Production of Bio-oil from Cigarette Butts and a Circular Economy System

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Industrial Engineering and Management

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"There are three principal means of acquiring knowledge... observation of nature, reflection, and experimentation. Observation collects facts; reflection combines them; experimentation verifies the result of that combination."

-Denis Diderot

"Imagination is more important than knowledge. For knowledge is limited to all we now know and understand, while imagination embraces the entire world, and all there ever will be to know and understand."

— Albert Einstein

Abstract

Global population is constantly growing and therefore greater pressure has been placed on natural resources, environment, and sustainability. Circular economy is a concept which when applied in business strategy enables the use of end-of-life materials to produce new solutions, contributing to a more sustainable and efficient economy. Worldwide, cigarette butts are among the most common type of litter. This type of waste represents a global threat to the environment and there are few solutions for its reuse and management. A complete literature review on the circular economy, energy recovery, current recycling solutions of cigarette butts, reverse logistics and municipal solid waste management is carried out to provide a theoretical background for a full understanding of the discussed matters and drive future work.

This research aims at filling the literature gap on the development of a solution for cigarette butts valorisation at an industrial scale within a circular economy perspective. The investigation adopted allowed the development of a practical solution for the valorisation of cigarette butts: the production of bio-oil and a logistics solution in order to integrate the collection of this type of waste in the municipal waste system, thus avoiding environmental pollution and facilitating its reuse.

Keywords: Sustainability, Circular Economy, Valorisation, Methodology**,** Bio-oil

Resumo

A população global está em constante crescimento e, por conseguinte, tem sido exercida uma maior pressão sobre os recursos naturais, o ambiente e a sustentabilidade. A economia circular é um conceito que quando aplicado na estratégia empresarial fomenta a utilização de materiais em fim de vida para produzir novas soluções, contribuindo para uma economia mais sustentável e eficiente. A nível mundial, as beatas de cigarro estão entre os tipos de lixo mais comuns. Este tipo de resíduos representa uma ameaça global para o ambiente e existem poucas soluções para a sua reutilização e gestão. Uma revisão completa da literatura sobre economia circular, recuperação de energia, soluções atuais de reciclagem de beatas de cigarros, logística inversa e gestão de resíduos sólidos urbanos é levada a cabo para fornecer uma base teórica para uma compreensão completa do tema em questão e impulsionar o trabalho futuro.

Esta investigação visa preencher a lacuna da literatura sobre o desenvolvimento de uma solução para a valorização das beatas de cigarro à escala industrial, segundo uma perspetiva de economia circular. A investigação adotada permitiu o desenvolvimento de uma solução prática para a valorização das beatas de cigarros: a produção de bio óleo e uma solução logística que visa integrar a recolha deste tipo de lixo no sistema municipal de resíduos, evitando assim a poluição ambiental e facilitando a sua reutilização.

Palavras-chave: Sustentabilidade, Economia Circular, Valorização, Metodologia, Bio-óleo

Acknowledgements

Now that I have come to the end, I look back on the road I have travelled until today and I realise what a privilege it is to have the possibility of studying and living in a country that, despite all the circumstances, can provide me with an excellent public education.

This dissertation has a little of all the conversations, analysis and research I have done during these last months, which means that it has a "hand" from all those who have crossed my path recently, starting with my family, my friends, Manuel from the Missão Beatão association, Andreas "Trash Traveller", Ana from the Zero Waste Lab Association, the President of the Cascais-Estoril parish Council Pedro Morais Soares, and all the members of the CERENA research centre, especially Sila, Suzete, Diogo, Salomé and David. By this, I mean that the work done is much more than a normal collection of information from banks of scientific articles, but it is a collection of experiences.

In a different way I will have to thank my supervisors.

Professor Ana Carvalho, the central person on this journey, who gave me the opportunity to work with her. Always trusted and believed in the ideas I proposed without ever doubting or giving up on any of them. In a practical, simple, and direct way she was always guiding me, and I am truly grateful for that. Without her supervision this outcome would not have been possible.

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1.Introduction

1.1 Problem motivation

Given the recent trends in population growth and the predictions about its evolution over the next decades (UN, 2019), understanding the extent to which demographic changes may affect the prospects of sustainable development is a priority. It is important to understand the main habits of the population and their consequences for the environment.

Environmental pollution is not a new phenomenon, yet it remains the world's greatest problem facing humanity, and the leading environmental causes of morbidity and mortality (Ukaogo, 2020) . One form of waste that has been brought to the public's attention in recent years is plastic waste. Since the 1950s, billions of tons of plastic have been produced with only a small fraction of this being recycled. Because of this, huge quantities of plastics end up in oceans, leading to ecological disasters (Tiseo, 2020). The world´s most littered plastic item is cigarette butts. Cigarette filters are made of plastic called cellulose acetate. This type of waste has a severe impact on the environment, not only because of the plastic but also the nicotine, heavy metals, and many other chemicals. Cigarette butts accumulate due to the poor biodegradability of the cellulose acetate filter, and all the toxicity threatens human life, marine ecosystems and the environment (Kadir, 2015)

With the increasing concern arising about landfills toxic incinerator emissions, there is a critical need for an alternative method for cigarette butts waste disposal which is sustainable and resilient. Based on the circular economy´s principles it is possible to create value-added alternatives for the reuse of cigarette butts, while reducing resources used, and the waste and leakage created and helps to reduce environmental pollution. The energy sector is undergoing major changes and developments to find new sustainable ways of producing energy. Energy production from waste (particularly plastics) is being explored and some processes such as anaerobic digestion, pyrolysis, hydrothermal liquefaction, and gasification are proving to be viable alternatives (Foster et al., 2021).

This Dissertation aims at filling the literature gaps on the development of an integrated process of cigarette butt's valorisation at an industrial scale by adopting a circular economy strategy. The goal is to develop a form of valorisation and logistics scenarios that enable the creation of a structured supply chain for this waste.

1.2 Master Dissertation Objective

This dissertation project aims at delivering a complete theoretical basis on the concepts regarding the characterized problem motivation. This research seeks to provide (1) Contextualisation, identification of the main problems, relevance of the topic and characterization of the tobacco market, (2) the state of art on circular economy, energy recovery, current recycling solutions of cigarette butts, reverse logistics and municipal solid waste management, and (3) statement of the future research objectives by establishing a methodology to adopt during the master´s dissertation development.

1.3 Master Dissertation Structure

The project is constituted of 5 chapters. The first chapter is an introduction to the work, which includes a problem motivation and sets the objectives of the study. The second chapter is a comprehensive literature review on tobacco market that aims at gathering exhausting information on this topic, also includes a contextualisation, identification of the main problems and the relevance of the topic. A description of these products is given, through a characterization of their essential features. The third chapter describes the state of art on circular economy, energy recovery, current recycling solutions of cigarette butts, reverse logistics and municipal solid waste management The fourth chapter includes the research agenda and methodology, also the objectives are presented to point out future research questions and structure the further study to be done. Chapter four describes the methodology and research agenda.

It is worth highlighting the fact that there are two approaches in the development of this dissertation: laboratory research and analysis and development of a logistics process. Thus, this chapter 4 is divided into three main sub chapters that describe the research methodology: Overview, Laboratory research and logistic process. Initially (4.1) the research is presented in a general way and the main steps to be taken as well. In the laboratory research (4.2) an overview of the process is given, the materials and equipment are described, the procedure for cigarette butt's characterisation is explained, bio-oil production is shown, solvent extraction is presented, and finally bio-oil characterisation is defined, In the third sub-chapter (4.3) is where the development of the logistics process is performed, which is divided into 3 parts: Municipal cigarette butts waste management proposal, Recycling company logistics optimization and Data collection.

The results and discussion are presented in chapter 5. It follows a similar structure to the previous chapter. In subchapter 5.1 the results of the laboratory part are presented. Firstly, the process yields are described for each bio-oil, then the results of the characterisation of the cigarette butts and the liquefaction products are presented and finally the Higher heating value of the bio-oils is analysed. In chapter 5.2 the results for the considered scenarios were discussed and presented, considering the flows and localization of the plants and lastly an analysis of the costs obtained by the developed model.

2.Tobacco Market

This chapter is divided into six sections. Section 2.1 provides an overview of the global tobacco market since its beginning until present days. Section 2.2 presents global consumption of tobacco products by region, main trends, and future perspectives and the composition of the cigarettes. Furthermore, in section 2.3 Actual cigarette butts waste management is introduced. Section 2.4 gives an overview of the cigarette butts pollution, presenting its components, toxicity, and main impacts in the environment. Lastly, section 2.6 characterizes the problem.

2.1 Global Market

Tobacco is a plant product containing mainly nicotine, cellulose, ammonia, and protein (Shahbandeh,2020), it began to be used millennia ago by the peoples of the western hemisphere, before contact with Europeans began in 1492 (Slade, 1997). The modern history of tobacco really starts with the design of the cigarette machine in the middle of the nineteenth century (Bonsack, 1881), since then most tobacco has been smoked in cigarettes, with cigars, pipes and chewing tobacco declining to relatively small proportions of the global consumption (Gerlach *et al.*, 1998). During the past two decades, tobacco use has dropped from 1.397 billion in 2000 to 1.337 billion in 2018 (World Health Organization, 2019), even so tobacco is still considered an epidemic and one of the greatest public health threats the world ever faced, killing around 8 million people a year (World Health Organization, 2020).

Tobacco is produced mainly in regions with mild and sunny climate: China, India, and Brazil. Its production was 2241, 762.27 and 749.91 metric tons in the year of 2018, respectively (Shahbandeh, 2020). Since 2000, the area of tobacco harvested (189,967 ha) has never been higher than this year. Beyond 2004, there were some fluctuations, with a peak of harvested area of 153116 ha in 2014. Finally, in 2019 the lowest ever figure of the last two decades was reached, 91912 ha (Shahbandeh, 2020).

Higher taxation and increasing health awareness among consumers have led the tobacco industry to change in recent years, mainly with the introduction of e-cigarettes on the market (Michal and Jeffrey, 2016). In Figure 1, It is noticeable that the tobacco revenue growth in percentage have the same pattern on these different products: cigarettes, smoking tobacco, cigars, and e-cigarettes. In addition, it can be seen that novel and risk-reduced products present the greatest revenue growth all over the studied period, evidencing the evolution of the tobacco market, mentioned above. In 2020, tobacco revenue growth of cigarettes decreased from 2.1% to 0.6%, as well as e-cigarette's revenue growth fall to 6.8%.

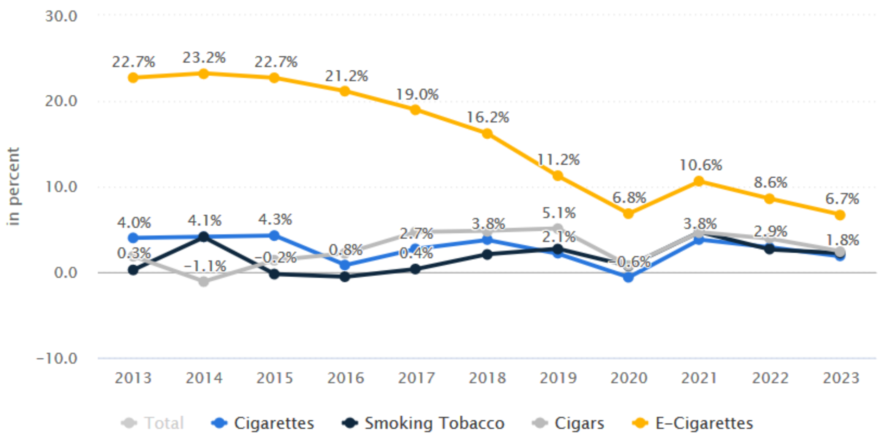

Figure 1-Tobacco revenue growth in percentage on different products- Statista December 2020

2.2 Consumption of tobacco products

Two of the most interesting tobacco products for this project are: cigarettes and e-cigarettes. However, this investigation will focus on normal cigarettes.

A cigarette is composed by tobacco, chemical additives, a filter, and a paper wrapping. Nowadays, there are 93 known potentially harmful chemicals in cigarettes, the most known are: nicotine, cadmium, lead, acrolein, benzene, carbon monoxide and ammonia (FDA, 2020). Cigarettes account for 96% of the global sales of manufactured tobacco in terms of value (Mackay et al., 2006).

Even though there is a lot of information these days about the consequences of smoking, according to Euromonitor estimation in 2016, still 5.5 trillion cigarettes were consumed worldwide (Elflein ,2019). Figure 2 represents the number of tobacco smokers among those 15 years and older worldwide from 2000 to 2025 by region. First of all, it is noticeable a constant decrease during the period between 2000 and 2020, as well as it is expected to maintain the pattern until 2025. The majority of tobacco smokers are from the Western Pacific, followed by South-East Asian, European, Americans, Eastern Mediterranean and African.

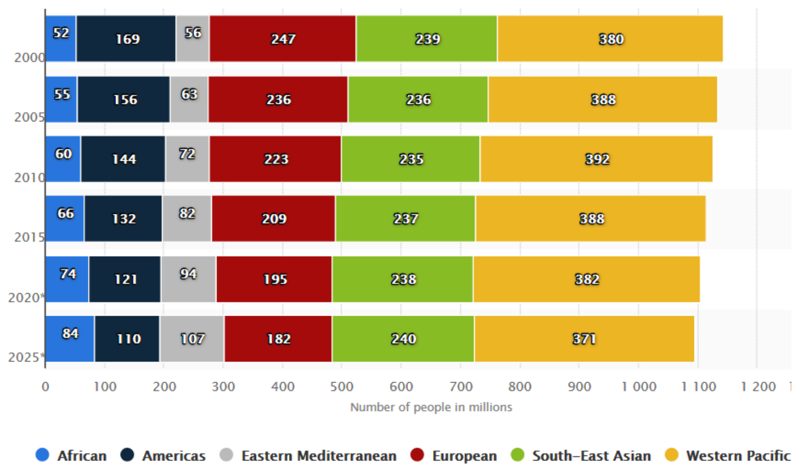

Figure 2-Number of tobacco smokers among those 15 years and older worldwide from 2000 to 2025-Statista October 2020

Figure 3 shows the global cigarette consumption per region between 1999 and 2016. The trend highlights the regions affected by higher growth (China and South-East Asia Region - SEARO) and those characterized by a decline (European Region -EURO, Americas - AMRO, Western Pacific Region - WPRO - excluding China).

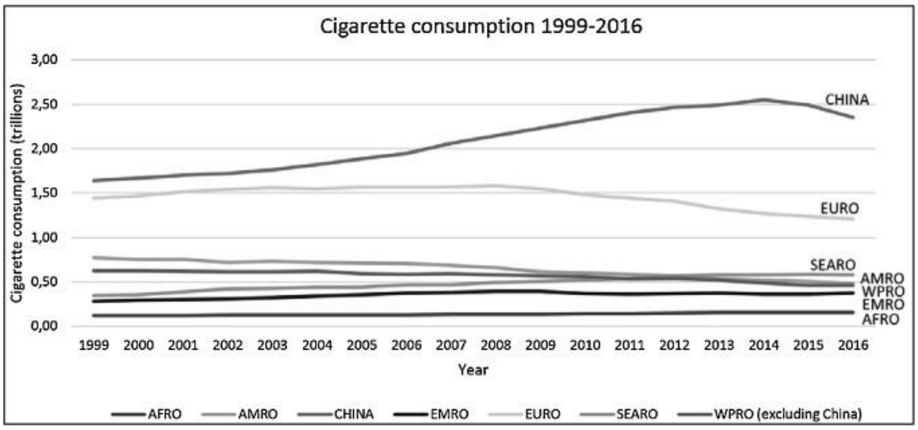

Figure 3-Trend of global cigarette consumption per region (authors elaboration from Tobacco Atlas data-2006).

Electronic cigarettes or so-called e-cigarettes are a relatively new development on the tobacco market, 21% of US high school students reported having used e-cigarettes in 2018 (Statista Research Department,2020). It could have different shapes, normally it holds a battery and a heating element that could be a liquid containing nicotine or a regular cigarette (heated tobacco). The e-cigarette also contains potentially harmful substances including, nicotine, ultrafine particles that can be inhaled deep into the lungs, flavoring such as diacetyl, a chemical linked to a serious lung disease, volatile organic compounds, cancer-causing chemicals, heavy metals such as nickel, tin, and lead (CDC, 2020).

2.2.1 Composition

Modern commercially manufactured cigarettes are composed by the following main elements presented on figure 4.

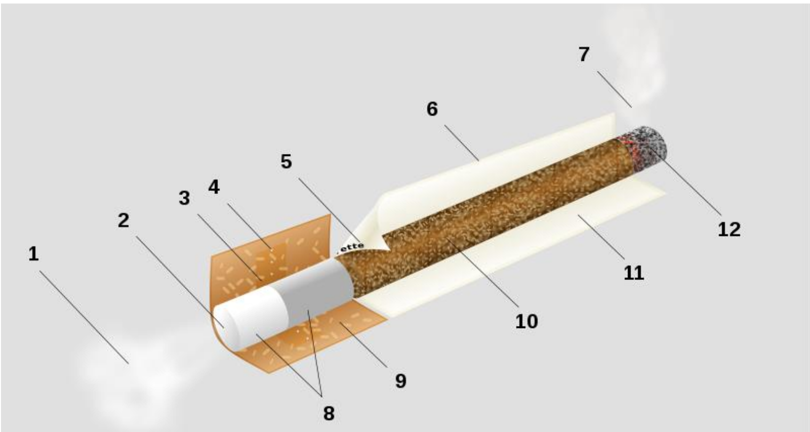

Figure 4-Composition of a Cigarette Adapted from Kurmas & Mohajerani, 2020

In order to systematize all the different elements of the cigarette and their descriptions, table 1 is presented (Kurmas & Mohajerani, 2020).

Table 1- Cigarette's composition description

NUMBER	ELEMENT	DESCRIPTION
1	Mainstream smoke	Mainly composed by PAHs (Polycyclic Aromatic Hydrocarbons), Nitrosamines, Carbon monoxide, Nicotine, Ammonia, Acrolein, Isoprene, Benzene and Toluene
2	Filtration material	It is used activated charcoal and some other materials
3	Adhesives	Adhesives are used to hold the cigarette paper around the tobacco and are known as side stream adhesives. Ethlene-vinyl acetate (EVA) and polyvinyl acetate (PVA) are just two of the adhesives used by tobacco companies.
4	Ventilation holes	Reduce the taste of the cigarette. If unblocked, dilute inhaled smoke with air
5	Ink	---
6	Adhesive	Adhesives are used to hold the cigarette paper around the tobacco and are known as side stream adhesives. Ethlene-vinyl acetate (EVA) and polyvinyl acetate (PVA) are just two of the adhesives used by tobacco companies
7	Side stream smoke	Side stream smoke contains smaller particles than mainstream smoke. These tiny toxic particles are more easily absorbed deep in the lungs and other cells in the body.
8	Filter	Made from bundles of thin, hair-like fibres (Cellulose acetate). Designed to trap smoke, but only a small proportion.
9	Tipping Paper	Wraps around the filter, connecting it to the rest of the cigarette.
10	Tobacco and ingredients	Manufacturers can add hundreds of ingredients to a cigarette to make smoking more appealing and to mask the harshness of smoke
11	Cigarette Paper	Holds the tobacco filler. Chemicals are added to the paper to control how fast the cigarette burns
12	Burning point and ashes	Cigarette ash is a bit unique among the plant ashes because of the potassium nitrate and other substances added to the tobacco in a cigarette. The ash is associated with a significant amount of highly birefringent small crystals.

2.3 Cigarette Butts Waste Management

Tobacco products, such as cigarettes and e-cigarettes mentioned earlier, produce large amounts of waste, often referred to as butts. As a result of trillions of cigarettes consumed, billions of cigarette butts are being thrown away in the world daily. According to two separate reports, the ratio of littered butts to the cigarette consumption was about 76% in 2013 (Patel et al., 2013) and 84% in 2015 (Lee and Lee, 2015), indicating the effect of smoker's behaviour on the amount of these litters. Cigarette butts are commonly found in coasts, roads (Haseler et al., 2018), aquatic and sea environments (Becherucci et al., 2017), urban and public areas (Chevalier et al., 2018). It is recognized as one of the most common and epidemical wastes (Pon and Becherucci, 2012) and contributes to the largest number of wastes in the world (Micevska et al., 2006). The estimated annually discarded waste from global cigarette consumption could be anywhere between 340–680 million kg, besides almost two million tonnes of paper, ink, cellophane, foil, and glue that are used in tobacco product packaging. More than 40% of all items collected during urban clean-ups and removed from public areas such as beaches and parks are cigarette butts and related products (Bonanomi et al., 2015; Ariza et al., 2008).

As there is no regulation for the collection and treatment of butt waste so far, we are at a stage where it is crucial to adopt practices in the management of butt waste, raising awareness among consumers and producers in order to avoid further dispersion of this type of waste in the world. Many studies have been carried out with the purpose of finding effective management solutions for this waste. Conventional methods such as landfilling or incineration are neither universally sustainable nor economically feasible for this purpose (Bandi et al., 2018; Mohajerani et al., 2016).

Recycling CBs is difficult because there are no easy mechanisms or procedures to ensure efficient and economical separation of the butts and appropriate treatment of the entrapped chemicals (Mohajerani et al., 2016).

Numerous proposals have been made to prevent or mitigate cigarette butt disposal, including labelling filters as non-biodegradable, deposit and return programmes, waste fees, litigation against the tobacco industry to recover clean-up costs, fines levied against consumers or tobacco companies, mandated filter biodegradability, a ban on filters and consumer education (Novotny et. al, 2009)

The fact is that industry has been concerned for decades that cigarette litter might increase the social unacceptability of smoking, inspire support for tobacco control, or result in legislation requiring them to take fiscal or practical responsibility for cigarette waste disposal. As a policy response, the industry has sponsored anti-littering groups, distributed portable ashtrays (frequently branded) and installed permanent ashtrays in downtown areas of numerous cities (Smith et. al, 2010).

Some efforts to establish a cigarette butt recycling programme has been made, however this effort and other clean-up campaigns reached only a small portion of the tobacco product waste.

For example, the Ocean Conservancy reports that approximately 52 million cigarettes have been picked up globally in 27 years of clean-ups (Ocean Conservancy, 2011), at the same time trillions of cigarette butts are thrown to the ground yearly. This means that downstream solutions are not effective in reducing tobacco product waste in the environment.

Not only clean-up efforts reach only a small proportion of cigarette butts waste, but also given a high number of cigarette butts, their small size and widespread dispersion, the collection of them is very costly. An economic estimate was performed and showed that the cost of cleaning up and collecting littered cigarette butts in streets and parks in San Francisco was 0.5-6 million dollars annually (Rath et al., 2012)

The truth is that many points out that downstream processes are not effective and are expensive. Many believe that the solution will pass through other types of actions such as: several legal measures like raising cigarette tax, production of cigarette filters using degradable material, raising awareness among individuals about the importance of cigarette butts and prevention of cigarette smoking and the use of portable ashtrays (Torkashvand et al., 2020).

Due to the lack of practical operational aspects in this area, companies and associations started collecting cigarette butts separately, leading to a new waste stream exclusively consisting of these materials, whereas they were previously mixed with household and municipal waste. European List of Wastes (EC, 2000, EU, 2014b) does not propose a specific entry for cigarette butts. Consequently, cigarette butts should be attached to the 20 01 99 entries (i.e., “Municipal wastes including separately collected fraction/Separately collected fraction/Other fractions not otherwise specified”). Therefore, it is necessary to determine the fifteen hazardous properties defined in the Waste Framework Directive (EU, 2008) to conclude on their classification.

As a consequence of the actual classification and inefficient treatment by public authorities, some associations and companies propose to collect them separately and to enhance public education, in order to prevent cigarette butts impacts on the environment.

In Europe, *Mégo* is a sorting and recycling service for cigarette butts (used filters), a unique solution in France. The objective of this national service is to collect cigarette butts to recycle them. This offer allows an external cleanliness in favour of the environment. This service is suitable for small companies, associations and individuals who want a simple and inexpensive solution for sorting cigarette butts. This company provide bags, portable and recyclable ashtrays, information and awareness posters, stickers, and instructions on how to send the package back to them. Once the waste has been recycled, a detailed report is sent with the impacts avoided and the carbon footprint of the operation (EU, 2021).

Terracycle is an innovative recycling company that has a cigarette waste recycling program with funding from Santa Fe Natural Tobacco Company, the waste collected through this program is recycled into a variety of industrial products, such as plastic pallets and any remaining tobacco is recycled as compost. Nowadays, this program accounts for 26590 participating locations across the world (Terracycle,2021). Due to the position still adopted by the state and the tobacco industry in most countries, there is no defined chain for butt management. Today we have a fragmented or almost non-existent recovery or treatment chain. The fact that the management chain for this waste is almost non-existent makes its valorisation very complicated, so solutions for its reuse will always involve a major logistical and institutional challenge. For this reason, most solutions developed to create value through butts are difficult to implement.

2.4 Cigarette Butts Pollution

Cigarette butts are made of about 95% poorly degradable microscopic-sized white fibres massed together (about 12,000 per filter with about 30,000 dernier), characterized by a Y-shaped cross-section (Du et al., 2015). Cellulose acetate fibres are linked to each other through the glycerol triacetate, which is a plasticizer (Hamzah and Umar, 2017). A filter, after its use, has absorbed smoke, trap tar, toxic chemicals, and particle smoke. Its chemical composition depends on the type of tobacco used, the cigarette paper, category, and effectiveness of the filter as well as the degree of tip ventilation. It also depends on the filter design. Tests performed by Strain et al., 2015, showed presence of many carcinogenic hydrocarbons and alcohols that exist in tobacco smoke. The main problem associated with cigarette butts is their slow degradation rate and the high concentration of toxic content. Typically, cellulose acetate possesses poor photo- and bio- degradable properties, making cigarette butts persistent in the environment. The methods and times required for this process depend on the degradation mechanism, of which there are different types, e.g., photodegradation, biodegradation, and mechanical processes or a combination of these as typically occurs in outdoor environments due to different factors (Marinello et al., 2020). According to Puls et al., 2011, cellulose is degradable thanks to organisms that utilize cellulose enzymes. At the other hand, Haske-Cornelius et al., 2017, state that cellulose acetate-based cigarette filters do not biodegrade under most circumstances because of their compressed make up and the presence of acetyl molecules. In 2011, Moerman and Potts, 2011, investigated the leaching behaviour of heavy metals in cigarette butts. The main objective of the study was to determine the concentration of leached metals and the effect on the surrounding environment. The variable relationships for the selected metals Ba, Zn and Cu can be seen figure 5. This indicates that a piece of cigarette waste is a point source of metal contamination for at least one month. Furthermore, it suggests that the longer the waste remains in the environment, the greater the contamination of Ba, Fe, Mn, and Sr (Moerman and Potts, 2011).

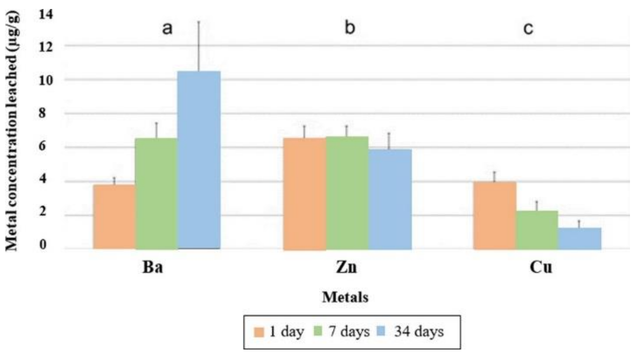

Figure 5- Relationships observed between metal concentration leached from smoked cigarettes and soaking time in aqueous solution (Adapted from Moerman and Potts, 2011)

Emissions from cigarette butts into water can be a fast process. Standardized cigarette butts produced with a smoking machine leached 7.3 mg of nicotine per g of butts into 1 L of purified water, of which 50 % was released in the first 27 minutes during the experiment (Green et al. 2014). The same study also found that the cumulative nicotine release from fifteen consecutive rainfall events with 1.4 mm of precipitation for each event was 3.8 mg of nicotine per g butt, of which 47 % was released during the first event (Green et al. 2014).

Many scientific studies were made during recent years about the effects on fish exposed to cigarette butts on salt and freshwater Slaughter et al., 2011,also on microbial communities Singh and Kathiresan, 2015, and aquatic organisms from different trophic levels, Oropesa et al., 2017. Conclusions demonstrate that nicotine poses an important risk to aquatic organisms.

Cigarette butts littered on streets commonly get washed away into stormwater drains and end up on beaches, or in rivers and harbours, leaching toxic chemicals (Araújo and Costa, 2019). To systematize the main impacts of cigarette butts the following figure 6 was developed.

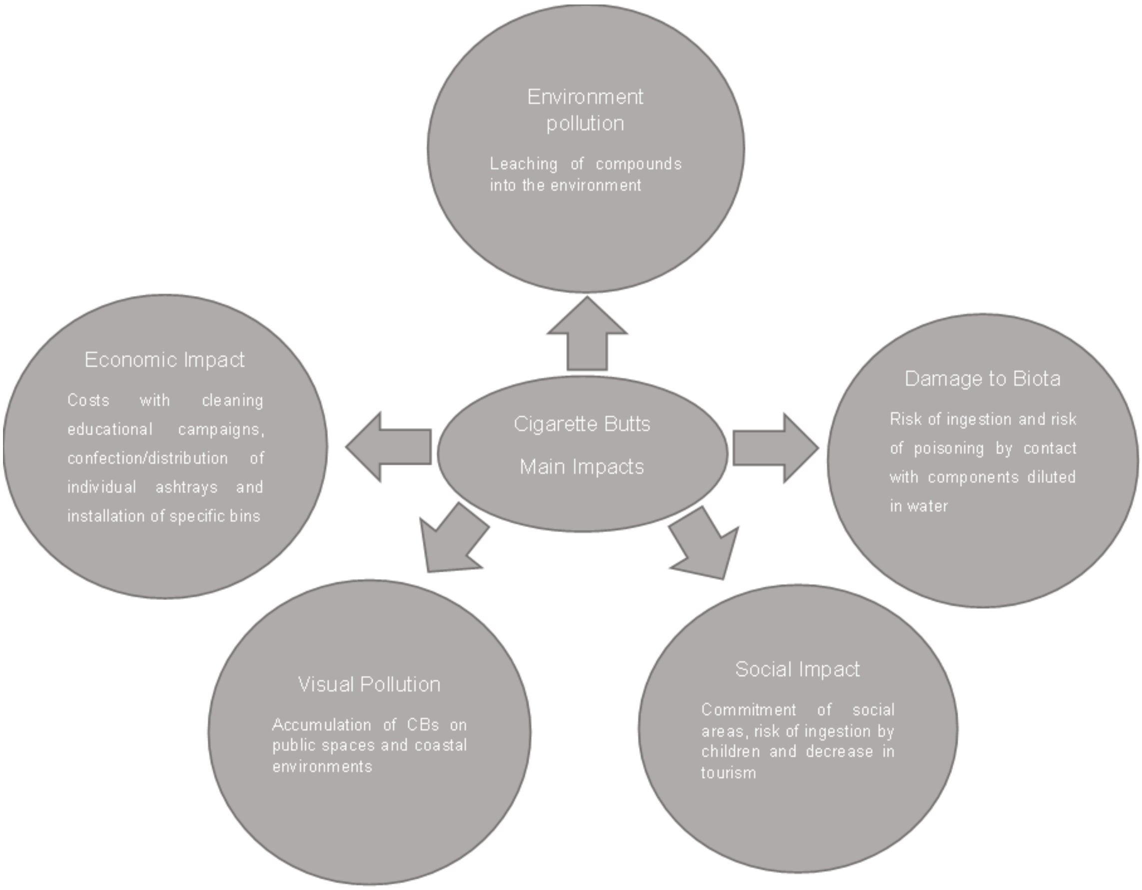

Figure 6- Cigarette Butts Main Impacts- (Adapted from Araújo and Costa, 2019)

2.5 Problem characterization

Tobacco consumption is not expected to slow down significantly in the coming years and the attitude of the state and the consumer towards this product will tend to continue soon.

The two facts mentioned above combined with the non-existence of a specific reuse chain for this product has therefore serious impacts on both society and the environment. Cigarettes have as constituents many chemicals that are harmful and toxic to the environment and most of them end up on the ground of cities, in the sea or somewhere in nature. To cope with the excessive and unwanted volumes of cigarette butts it is extremely important to review its entire value chain and create reuse solutions that are sustainable from an economic and ecological point of view. The solution should not only provide a practical way of recycling cigarette butts but also logistics scenarios in order to prepare a solid supply chain that will enable its recovery in a structured way.

This research will focus on energy recovery using cigarette butts and possibly other types of waste for their integration. Accordingly, this research focuses on the design of processes, which may or may not already be used by certain companies, and which may eventually be adapted or improved. In addition, it aims to understand the constraints and variables of certain processes to find the best possible solution for the case under study.

2.6 Conclusions

Tobacco consumption will not vary greatly according to the statistics presented by some sources. The changes expected by the year 2025 are not very substantial when we look directly at the world picture. Apart from this, the management of cigarette butt waste is almost non-existent worldwide, and the initiatives that are beginning to appear come from associations and private companies. It is believed that cigarette butts recycling is very complicated since there are no efficient mechanisms or procedures to ensure a proper treatment.

Not only the facts mentioned above are important to characterise the problem, but also the pollution caused by this type of waste. The truth is that not only the plastic filter constituents are a threat to the planet, but also all the chemicals present in cigarette butts. The impacts of cigarette butts are noted on the economic, social and environmental levels.

Nowadays, we have a fragmented or almost non-existent treatment or recovery chain for this type of waste, which makes its valorisation complicated and therefore its reuse involves a major logistical and institutional challenge.

3. State of Art

This chapter provides the state of art and summarizes the relevant insights acquired from the literature review. In section 3.1 circular economy definition and concepts are presented and an overview of the model is showed. Section 3.2 introduces current recovery solutions for cigarette butts and its applications. A specific way of creating value through waste is showed in section 3.3, that is energy recovery. Finally, section 3.4 presents reverse logistics concepts and its application in municipal solid waste management.

3.1 Circular Economy

Organizational concern regarding environmental management has been growing worldwide. Environmental improvements in business have been encouraging companies to think and act towards reducing the negative effects from ill environmental performance, from both production and consumption ends (Barros et al., 2021). The circular economy has been increasingly seen as a possible solution to pursue a more sustainable development (Geissdoerfer et al., 2018).

Ultimately, circular economy refers to the idea of extending the useful life of products, materials, or resources (Gregson et al., 2015). A central topic in the concept of circular economy is the use of resources within closed-loop systems, reducing pollution or avoiding resource leakage while sustaining economic growth (Winans et al., 2017). The main point of circular economy concept is to capitalize on material flow recycling and to balance economic growth and development with environmental and resource use (Zhu et al., 2010).

The concept does not only pass by the production of the products and its end life, but in its best form, it encompasses a “cradle to grave” approach or a “life cycle” approach from material design, production, use and disposal (Curran and Williams, 2012; Matete and Trois, 2008). It is mainly related with eliminate inefficiency by way of total recovery of resources, from whatever is discarded through the supply chain (Greyson, 2007).

A circular economy seeks to rebuild capital, whether this is financial, manufactured, human, social or natural. This ensures enhanced flows of goods and services (MacArthur, 2013). The system diagram illustrates the continuous flow of technical and biological materials through the ‘value circle’. Figure 7 shows technological and biological nutrient-based products and materials cycle through the economic system.

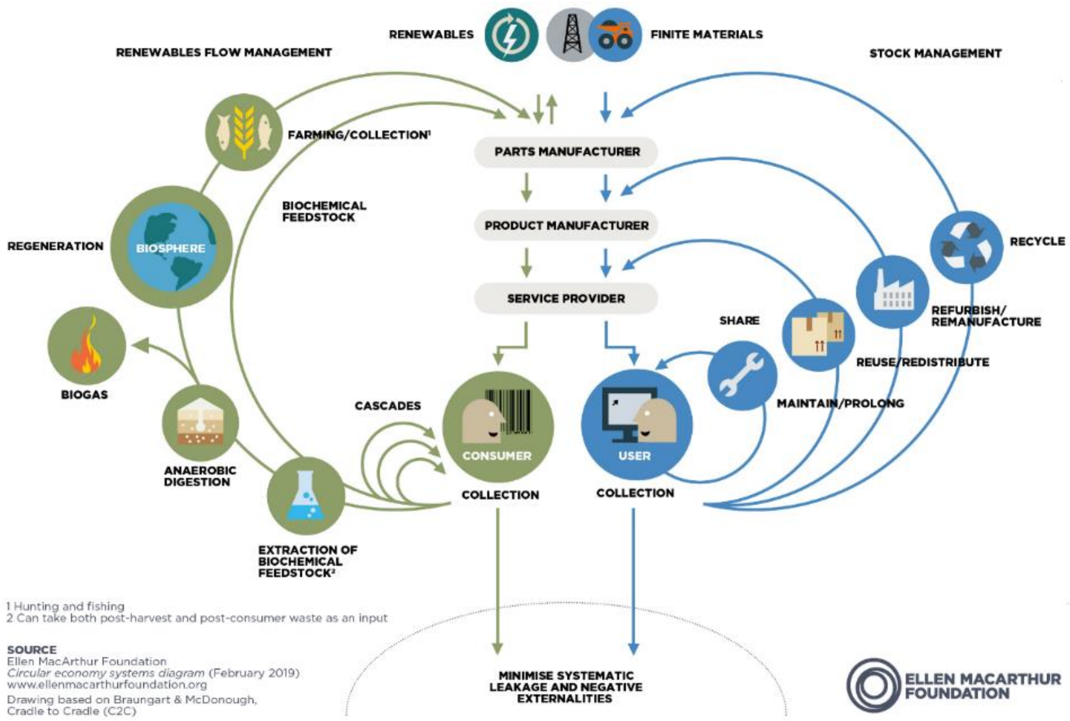

Figure 7-The circular economy-an industrial system that is restorative by design- Source Ellen Macarthur Foundation

The model begins with the extraction of resources which could be biological or technical depending on its nutrients and characteristics. Both are represented in the model, where the green one corresponds to the biological cycle while the blue one corresponds to the technical cycle. Basically, the extraction of resources is usually done by the supplier (parts manufacturer) and then the producer (product manufacturer) manufacturers the final product according to some specifications and these products are delivered to service providers who sell the products to consumers or users, depending on the cycle, since biological products are consumed, and technical products are used. When the product is no longer suitable after consumer and user stage, has two possible destinations: (1) circular path through recovery cycle or (2) disposal and landfilling purposes.

Circular economy has heavily relied upon the principles of 3RS: Reduce, Reuse and Recycle, being these three principles regarded as the founding principles of the sustainable waste management system (Mason et al., 2003; Colon and Fawcett, 2006, Murphy and Pincetl, 2013). It is aimed at optimum production by utilizing reduced natural resources, producing minimum pollutions, emissions and wastes by utilizing 3R principles (HQ et al., 2014).

Jawahir and Bradley, 2016, based on work developed by Zhang et al.,2013, reinforced the importance of the inclusion of a 6R-methodology rather than 3R in the circular economy conceptualization. This approach offers a closed-loop, multiple product life-cycle system as the basis for sustainable manufacturing (Joshi et al., 2006).

The definitions of the six concepts are:

(1) **Reduce:** Aims to reduce the input of raw materials, the primary energy, and the waste through the improvement on production efficiency (Su et al.,2013).
(2) **Reuse:** Production of new components through products and components after its first life cycle, for subsequent life cycles (Jawahir and Bradley, 2016).
(3) **Recycle:** "Any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes" (Ghisellini et al., 2016)
(4) **Recover:** Process of collecting products after its first use, disassembling, sorting and cleaning for utilization in subsequent life cycles of the product (Jawahir and Bradley, 2016).
(5) **Redesign:** involves the act of redesigning next generation products (Jawahir and Bradley, 2016) and the processes of the whole circular chain to increase its efficiency (Ellen MarcArthur Foundation, 2012)
(6) **Remanufacture:** Re-processing of already used products to restore their original state or a like-new form through the reuse of as many parts as possible without loss of functionality (Jawahir and Bradley, 2016).

Figure 8 illustrates the natural sequence of the 6R applications within the entire life cycle with several decision points and multiple closed-loop options (Zhang et al., 2013). Initially, if the material cannot be recovered for use as either material or energy it goes to landfill. On the other side, if the end-of-life products are recoverable, the first activity to consider is reuse and they can be directly used for assembly to make new products. Remanufacture is the next activity to consider if the components could not be reused directly. Depending on the damaging and their original specifications, components are restored by remanufacturing if they are in good conditions or by recycling if not. After recycling processes, the materials can be recovered and reused in the form of raw materials to make the same or different products. By analysing this figure, virgin materials would no longer needed to produce the next generation products and a multiple closed-loop material flow could be achieved with this 6R methodology (Zhang et al., 2013).

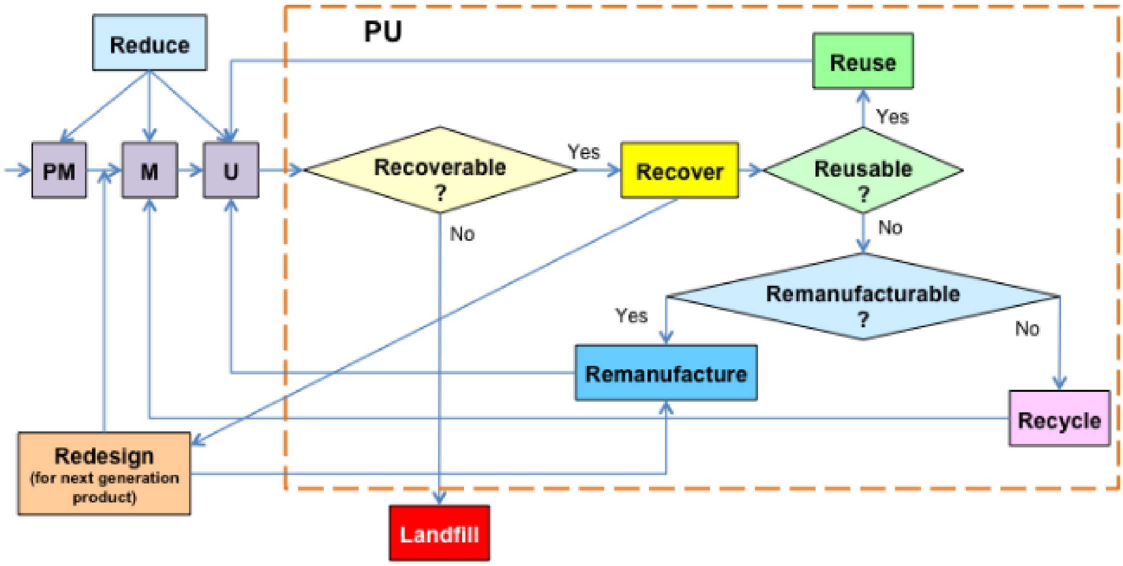

Figure 8- The 6R decision flow diagram across four life-cycle stages- Adapted from Zhang et al., 2013

3.2 Current recovery solutions for cigarette butts

Identifying a recycling methodology for this kind of waste would reduce the release of dangerous materials into the environment and to the ecosystems and would promote the recovery of materials in line with the circular economy and sustainable development. (Marinello, et. Al, 2020).

As noted above, circular economy promotes the use of waste as a resource to produce new products or materials. In this chapter a literature review of possible butt recovery solutions will be developed, including recent studies on cigarette butts recycling solutions which used this waste as input for physical and or chemical treatment in order to obtain second raw materials, semi-finished products and finished goods. These 9 studies were assessed through a literature review on cigarette butts recovery solutions, where the main focus was to understand what have been addressed by the authors and researchers. Inside the vast list of studies, nine documents were selected: (1) Mohajerani et al., 2016; (2) Maderuelo-Sanz et al., 2018; (3) Wadalkar et al., 2018; (4) Xiong et al., 2018b; (5) Ghosh et al., 2017; (6) Ogundare et al., 2017; (7) Anmei et al., 2018; (8) Ifelebuegu et al., 2018; (9) Wang et al., 2016.

The goal of the literature review was to assess the: applied technology and process used, operating conditions, level of implementation, output and application of these different solutions.

From table 2 it is possible to verify all information in the different studies, under the same goal of recycling cigarette Butts.

Table 2- Analysis of different solutions for cigarette butt's recovery

	Solution	Applied technology and process used	Operating conditions	Level of implementation	Output and Application
Physical	**Fired clay bricks (1)**	Cigarette Butts (CBs) were disinfected and mixed in different percentages with brown silty clayey sand, dried and finally fired	Disinfection at 105 ºC for 24h. Mixing Time 10-15 min. Fired in furnace at 1050 °C for 3h.	This research refers that the process is easy scalable and proposes the inclusion of 1% CBs content in fired clay bricks throughout the brick-manufacturing industry.	Fired Clay Bricks with CBs content < 2.5% did not see large reductions in their compressive strength so that can be used in construction. The main advantage arising from the incorporation of CBs in terms of the properties of the brick, was the reduction in dry density and increase in porosity. Resulting in bricks that are lighter and easier to handle.
	Sound porous absorber (2)	CBs were dried to disinfect and to remove the humidity. Then cellulose acetate was manually separated from the outer and inner paper and was shredded into short fibres which were subsequently mixed. After this initial treatment the blend is compacted between a grid and the hard back termination of the impedance tube o reach a given bulk density.	Disinfection at 80ºC for 72h.	Research is made in a pilot scale and there is no reference about scalability of the process.	Sound absorber , a porous or fibrous material, able to absorb sound energy. It is more effective by increasing bulk density, increasing porosity, and reducing flow resistivity. Major application in building and structures.
	Blocks for paving (3)	Cigarette butts were sun dried to disinfect them. CBs were grinded and then mixed with cement, fine aggregate, coarse aggregate, water and admixtures. Last process- Curing	Disinfection (sun dried) for 3 days. Air cured for 28 days.	Research is made in a pilot scale and there is no reference about scalability of the process.	The product described by the authors is a precast concrete block for paving mixed with CBs which, according to the tests performed increases water absorption and flexural strength , while there are no significant variations in the compressive strength. Major application: Infrastructure
Chemical	**Superhydrophobic adsorbent (4)**	Fabrication of hydrophobic SiO2 particles, by ultrasonic dispersion, centrifugation and drying in an oven. Then superhydrophobic Cigarette Filter was fabricated by ultrasonic dispersion, magnetic stirring and finally dried in a vacuum oven. After these processes, samples were characterized.	In the fabrication of hydrophobic SiO2, suspension is dried in an oven for 30 min at 80ºC. In the fabrication of superhydrophobic cigarette filter, magnetic stirring is made at 70ºC for 4h and placed in a vacuum oven for 72h at 30ºC.	Research is made in a pilot scale, however authors have demonstrated its cost-effective, highly selective and environmentally-friendly properties. It could be concluded that is a scalable solution.	Cellulose as a superhydrophobic absorbent for oil spillage clean-up. Major application in environmental engineering. Could be also applied to oil and water separation not only to reduce environmental pollution, but also to address chemical leakage.
	Electrically conducting material (5)	Filters are separated. Pre-treatment is made in a dryer. After pre-treatment, one step Pyrolysis process in a muffle furnace is made and then the pyrolyzed product is cooled down.	Pyrolysis at 900ºC for 2h. Cooling down to room temperature.	Research is made in a pilot scale, however authors have demonstrated its cost-effective and promising properties . So, it may be interesting to scale the process.	Electrically conductive device that have the capability to supply high levels of power and energy. Applications such as electrical vehicles, micro sensors, and portable electronics.
	Nanocrystalline Cellulose (6)	Manually separation of the filters and then ethanolic extraction, followed by hypochlorite bleaching, alkaline deacetylation, and conversion into NCC by sulfuric acid hydrolysis.	Ethanolic extraction for 24h at room temperature. Bleaching for 6h at room temperature. Deacetylation for 24h at room temperature.	Research is made in a pilot scale. Authors revealed that this process has demonstrated proof-of-concept and future applications, yet there is necessary further investigation to scale the solution.	The mechanical and chemical properties of the nanocellulose make it extremely suitable for different types of applications. The authors describe the isolation of nanocrystalline cellulose from CBs with important properties, such as: biocompatibility, biodegradation, high strength, specific surface area, high crystallinity index, low toxicity, and density. Major application in chemical and medical industries.
Physico-Chemical	**Oil-Absorbent material (8)**	Cigarette filters were first cleaned and then shredded in ethanol under ultrasonication . Then were hydrolysed with sodium hydroxide solution. Then, were dried in an oven. Using thermal vapour deposition method filters were coated and then heated in an oven again. After morphology changes of the product, adsorption tests were performed.	Ultrasonication for 1h. Drying in an oven at 70ºC for 24h. Final Heating in an oven at 70ºC for 4h.	Research is made in a pilot scale. Due to its low costs, easy and high efficiency operations the material has a very good chance to be scalable and widely used.	Oil-absorbent material, which can be used to mitigate the effects of possible oil spills in aquatic environments. The material described by the authors, obtained from CBs, has demonstrated high absorption capacity and a good oil-saving rate, as well as being fabricated in a green and easy manner.
	Carbon Quantum Dots (CQDs) (7)	Hydrothermal method: First step used in the process was washing cigarette filters with water and then dried them in oven. Then, cigarette filters were transferred to an autoclave and heated in an oven. After the reaction, the autoclave was cooled, and the solution was filtered through a membrane filter and diluted for further use. CQDs were then used to detect Sudan I (colorant) in chilli powder, chilli sauce and tomato sauce. CQDs solution and amounts of.	Cigarette filters dried in oven at 60ºC. After the autoclave process, were heated at 200ºC for 6h.	The level of implementation of this solution will be on a laboratory scale due to its final application.	Carbon Quantum Dots (CQDs) which are a recent type of carbon nanomaterial that exhibits strong fluorescence depending on the size and excitation wavelength. CQDs are used in the chemical field to exploit their fluorescence in chemical analyses and to detect synthetic colorants in foods (Sudan I)
	Hybrid Electrode Material (9)	The waste cigarette butts were collected and used directly to adsorb NH_4VO_3 in a NH_4VO_3 solution under magnetic stirring to obtain cigarette butt and NH_4VO_3 complex. After that, with a heat-treatment in the mixed atmosphere of N_2 and NH_3, NH_4VO_3 transformed to VN, and meanwhile the cellulose fibres generated carbon fibres. As a result, the carbon fibres and vanadium nitride (CFVN) was obtained. CFVN was further used as active materials to fabricate supercapacitor device.	Dissolution was made at 60ºC. Drying at 60ºC under airflow for 24h. Pre-heating under airflow at 270ºC for 1h and then heated a mixed atmosphere of N2 and NH3 at 800ºC for 1h.	Research is made in a pilot scale. Authors believe this product meets the needs of the market for energy storage devices.	Hybrid electrode, a particular composition of the electrodes used in superconsenders that allow to improve the performance of traditional electrodes by simultaneously using two charge storage mechanisms, without compromising the structural integrity and operational life of supercapacitors. Authors believe that this material could be used as a precursor to fabricate the active material for supercapacitor electrode.

Nine different papers were analysed, and all provide different types of solutions for the treatment and recycling of cigarette butts. Comparing the authors´ approaches to the treatment of this waste, in most tests only smoked cigarettes were used often without providing comparative analyses of the same non-smoked material. The solutions are mainly solid materials used in numerous economic and productive sectors, especially in the field of building materials, environment, and chemistry.

In fact, laboratory experiments do not require large quantities of samples. However, the logistical aspect associated with the collection and handling of cigarette butts is an extremely critical element of the process, since it is crucial to understand what makes the product developed ineffective. The treatment processes described all take place on a laboratory pilot scale. However, a large-scale analysis or experimental application is lacking, which would simulate the operational process with greater quantities and with the critical, operational, economic and legislative barriers that characterize a pilot case. All the papers provide detailed information on the characteristics of the resulting materials and performance under operating conditions. Nevertheless, no author provides detailed information regarding the economic sustainability of the process or how to make these products suitable for the market.

It is necessary to research possible solutions that are sustainable, economically feasible and scalable.

3.3 Energy recovery through solid waste

The energy sector is a possible way to explore the development of solutions for value creation through cigarette butts, since energy recovery plays an important role in modern municipal solid waste management systems. Biochemical and thermochemical waste-to-energy technologies can exploit the energy content of municipal solid waste, thus replacing fossil fuels and diverting waste from landfills (Maria et al., 2018). Sustainable waste management is a global challenge and urgently in demand under the pressure of increasing waste production. The global waste generation will reach 6 million tonnes/day by 2025 (World Energy council, 2016) coinciding with a growing global population with a rate of 1.18% each year (IEA, 2015). Municipal solid waste treatment has been studied in recent years in order to contribute to greenhouse gas emission reduction, economic benefits, technological applications and overall performance of one municipal solid waste treatment system.

The combination of high-quality recycling and efficient energy recovery processes could reduce emissions (Yi et al., 2018), due to the waste, that cannot be recycled in a technically or economically viable way, could be used to generate energy (CEWEP, 2020), besides providing a substitute for fossil fuel combustion (Iqbal et al., 2019). Developed countries have been working on reduce landfills dependency by combining recycling with biological treatments such as composting and anaerobic digestion together with thermal conversion into energy. Mazzoni et al., 2017, believes that a waste management plan can include the waste-to-energy technologies, which comprise thermochemical treatments such as pyrolysis, gasification, and combustion.

According to Korai et al., 2016, the energy recovery potential from Municipal Solid Waste depends on the waste amount that is incinerated, its heating value, and the combustion process efficiency. Sampling and sample preparation are critical steps in these processes, since spatial (local, regional, national) and temporal (week, month, year) variations must be considered (Edjabou et al., 2015). Due to the heterogeneous character of municipal solid waste understanding physical and chemical combustion behaviour becomes very difficult, as many complex reactions take place during the process, which are implicit on the oxidation at high temperatures of the organic substances present (Reddy et al., 2016).

As it can be seen in figure 9, in the EU in 2018, more than a half (54.6 %) of the waste was treated in recovery operations: recycling (37.9 % of the total treated waste), backfilling (10.7 %) or energy recovery (6.0 %). The remaining 45.4 % was either landfilled (38.4 %), incinerated without energy recovery (0.7 %) or disposed of otherwise (6.3 %) (Eurostat statistics, 2021).

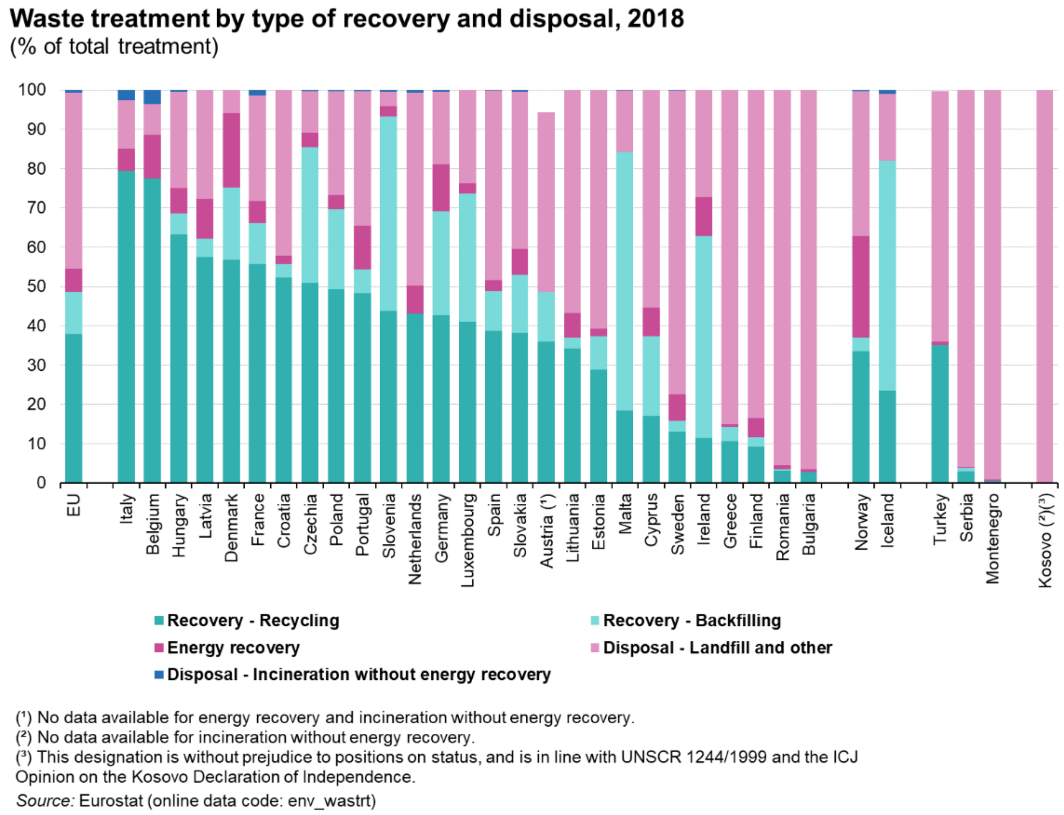

Figure 9- Waste treatment by type of recovery and disposal (Eurostat, 2021)

The amount of useful energy obtained from waste-to-energy resources depend on the conversion efficiency of the applied technology (Istrate et al., 2021).

Foster et al., 2021, discussed the waste-to-energy conversion technologies in the UK, namely anaerobic digestion, gasification, pyrolysis, and hydrothermal liquefaction.

Anaerobic digestion is considered one of the most promising strategy for organic waste treatment (Istrate et al., 2021). On average a state-of-the-art anaerobic digestion facility can reach 70% of the methane potential and a methane content in the biogas of 55% v/v (Moller et al., 2009). The biogas production rate for the 2030 scenarios ranges from 111 to 149 m^3 biogas t^{-1} of organic waste collected separately and from 102 to 126 m^3 biogas t^{-1} of residual organic waste (Istrate et al., 2021). This biogas could be converted into 212 – 285 kWh t^{-1} organic waste collected separately and 198 – 242 kWh t^{-1} residual organic waste in an internal combustion engine, within the ranges reported in the literature (Slorach et al., 2019).

Gasification is a partial oxidation process of organic substances, using high temperatures of around 500–1800 °C. Partial oxidation is achieved by limiting the oxygen exposure at those temperatures so the gases produced known as 'syngas' do not combust but instead can be collected and stored for later use (Foster et al., 2021). Syngas is constituted by H_2, CH_4,CO, CO_2, H_2O and N_2 with trace amounts of other hydrocarbons like propane and ethane. It could be used in the chemical industry, as a fuel to produce heat and electricity or conversion into ethanol (Clarke Energy, 2019).

Pyrolysis process is a thermal degradation similarly to gasification where partial oxidation is used to maintain the thermal conditions, and 3 products are obtained: solid coke, pyrolysis gas and pyrolysis liquid (Foster et al., 2021). Comparatively to gasification, pyrolysis works on lower temperatures of around 300–700 °C (Lam et al.,2016). One of the main advantages of pyrolysis against other processes is the higher energy density of the products produced, typically, the pyrolysis gas, liquid and coke have calorific values of 5–16 MJ/kg, 22–25 MJ/kg and 33 MJ/kg respectively (Foster et al., 2021).

Hydrothermal liquefaction is the thermochemical conversion of biomass into oils referred to as 'biocrude oil' and the main advantage of this process is that water has a high dissociation constant at the operating conditions used in the process, providing means for processing wet biomass without drying (Foster et al., 2021). The process is performed in a pressurized environment from 4 to 22 MPa, which avoids oxygen and heats to elevated temperatures between 250 and 374 °C (Elliott, 2015). Biocrude oil obtained from pig manure and digestate sludge at operating conditions of 300 °C, 10–12 MPa and 30 min reaction time, yielded 30% and 9.4% respectively with calorific values of 34.7 MJ/kg and 32 MJ/kg (Vardon et al., 2011).

Foster et al., 2021 assessed the main advantages and disadvantages of the different waste-to-energy processes. Based on his research table 4 was performed:

Table 3- Advantages and disadvantages of waste-to-energy processes

PROCESS	ADVANTAGES	DISADVANTAGES
ANAEROBIC DIGESTION	• No need high temperatures and complex systems • Processes wet biomass	• Limited feedstocks • Economic concerns (Large plant waste treatment)
GASIFICATION	• Low flue gas volumes • Low levels of Sox and NOx • High thermal efficiency	• Preparation and pre-processing • Economic concerns (Higher temperatures)
PYROLYSIS	• Low flue gas volumes • Low levels of Sox and NOx • Product with higher energy density	• Preparation of feedstock-reduce particle size • Higher waste residue
HYDROTHERMAL LIQUEFACTION	• Processes wet biomass • Bio crude oil can be refined to match petroleum-based fuels from waste streams	• Only validated in the laboratory environment • Expensive process (Components to operate in a corrosive environment)

As referred in Fuel Cells Bulletin, 2020, the Powerhouse Energy group has developed an exclusive technology (DMG), an innovative and highly efficient thermal conversion of waste into energy. DMG is a new type of Chemical Recycling, a form of Advanced Thermal Conversion Technology that takes unrecyclable plastics and recovers the maximum amount of calorific value (energy) through an innovative approach to waste management. The process involves the plastic being heated to very high temperature and then vaporises into a mixture of gases. Further heating within the chamber reforms the molecules into a synthetic gas “syngas”. There is no burning in the process since the chamber operates in oxygen absence. However, a non-combusting oxidising agent in the form of steam is added to control the process and the quality of the syngas. The resulting gas is similar in calorific value to the natural gas. It is important to refer that a small portion of the syngas produced is used to heat the thermal conversion chamber, making the whole process self-sustaining (Powerhouse,2021).

As it can be seen in figure 10 , a by-product of the process is heat that can be captured and made available for sale. The energy rich syngas is then processed to generate electricity and sustainable hydrogen using a series of engines that generate electrical power.

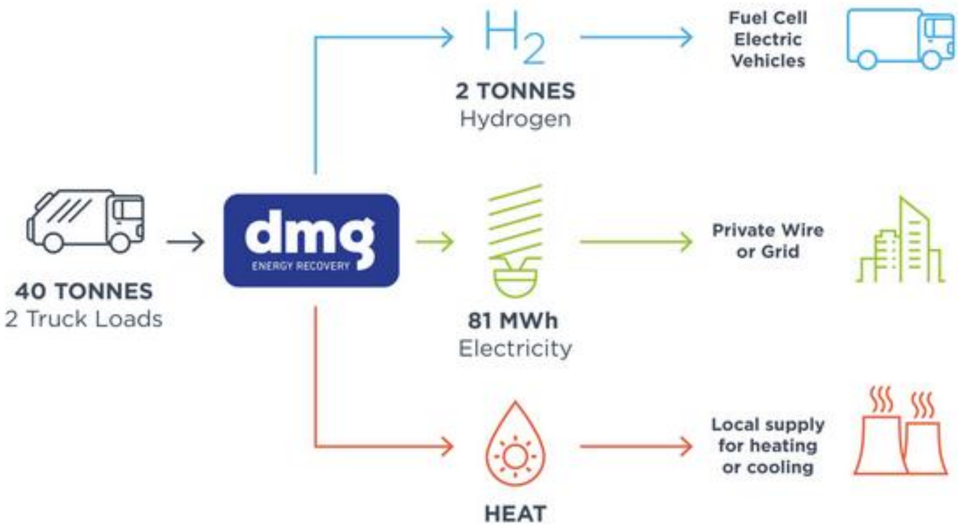

Figure 10- DMG products and applications (Powerhouse, 2021)

As presented above, pyrolysis and hydrothermal liquefaction are two possible solutions for energy recovery through waste. Both processes are used approaches to convert biomass or organic wastes into liquid bio-oils or other fuels and value-added chemicals (Araujo, 2018; Baloch, 2018; Li, 2015; Lian, 2017). Among all the energy sectors, transport sector, which mainly relies on liquid fuels, consumes the largest part of the energy, and is predicted to reach nearly 3.3 billion worldwide by 2040 (Capuano,2000). High-power transport vehicles, such as aeroplanes, long-haul trucks, and ships, will still require high energy-density fuels, consequently potential alternatives to liquid fuels are required to meet the energy demand and the most alternatives could be renewable and sustainable fuels or fuels that can be produced from renewable feedstocks and their combustion produces less greenhouse emissions (Kumar, 2021). In addition, it has been also reported that the combustion of fuels produced from waste emits lower amount of NO_x and SO_x compared to conventional liquid fuels, like bio-oil or bio-based jet fuel, which consequently could help to reduce greenhouse emissions (Khodier, 2009). A study performed by Oasmaa, 2001, demonstrated the comparison of bio-oil combustion with heavy fuel oil in an industrial boiler and results showed that NO_x emissions for bio-oil were 88 mg/MJ, while the combustion of heavy fuel oil produced NO_x emissions of 193 mg/MJ.

Bio-oil upgrading is essential to produce bio-oil as a transport fuel or for its direct use in the boilers and turbines for heat and power generation (Kumar,2021). Upgrading processes include different strategies to improve bio-oil properties, mainly based on the feedstock treatment, such as dry torrefaction (Bert, 2017), wet torrefaction (He, 2018), acid and alkali treatment (Cao, 2019), steam explosion (Wang, 2011) and downstream treatment such as emulsification (Leng, 2018), solvent addition (Li, 2016) and filtration (Javaid, 2010).

Bio-oil obtained from thermochemical techniques could also be a suitable feedstock for steam reforming for production of H_2 or a mixture of CO and H_2, called syngas (Adeniyi, 2019). H_2 produced from steam reforming of bio-oil can be further used as a clean fuel, while syngas can be further used on the Fischer-Tropsch process for production of hydrocarbons (Kumar, 2021).

Extensive research has been carried on both pyrolysis and hydrothermal liquefaction for optimization process parameters and selection of biomass feedstock to obtain higher yield and quality bio-oil. Energy conversion rate of the pyrolysis and hydrothermal for a biomass feedstock at any temperature can be obtained using (1) and (2) (Kumar, 2021):

(1) $$\eta = \frac{Qr - Qp}{Qb} \times 100\%$$

Qr-*Heat recovered*
Qp-*Heat obtained by pyrolysis*
Qb-*Heat obtained by the biomass*
mg-*Mass of gas*
ml-*Mass of liquid*
mc-*Mass of char*
HHV g- *Higher heating value gas*
HHV l-*Higher heating value liquid*
HHV c-*Higher heating value char*

(2) $$Qr = HHV\ g \times m\ g + HHV\ l \times m\ l + HHV\ c \times m\ c$$

Comparative studies suggest that hydrothermal liquefaction produces better bio-oil quality compared to pyrolysis (Choi, 2019), since it showed better thermal stability and higher heating value when compared to the pyrolytic oils (Jena, 2011).

3.4 Reverse Logistics and municipal solid waste management

To achieve a process that allows energy recovery using cigarette butts it is necessary to have a logistics system that enables the creation of a closed loop supply chain. A closed loop supply chain is achieved by implementing reverse logistics. Reverse logistics has gained increased importance as an environmental, profitable, and sustainable business strategy due to the importance of such operations for firms in every industrial sector. The concept of reverse logistics has not been defined precisely, probably due to its rapidly growing and importance role.

To systematize information of recent literature about reverse logistics definitions, table 5 was performed.

Table 4- Reverse logistics definitions review

AUTHORS	DEFINITION
THIERRY ET AL., 1995	"all those activities that encompass the management of all used and discarded products, components, and materials that fall under the responsibility of a manufacturing company. The objective of product recovery management is to recover as much of the economic (and ecological) value as reasonably possible, thereby reducing the ultimate quantities of waste"
KROON AND VRIJENS, 1998	"Reverse Logistics refers to the logistics management skills and activities involved in reducing, managing and disposing of hazardous or non-hazardous waste from packaging and products"
STOCK, 1998	the role of logistics in product returns, source reduction, recycling, material substitution, reuse of materials, waste disposal, and refurbishing, repair and remanufacturing".
CARTER AND ELLRAM, 1998	"Reverse Logistics is a process whereby companies can become more environmentally efficient through recycling, reusing and reducing the number of materials used. Viewed narrowly, it can be thought of as the reverse distribution of materials among channel members. A more holistic view of Reverse Logistics includes the reduction of materials in the forward system in such a way that fewer materials flow back, reuse of materials is possible, and recycling is facilitated".
ROGERS AND TIBBEN-LEMBKE, 1999	"The process of planning, implementing and controlling the efficient, cost effective flow of raw materials, in-process inventory, finished goods and related information from the point of consumption to the point of origin for the purpose of recapturing or creating value or for proper disposal"
DOWLATSHAHI, 2000	"a process in which a manufacturer systematically accepts previously chipped products or parts from the point for consumption for possible recycling, remanufacturing or disposal."
HILLEGERSBERG ET AL., 2001	"The logistics of return flows, called Reverse Logistics, aims at executing product recovery efficiently"
DE BRITO AND DEKKER, 2004	"The process of planning, implementing and controlling backward flows of raw materials, in-process inventory, packaging and finished goods, from a manufacturing, distribution or use point, to a point of recovery or point of proper disposal"
RL EXECUTIVE COUNCIL, 2019	"RL is the process of moving goods from their typical final destination to another point, for the purpose of capturing value otherwise unavailable, or for the proper disposal of the products".

Logistics processes include both forward logistics and reverse logistics. Reverse logistics covers a series of operations within a supply chain system which involves product returns from downstream members to the upstream, product reprocessing, and remanufacturing. In fact, proper reverse logistics management is related to many different measures which are implemented in the supply chain (Alshamsi and Diabat, 2015). Many organizations face challenges in implementing their reverse policies. For a successful reverse logistics, it is very important to understand failures that affect the reverse chain and perfectly define the expected objectives to be achieved. This concept plays a key role in promoting an environmentally friendly operation, since with the collection and reuse of disposed products, the generation of new waste is avoided, as well as its incorrect disposal in the environment (Guarnieri et al., 2020).

To meet the needs of society, natural resources are transformed into processed products that are discarded when they reach the end of their useful lives. In other words, these resources reach the ends for which they were created, generating what is called solid waste. The growing increase in the disposal of this material in the environment is due to the disordered growth of the population and income per capita, related to the inadequate production and consumption process, leading to the deterioration of the natural environment (Hajar et al., 2020). Peña-Montoya et al.,2020, states that there is complementary relationship between sustainable solid waste management and reverse logistics, which can be observed in practices widely disseminated in the literature. Moreover, the main articles on sustainable solid waste management provide significant information that confirms this relationship.

One of the main goals of reverse logistics is the creation of waste flows characterized by both ecological efficiency and economic effectiveness. To do so, it is necessary to form closed loop systems through the integration and coordination of activities and information concerning waste materials in an economic system. Solutions applied in the creation of closed loop systems, also with reference to municipal waste, include:

1. Technologies for the recovery of energy from waste (Soltani, Sadiq and Hewage, 2017; Fernández-González, Grindlay, Serrano-Bernardo, Rodríguez-Rojas & Zamorano, 2017)
2. Tightening the system of waste management with respect to effective separate collection of waste, reduction of illegal landfills, building facilities for processing waste and the reduction of environmental hazards connected with the transportation of waste (Wolniakowska and Ławińska, 2016; Zlamparet, Tan, Stevels and Li, 2018),
3. Application of lean production to realize and shorten the processes of regeneration (Kurilova-Palisaitiene, Sundin and Poksinska, 2018),
4. Raising ecological awareness (Bittar, 2018),
5. Optimization of pricing and brand investment decisions regarding remanufactured products (Choi, 2017),
6. Introduction of digital technology into remanufacturing processes (Yeo, Pepin and Yang, 2017),
7. Implementation of product life-cycle management (Miah, Griffiths, McNeill, Halvorson, Schenker, Espinoza-Orias, Morse, Yang and Sadhukhan, 2018).

Bing,et. al, 2016 research challenges in municipal solid waste logistics management and proposed that the decision-making process should be divided into two levels as presented in figure 11. External drivers or incentives that can influence decision making on the reverse logistics network and processes were identified by Bekker et al., 2004: economics, legislation, and extended responsibility (public, social and economic). Despite the obvious environmental gain from waste recycling, collection and transportation of recovered products have an environmental burden due to greenhouse gas emissions, and so minimizing this burden is important in order to increase the total environmental gain from recovery (Tsoulfas and Pappis, 2006). To meet the future demand of sustainable development, the output of the decision making on municipal solid waste management is a sustainable performance (Figure 11).

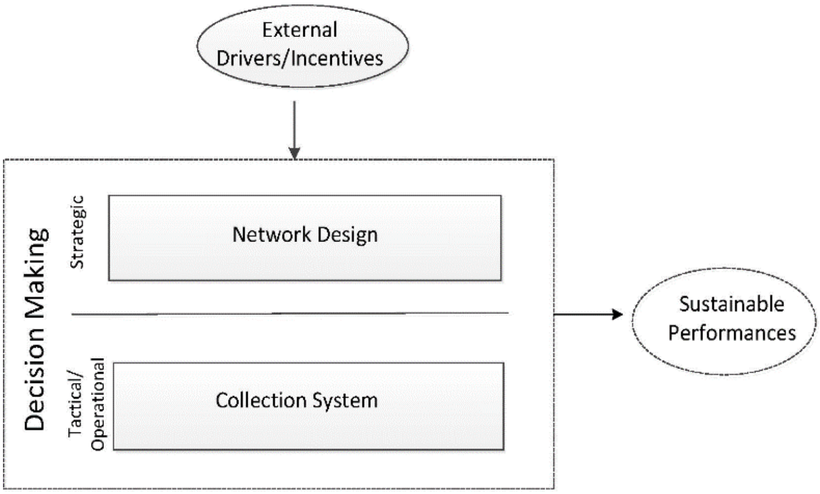

Figure 11-Framework of reverse logistics for household waste recycling (Bing,et. al, 2016)

At the strategic level, decisions are made at the network design of a recycling network which includes the process of collection, separation, sorting, and re-processing (Figure 12). The separation of recyclable waste is done at collection point while in other cases the waste is collected and sent to a separation center for this procedure. After this process, the waste is sent to a sorting centre, where further sorting by colour and composition is conducted. At cross-docking centers is where transhipment and baling of waste is done. Then, sorted waste will be transferred to specialized treatment facilities to be re-melted or transformed for recycling (Bing,et. al, 2016).

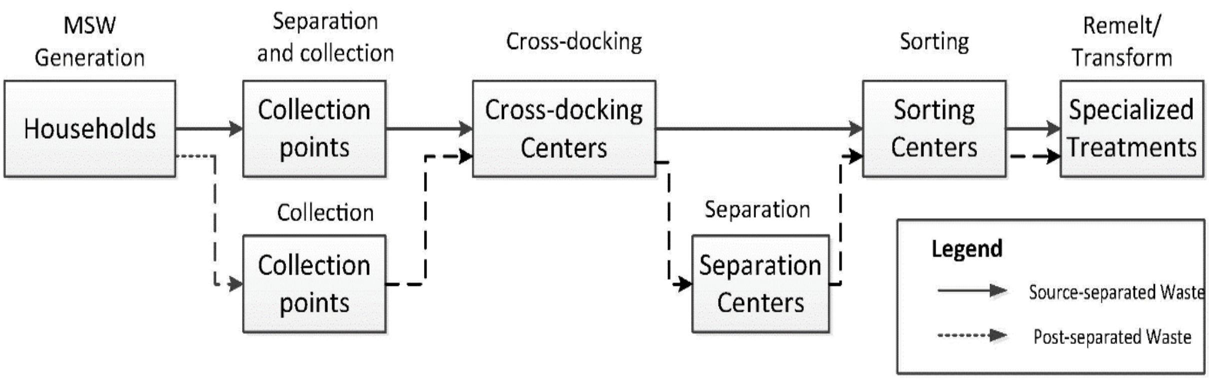

Figure 12-Recycling network flow of municipal solid waste (Bing,et. al, 2016).

3.4.1 Risks and Uncertain demand on logistics (Waste management)

As we are dealing with a waste product, and therefore its flow is not constant in terms of quantity and quality, it is important to analyse the risks and uncertainty associated with this issue in the logistics process. The complexity of the green supply chain has increased from being an open-loop supply chain to being a closed-loop supply chain, from being a single supply chain to being a network supply chain, assuming deterministic demand mostly infeasible. More research is required to investigate complex green supply chains models with stochastic demand, dynamic rather than static networks, and asymmetric information (Keyvanshokooh et al., 2013; Lieckens and Vandaele, 2007; Niknejad and Petrovic, 2014; Pishvaee et al., 2011; Zhang et al., 2014).

Within the topic of cigarette butts reuse solutions and promotion of the circular economy it becomes very important to assess and investigate how to deal with risks and uncertainty of demand in the supply chain and how this affects the logistics processes.

According to ISO (2009), organizations of all types and sizes face internal and external influences and factors that brings uncertainties towards their goals. Thus, the effect that these uncertainties present on the process of achieving the objectives of an organization is called *risk* (ISO, 2009). According to several theories, companies tend to protect themselves to mitigate different types of risks, such as credit rationing, information asymmetry and financial difficulties (Bodnar, 2019). Saglam et al., 2020, highlights other types of risks that companies are exposed to, such as supply risks, logistical risks, relational risks, and demand risks. In addition to these typical risks, increasing awareness for sustainable practices brings additional risks. Considering the dimensions of sustainability, these risks include environmental, economic, and social risks. On the economic side, this perception is also shared by Nguyen and Vo, 2020, who argue that corporate risk management improves issues related to companies' financial vulnerability.

In waste management logistics, there are transportation issues of the used materials going through a collection of units regarding recycling process, such as refurbishing, remanufacturing, disassembly, and disposal (Tsao et al., 2017). From the view of supply chain, the resulting network is known as closed-loop supply chain, where the product lifecycle management is integrated with its logistics solutions comprehensively (Govindan et al., 2015). Product data throughout the whole lifecycle should be tracked whether they have reached their end-of-life in order to design and optimize such a network.

Uncertainty is a significant factor encountered in forward and reverse logistics network design that could be originated from both physical and information flows. Lee and Dong, 2009, affirm that there is a higher level of uncertainty for product recycling system when compared to the forward logistics modelling. Uncertainty could be found in market demand, processing capacity of each facility, return quantity of the recycled materials, quality variation of the return flow and relevant cost parameters (Yadollahinia et al., 2018).

Stochastic programming formulates the uncertain sources based on random characteristics using probability distributions (Chen et al., 2007). Programming using fuzzy set theory provide more tools to handle the uncertain scenarios in the real world and have been increasingly studied to deal with the close loop supply chain and reverse logistics problems in the last decade. There are generally two types of scenarios regarding the uncertainty, that is flexibility in constraints and epistemic uncertainty in data, which are handled by flexible programming and possibilistic programming (Wu et al., 2018).

3.5 Conclusions

Circular economy is seen as a strategy for sustainable development. The central topic of this concept is the use of resources in closed loop systems, reducing pollution, avoiding resource mismanagement while contributing to economic growth. Based on the 6 concepts of the circular economy, it is possible to create solutions that enable the reuse of different materials. In this third chapter it was analysed the solutions that exist today for the valorisation of cigarette butts, and it is possible to conclude that exist some solutions in the literature with good results. However, all the solutions presented lack of detailed economic and sustainability analysis, and moreover none of them were realized with the possibility of being scalable to industrial level. As most of the solutions are in an embryonic phase, it is very interesting to develop new strategies for the recovery of this waste.

Since the energy sector is in great expansion and development, new sources of energy have been evaluated, and for this reason the recovery of energy from waste by different processes such as anaerobic digestion, gasification, pyrolysis, and hydrothermal liquefaction have been widely developed. These processes could possibly be applied to cigarette butts in order to produce energy.

To achieve a process that allows energy recovery from cigarette butts it is necessary to have a logistic process that enables the creation of a closed loop supply chain. For that, it is fundamental to have a structured and sustainable management of this waste, which complemented with reverse logistics allows the creation of efficient waste flows to have an efficient process integrated in an organised chain. The reverse logistics of cigarette butts, whose quantity and quality varies according to spatial and temporal location, is complex and for this reason it is very important to assess and investigate how to deal with risks and uncertainty of demand in the supply chain.

4.Research Agenda and Methodology

4.1 Research Scope

During the last years circular economy has been receiving greater attention from companies, which recognize that this concept contributes to a profitable and sustainable alternative to traditional business. Circular economy is seen as a remarkable opportunity for companies to respond proactively to environmental regulations, since the use of resources within closed-loop systems allows to reduce pollution, avoid leakage while sustains economic growth.

This concept is seen as a future solution for sustainability on a global level. Its advantages are undoubted, however many of its applications lack research and scientific evidence at logistics and supply chain resilience level. The literature shows that the use of cigarette butts for value creation is possible, but studies lack consistency as they are rarely performed on a scale beyond the laboratory and many lack economic and sustainability analysis. Furthermore, all the solutions found are in an embryonic state and we should investigate new ways of valorisation. The energy sector is growing fast, and it has been concluded that other energy sources will play a major role in the future, consequently energy recovery from cigarette butts could be a good way to contribute and develop alternative resources. The studies carried out at the cigarette butt recycling level do not include logistical scenarios that make it possible to access the material to produce the final product in a uniform and structured manner. Using circular economy concept and supply chain management, the future study aims to develop a solution to create value through cigarette butts. The research questions for the following work will be:

(1) What is the most efficient way to valorise cigarette butts?
(2) Energy recovery from butts is a viable and sustainable process?
(3) Which supply chain decisions increase the sustainability and efficiency of the logistics process?

Figure 13 provides an overview of the research. The methodology of this work will be divided into two parts: laboratory research to develop a practical solution for cigarette butt's valorisation and an analysis of a logistic process and development of an optimization model to minimize the costs of a company that will recycle cigarette butts according to the solution found in the laboratory. The initial part of the scheme highlights the logistical issue of the research. In this study, a logistical process of cigarette butts' collection at the municipal and district level is going to be proposed, which will enable the development of the cost optimization model of the company that will valorise this type of waste. The second part of the diagram depicts the laboratory procedure of developing the solution for waste valorisation. Initially the cigarette butts are characterized to access the main components and properties. This characterization allowed understanding that the liquefaction process would be feasible to produce a bio-oil. Next, the production of the bio-oil was optimized by changes in the experimental procedure. To finally understand the quality and potential application of the bio-oil, its characterization was performed.

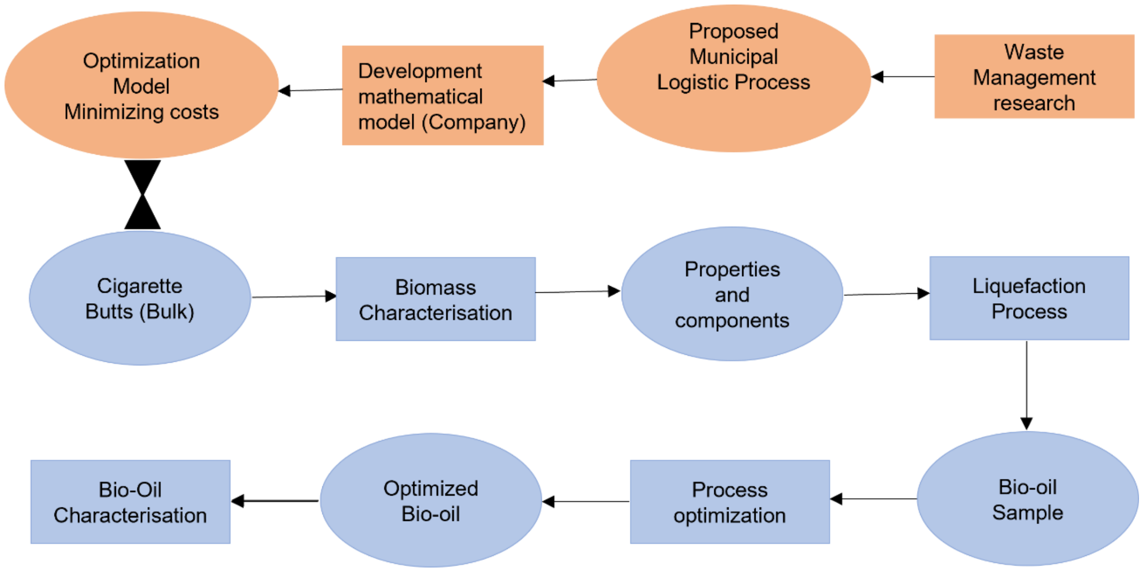

Figure 13- Research overview

4.2 Laboratory Research

4.2.1 Overview

Chapter 4.2 details the experimental procedure and is divided into 5 subchapters. Each subchapter relates to a specific process implemented during laboratory research. A diagram with an overview of the process is presented in figure 14 below. In the diagram is represented, in a simplified form, the process that led to the investigation of a solution for the valorisation of cigarette butts. Initially this type of waste was characterized through analyses such as Fourier transform infrared (FTIR) spectroscopy, Thermogravimetry (TGA) and Gel permeation chromatography (GPC). After initial characterisation and result's analysis it was concluded that liquefaction is a good approach for cigarette butt´s valorisation, since cellulose acetate (main filter component) is a very good source of organic carbon and can be converted into high valued liquid products by suitable thermochemical conversion methods.

After this initial characterisation stage, the liquefaction reactions were carried out. The liquid obtained from the reaction was subsequently filtered to produce bio-oil and later characterized using the techniques mentioned above and elemental analysis to obtain higher heating values for each bio-oil.

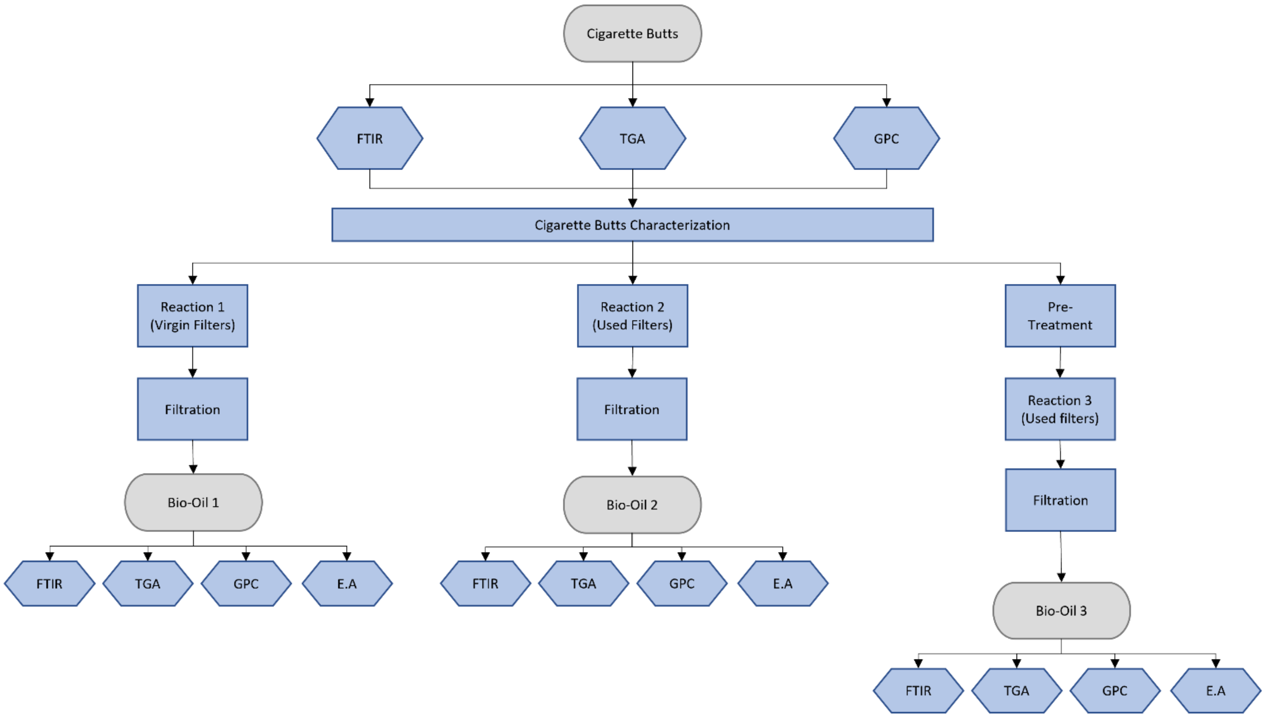

Figure 14- Laboratory Research Overview

4.2.2 Materials and Equipment

The material and equipment provided belong to the CERENA (Centro de Recursos Naturais e Ambiente) research centre. A variety of material was used during the investigation. Table 6 shows the complete list of equipment by category used throughout the work. Material and equipment used can be divided into two categories: processing and material characterisation.

For the reaction were used cigarette butts or virgin filters, 2-Ethylhexanol and *p*-Toluenesulfonic acid.

Cigarette butts were randomly collected in different locations in the city of Lisbon. The virgin filters used in the tests were purchased and are from brand “Smoking”. For the liquefaction reaction were also used *2-Ethylhexanol*, used as solvent in this study, and *p*-Toluenesulfonic acid used as catalyst.

In figures 15 and 16 it can be seen the assembly of the material used for reaction and filtration processes; in both cases processing material was used which is described in table 5.

Table 5-List of most important material and equipment used in the laboratory

Material and Equipment Category	**Equipment**
Processing	Heating Mantle
	2 L glass reactor with 4 tubing and quick closure clamps
	Thermometer
	Condenser
	Heidolph RZR 2102 control electric stirring motor
	Buchner filter
	Vacuum Machine.
	Buchner filter
	Vacuum Machine.
	Shaft with Teflon paddles
	Seal for agitation shaft
	Vacuum Machine.
	Thermocouple
	Honeywell temperature controller with thermostat
	2l Kitasato balloon
	Büchner funnel
	Dean-Stark
	Filter paper
	Vacuum pump, Ilmvac GmbH, type P 12 Z
	Blue M Furnace, Thermal Gravity Stabilizing Furnace OV-18C
	IKA VWR rotary evaporator
	IKA RV10 vacuum controller
	IKA HB10 heating bath with silicone oil
	Vacuubrand 2c vacuum pump
	Neslab endocal condenser
	500 ml flask for solvent collection
Characterisation	JASCO CO-4061 columns
	JASCO PU-4180 pump
	JASCO RI-4030 refraction detector
	UV and visible detector JASCO UV-4075
	PerkinElmer Spotlight 200i FTIR
	Hitachi STA7200 Thermal Analysis System

Figure 16-Processing equipment

Figure 15- Processing equipment

For material characterisation the available equipment allowed the determination of chemical composition, moisture contents and thermal behaviour analysis. For chemical analysis a PerkinElmer Spotlight 200i FTIR (Figure 17) with Attenuated Total Reflectance (ATR) was used. This allowed to obtain the infra-red spectra of several material samples to compare them and assess molecular bonding elements with the peaks shown. For thermal stability and degradation analysis the equipment used was a Hitachi STA7200 Thermal Analysis System (Figure 18). Finally, for the determination of the average molecular weight of the samples the equipment for GPC shown in figure 19 was used.

Figure 17-Hitachi STA7200 Thermal Analysis System (Hitachi, 2021)

Figure 18-PerkinElmer Spotlight 200i (PerkinElmer, 2021)

Figure 19- Column equipment GPC(Jasco, 2021)

4.2.3 Cigarette Butts Characterisation

Step 1- FTIR analysis

Fourier transform infrared (FTIR) spectroscopy is a form of vibrational spectroscopy that is useful in the study of a variety of soil chemical processes. It is crucial to use this technique to characterise the cigarette butts before proceeding with the development of the valorisation process itself. This analysis is useful as a quantitative analytical method and as a tool to determine bonding mechanisms in solids and on surfaces since molecular vibrations can be related directly to the symmetry of molecules and so it is often possible to determine the composition of determined materials (Peak, 2005). The analysis was performed using both clean filters and a used filter-cigarette butts. The spectrum obtained is represented by the transmittance index as a function of wavenumber and can be divided into three distinct zones, these being the far-infrared zone (<400 cm^{-1}), the mid-infrared zone (between 400 cm^{-1} and 4000 cm^{-1}), and the near-infrared zone (between 4000 cm^{-1} and 13000 cm^{-1}). In the present dissertation, frequencies in a range from 600 cm^{-1} to 4000 cm^{-1} were used, the range where the bond vibration energies of the most important components of the analysed samples are located based on records from previous literatures. In the following table are wavenumber ranges corresponding to typical absorbance peaks for some functional groups of bio-oils.

Table 6- FTIR functional group compositional of different bio-oils (Hassan,2009)

Group	Absorbance	Class of Compounds
O-H (stretching)	3050-3600	Phenols, alcohols, water
C-H (stretching)	3000-2800	Alkanes
C=O (stretching)	1750-1650	Ketones, Quinones, Aldehyde groups, carboxylic acids
C=C (stretching)	1680-1580	Alkenes
C-H (bending)	1470-1350	Alkanes
C-O (stretching)	1300-950	Primary, Secondary, and Tertiary alcohol aromatic groups
C-H (bending)	900-700	

Step 2- TGA analysis

Thermogravimetric Analysis (TGA) is a technique in which the mass of a given substance is monitored as a function of temperature or time while it is subjected to a controlled atmosphere at various temperature levels. TGA measures the mass of a sample while it is heated or cooled in a furnace. This device consists of a sample plate supported by a high-precision balance where the heat treatment takes place, the furnace, temperature controller, furnace atmosphere controller, and data logging system. TGA machine relates to a computer for special data processing and analysis. A Hitachi STA7200 machine was used in this study. Approximately 4.106 mg of the filter was taken from random cigarette butts for the first analysis and 4.522 mg of a clean filter was used for the second analysis. For each TGA experiment was used a flow of 100 mL/min of nitrogen. The heating programme consisted of an initial holding for 3 min at 30°C, then a ramp at 5 °C per min from 30°C to 240 °C, followed by an isothermal at 240°C for 5 min and finally a ramp at 5 °C per min from 240 °C to 600 °C.

Step 3- GPC analysis

Gel Permeation Chromatography is a technique used to determine the average molecular weight distribution of a polymer sample. It is also possible to obtain qualitative data about the branching of long chains and/or determine the distributional composition of copolymers. This technique is based on separating the molecular structure of the sample according to size or hydrodynamic radius. The device for this type of analysis consists of a pump that drives the solvent (THF) through the instrument, an injection port to introduce the sample, the column to contain the stationary phase, detectors to detect the compounds leaving the column and software to control the different zones of the column and display the results.

In the present dissertation, the molecular weight distribution of bio-oil was determined on a column with the following equipment:

- JASCO PU-4180 pump;

- JASCO CO-4061 column;

- JASCO UV and visible detector UV-4075;

- JASCO RI-4030 refraction detector;

- Chrom NAV GPC software.

Initially, 0.0614g of virgin cigarette filter was dissolved for about 20 minutes at room temperature and at 400 rpm in 60 mL of tetrahydrofuran and 0.0694g of used cigarette filter in 70 mL of tetrahydrofuran . After making sure that the samples were fully dissolved in the solvent, they were injected one at a time into the GPC instrument. With the results obtained by the computer it was possible to plot the chromatogram and molecular weight distribution curve for the two samples.

4.2.4 Bio-oil Production

After the characterization of cigarette butts and consequent analysis of the results, it is concluded that liquefaction may be a viable option for their valorisation to produce a bio-oil using a batch reactor. This sub-chapter will describe the process used to produce the bio-oil in the laboratory.

1st Experiment

In the first experiment virgin filters were used. The pre-treatment of the filters was simply to split them into smaller pieces. The operating conditions considered were:

Temperature: 160ºC

Reaction duration: 4 hours

It was used a biomass-to-solvent ratio of 1:5 and 3% of catalyst of the total weight (biomass+solvent). Therefore, it was weighted:

Virgin filters (Biomass)- 25,04 g

2-Ethylhexanol (Solvent)- 125,04 g

***p*-Toluenesulfonic acid** (catalyst)- 4,5 g

2nd Experiment

This experiment was performed using exactly the same main steps as the first experiment. However, the biomass used was cigarette butts picked up from random locations. The pre-treatment performed was to split the cigarette butts into smaller parts.

It was used a biomass-to-solvent ratio of 1:5 and 3% of catalyst of the total weight (biomass+solvent). Therefore, it was weighted:

Cigarette butts (Biomass)- 25,17 g

2-Ethylhexanol (Solvent)- 126,12 g

***p*-Toluenesulfonic acid** (catalyst)- 4,52 g

3rd Experiment

In this experiment the same conditions and main steps were used as in the previous two experiments. The biomass used was cigarette butts collected at random locations. However, the pre-treatment performed involved removing the wrapping paper present in the filter and also tobacco remains. The final step of the pre-treatment was splitting the filter into lower parts.

It was used a biomass-to-solvent ratio of 1:5 and 3% of catalyst of the total weight (biomass+solvent). Therefore, it was weighted:

Cigarette butts (Biomass)- 25,35 g

2-Ethylhexanol (Solvent)- 125,40 g

***p*-Toluenesulfonic acid** (catalyst)- 4,5 g

Main Step 1- Hydrothermal Liquefaction

In all tests the same conditions were used, previously established. Regarding the mass proportions of reactants, the biomass and solvent were fed to the reactor in a 1:5 ratio. The catalyst added, corresponds to 3% of the total sum of solvent and biomass masses. As for the operating conditions, the reaction time and temperature parameters were set at 4 hours and 160ºC respectively.

The laboratory procedure began with the assembly of the reactor. This was placed on a heating mantle that in turn was connected to the temperature controller. On a Sartourius GP 3202 technical balance, the biomass (cigarette butts), 2EH solvent and APTS catalyst were weighed and promptly fed to the reactor. Next, the stirring shaft connected to the electric stirring motor was installed and the reactor was closed with the lid and locking clamp. The thermocouple connected to the heating mantle, the nitrogen current to render the interior atmosphere inert, and the Dean-Stark apparatus coupled with the condenser were inserted into the reactor tubing. The Dean-Stark apparatus allows the system to collect the water and solvent that evaporate during the reaction and condense into it, thus avoiding the possible total reflux. Once the system is installed, the agitation is started by the electric motor, the nitrogen valves that feeds the reactor and the condenser's mains water are opened, as well as the controller with a Set-Point set at 160ºC. This way the thermocouple reads the temperature within the reaction mixture and as soon as the desired value is reached. The controller suspended the heating, keeping the temperature at the constant Set-Point value. After 4 hours of reaction (started when the Set-Point is reached), the controller was turned off and agitation was maintained in order to accelerate the cooling process.

Main Step 2- Filtration

The mixture resulting from liquefaction process, consisting of a liquid phase and a solid phase is subsequently subjected to filtration for phase separation. The required equipment is described in section 4.2 and the filtration system used is represented in figure 16. When the reaction mixture in the reactor reached about 40°C, the system was disassembled, and the reactor was removed. The Kitasato flask was connected to the vacuum pump and the Büchner funnel covered with filter paper was placed in the right position. The pump was turned on, thus creating vacuum conditions inside the Kitasato flask. The contents of the reactor were poured into the funnel over the filter paper and separation began immediately. The solid phase (solid biomass residue) was retained on the filter while the liquid phase (bio-oil) was poured into the flask and stored in a properly labeled container. Filtration was again started, however this time the solid waste was washed with acetone to remove the remaining bio-oil solvent content. The contaminated acetone was also stored for later recovery and reuse and the solid residue was placed in the oven for 24 hours at 110°C to evaporate traces of solvent, water and acetone.

Main step 3- Weighing the solid residue and calculating the liquefaction yield

With the dry solid phase, it is possible to determine the yield of the process, i.e., the mass of biomass resulting from its liquefaction in detriment of the initial amount of the same fed to the reactor. To do this, the following equation is used, considering that the calculation has errors associated not only with the experimental technique itself, but also accounts for the complete polymerization of compounds, which by itself does not provide a total yield.

$$(\mathbf{4})\, Liquefaction\ Yield\ (\%) = \left(1 - \frac{Mr}{Mi}\right) \times 100$$

Mr- Mass of the residue

Mi- Initial mass of biomass

4.2.5 Bio-oil Solvent extraction

The liquid phase resulting from the previous process is as already mentioned, composed of bio-oil and 2ET solvent used in liquefaction. It is imperative that the solvent must be removed to proceed the study of the properties of the bio-oil. The material used in this process is described in section 4.2. The liquid mixture previously stored in a container was transferred to a 500 ml flask that is installed in the rotavapor. The heating bath was turned on and when the temperature of the silicone oil reached 140°C (saturation temperature of the solvent), the flask is partially immersed in it. At that instant the rotor was turned on at a speed of 80 rpm thus starting the extraction process along with reducing the system pressure to the minimum possible value (about 11 mbar recorded). Since the solvent is more volatile than the bio-oil, it evaporates faster with decreasing pressure (at constant temperature), thus the 2ET rises through the column where the vapor meets the condenser walls where a cooling liquid passes. Therefore, the solvent condenses to the solvent collection flask and is available for reuse. When no further condensation of the solvent is observed, the operation is stopped, and the resulting concentrated bio-oil transferred to a storage tube.

4.2.5 Bio-oil Characterisation

After Bio-Oil Production, characterisation was carried out through **FTIR**, **TGA** and **GPC** using the same method and technology described above in the characterisation of virgin and used cigarette butts. After the solvent extraction, an analysis was held to obtain values of higher heating values (MJ/KG).

Higher Heating Value

The Higher heating value is considered the most important factor in qualifying a fuel, and it is difficult to determine its value for energy sources such as biomass due to the variety of chemical structure. Usually, the calorific value is specified by burning a sample in a calorimeter under controlled conditions.

Alternatively, the higher heating value can be obtained by performing an elemental analysis of the samples in order to identify the carbon, hydrogen, oxygen, nitrogen and sulphur contents and with these data, use an empirical correlation to estimate with maximum precision the desired parameters. In this dissertation the calorific value of bio-oil and solid waste samples was determined using equation 5. (Arshadi, et. al, 2008).

$$(\mathbf{5})\ HHV\ (MJ/Kg) = -5.5232 + 0.2373N + 0.4334C + 0.2360H + 0.3732S + 0.00083800$$

4.3 Logistic Process

It is clear that the solution found for the valorisation of cigarette butts will always depend on the availability of biomass for the process. For this reason, it is essential to analyse the management of cigarette butts at the municipal and district level and to optimize the interactions between municipalities, districts, and a (fictitious) recycling company.

This chapter intends to analyse municipal cigarette butt waste management under the prospective of circular economy in order to propose some principles for the efficient collection of cigarette butts.

4.3.1 Municipal cigarette butts waste management proposal

After contacting some associations such as *Zero Waste Lab*, *Biataki*, *Trash traveller* and *Missão Beatão* it was possible to see that there are many private initiatives that intend to manage this waste in order to minimize the pollution. However, the impact that these initiatives have is still small given the scale of the problem in question. The truth is that these initiatives seek to mitigate the problems caused by the lack of management of this type of waste.

Since it is obvious that the solution to this problem will have to go through the action of public entities, the city of Cascais was contacted with the objective of understanding what are the main obstacles and drivers to the management of cigarette butts. After two meetings with the president of the parish council of *Cascais Estoril*, Pedro Morais Soares, it was possible to reach some main conclusions:

1. The collection of cigarette butts is extremely important, and it is necessary to propose solutions to the problem.
2. It is believed to be an expensive and difficult process.
3. Citizens need to be made aware of the cause.
4. There is no form of valorisation, so there is no interest in collecting cigarette butts.

Based on the conclusions drawn and after some discussion some solutions may be considered. It is important to mention that this is a purely theoretical analysis that was not based on an exhaustive economic evaluation in order to sustain the hypotheses.

Currently in Portugal there is a Law no. 88/2019 stablishing (Diário da República n.º 168/2019, 2019):

- *The disposal in public space of cigarette butts, cigars or other cigarettes containing tobacco products is prohibited*.
- *Commercial establishments, namely catering and drinking establishments, establishments where recreational activities take place and all buildings where smoking is prohibited must have ashtrays and equipment for the disposal of undifferentiated and selective waste produced by their customers, namely receptacles with hinged lids or other devices that prevent the spreading of waste in public space.*

- *The establishments referred to in the previous number must also clean the waste produced in the commercial occupation areas and in a 5 m radius influence zone.*
- *It is the responsibility of the companies that manage public transport to place ashtrays near the boarding platforms, in areas where smoking is allowed.*
- *It is the responsibility of the municipalities, or the public transport stop concessionary companies to place ashtrays at these stops, according to their respective competences.*
- *For buildings intended for non-residential occupation, namely services, higher education institutions, hotel activity and local accommodation, the provisions of this article are applicable regarding the placement of ashtrays, cleaning, and waste disposal.*

Based on this law, conditions must be created so that it can be effectively enforced, foreseeing where this type of waste must be disposed (at the municipal level) and who is responsible for doing so. Therefore, it is suggested for the management of cigarette butts at the municipal level the incorporation of (removable) cigarette butts' containers in the waste containers available in the streets of the municipality. A 3D model was created in SketchUp program, figure 20, in order to make the proposal clearer.

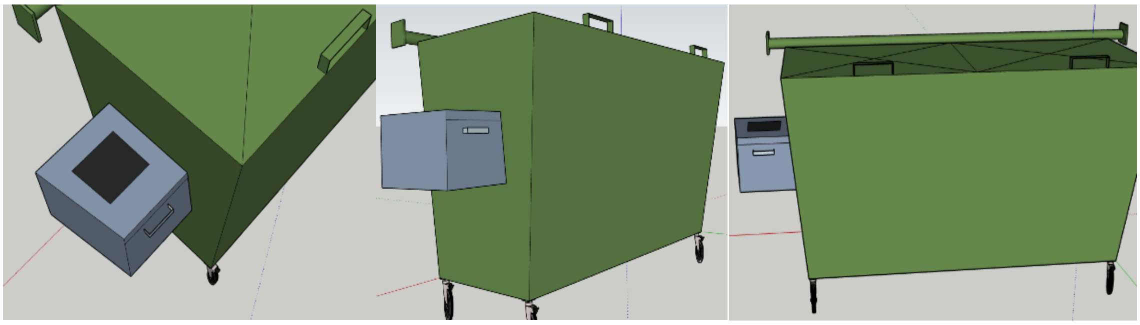

Figure 20- 3D model of cigarette Butt´s containers

Therefore, this proposal makes available to all population a specific place for the disposal of this waste, making its collection and processing more efficient. This proposal also suggests the existence of a specific place inside the municipal waste trucks for waste workers to deposit butts and prevent it from mixing with normal municipal waste.

Doing this will not require high initial investment, hiring new employees, new fleets, and new collection routes. The same resources are used as for normal municipal waste collection, possibly with an additional time during collection that should translate into mere seconds per waste collection activity. The proposal presented possibly solves the second conclusion discussed with the Cascais city council. However, a tax could still be applied to the citizens of the municipality, or even a tax on the sale of tobacco, to support the costs related to the management of this waste. Based on the work developed in this research, which allowed the creation of a solution for the valorisation of cigarette butts, it can be concluded that there is interest in collecting this type of waste, thus solving the problem described in 4.

The implementation of this proposal for the collection of cigarette butts at the municipal level allows for the existence of a company dedicated to its valorisation. Therefore, this company will be able to access the biomass to produce bio-oil by purchasing cigarette butts from different districts that integrate butts from the respective municipalities. An implementation scheme of the proposal is presented in figure 21.

Overall, once the management of this waste is implemented in the municipalities a recycling company may emerge with the objective of valorising the cigarette butts through the production of a bio-oil that can be treated in order to produce hydrogen and biofuel. Thus, this recycling company could have access to cigarette butts from different districts depending on the selling price and transportation costs.

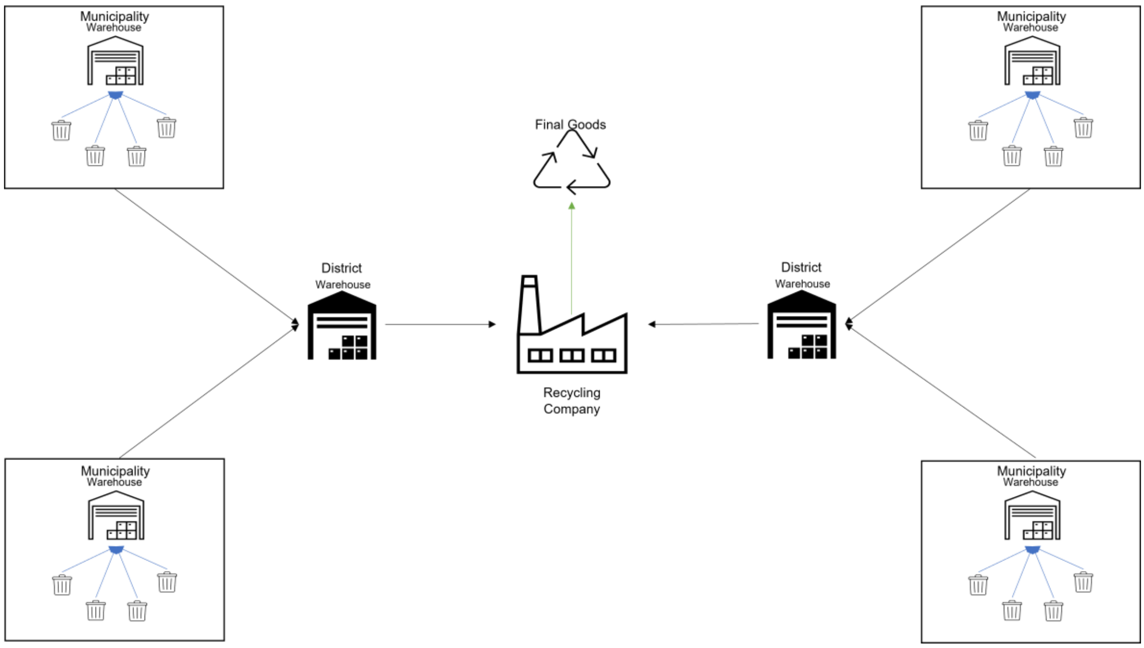

Figure 21-Implementation scheme of the proposal

4.3.2 Recycling company logistics optimization

The recycling company will have to perform an analysis to decide how much biomass and from which district it should buy the cigarette butts, considering the demand for the final product, the price of access to the biomass, and the transportation costs. In this chapter will be developed an optimization model that allows the company to make decisions in order to minimize costs. In the first part of this chapter the problem and the model are briefly described, initially the mathematical formulation is presented in detail.

Description of the optimization model

To solve this case, a decision support tool was developed at the strategic and tactical level from the recycling company's point of view. It was developed a mathematical model for the process represented in figure 21, considering the following data:

- Fixed locations of the district warehouses.
- Fixed locations of the recycling plants
- Implementation costs of each plant
- Demand by the different markets
- Distance associated with moving the Bio-oil from the plant to the markets
- Distance associated with moving cigarette butts from the warehouse to the plants
- Maximum capacity of each warehouse
- Maximum capacity of the recycling plants
- Yield of recycling process
- Production cost of Bio-oil
- Cost of biomass from the different districts

And intends to support the following decisions:

- Flow from each warehouse to each plant
- Flow from each plant to each market
- Opening the recycling plant or not
- Location of the plant Lisbon vs Porto

Mathematical model formulation

In this sub-chapter the model is described. Notation is introduced in order to present the *Indices*, *Parameters , Variables and objective function.*

Notation:

Indices

For each set, its elements are identified using the following indices:

- K: set of k *warehouses (each per district)* where the cigarette butts are stored $k \in K$, $k = 1,\dots,|K|$.
- I: set of i *Recycling plants* $i \in I$, $i = 1,\dots,|I|$.

- *S:* set of *s scenarios, s* $\in S$, *s* = 1,…, |*S*|.
- *M:* set of markets $m \in M$, *m* = 1,…, |*m*|;

Parameters

Based on the data provided, the parameters are defined below

- $prob_s$ - probability of each scenario
- CPW_k- Warehouse capacity
- CPP_i - Plant capacity.
- $Dists_{im}$ - distance from plant *i* to market *m*, in km
- $Distw_{ki}$ - distance from warehouses *k* to plants *i*, in km
- CT- transportation cost.
- P_k- Price/ton of cigarette butts from district warehouse *k*
- $Demand_{ms}$- Demand of market m in scenario s, in ton
- η - Bio-oil Process Yield
- CP - Bio-oil Production cost

Variables

Two types of decision variables are included in this formulation: continuous, and binary.

Continuous Variables

- XW_{kis} flow from warehouse *k* to plant *i* in scenario s, in ton.
- XP_{imss} flow from plant *i* to market *m* j in scenario s, in ton.

Binary variable

- $Y_{i,s}$- variable that assumes value 1 if plant *i* is open and 0 otherwise, in each scenario.

Objective Function

$$(\mathbf{6})\ Min \sum_{s} \text{probs} \sum_{k}\sum_{i} P_k \times \text{XW}_{kis} + \sum_{s} \text{probs} \times \text{CT}\left(\sum_{k}\sum_{i} Distw_{ki} \times \text{XW}_{kis}\right) + \sum_{s} \text{probs} \times \text{CT}\left(\sum_{i}\sum_{m} Distw_{im} \times \text{XP}_{ims}\right) + \sum_{s} \text{probs} \sum_{m} CP \times \boldsymbol{Demand_{ms}} + \sum_{i} CF_i \times Y_i$$

Constraints

$$(\mathbf{7}) \sum_{\boldsymbol{i}} \text{XW}kis = \sum_{\boldsymbol{s}} \frac{\boldsymbol{Demand_{ms}}}{\eta} \times \text{Y}i,s \qquad \forall\ k,m,i$$

$$(\mathbf{8}) \sum_{\text{k}} \text{XW}kis \le {}_{\text{CPWk}} \qquad \forall\ k,s$$

$$(9) \sum_{i} \mathrm{XP}ims \leq {}_{\mathrm{CPPi}} \times \boldsymbol{Yi,s} \qquad \forall\, i,s,m$$

$$(10) \sum_{i} \mathrm{XP}ims = _{\boldsymbol{Demand_{ms}}} \qquad \forall\, m,s$$

$$(11) \sum_{s} \boldsymbol{Y}_{\boldsymbol{i,s}} \geq \mathbf{1} \qquad \forall\, i$$

$$(12) \sum_{i} \mathrm{XW}kis \times \eta = \sum_{i} \mathrm{XP}ims \quad \forall\, k,s,m$$

Equation (6) represents the objective function of the mathematical model that contemplates the economic dimension of the logistic process. Thus, equation (6) consists in minimizing the total costs of the modelled supply chain. In this function are considered both the implementation costs of the facilities and the costs associated with the purchase of biomass, production, and transportation. In detail:

- The first parcel considers the costs associated with the acquisition of the biomass (cigarette butts), thus multiplying the price set by each warehouse in district *k* by the flow from each warehouse to recycling plants *i* times probability of each scenario *s*.
- The second parcel defines the costs related to biomass transportation. For this, the probability of each scenario is multiplied by the transportation cost and the distance from each warehouse to the recycling plants times the flow between the two.
- The third parcel defines the costs related to transportation of the final products. The probability of each scenario is multiplied by the transportation cost (assumed to be equal to the transportation of raw materials) and by the distance from each recycling plant to each market times the flow between the two.
- The fourth parcel provides the costs associated with production depending on market demand. Thus, the probability of each scenario is multiplied by the cost of production times the demand for the Bio-oil.
- The last parcel defines the fixed costs associated with opening the factories. For this, the fixed costs of opening are multiplied by the binary variable that defines whether the factory opens or does not open.

The remaining equations of the model define the constraints imposed. Equation (7) refers to the sum of the flow from the warehouses to the recycling plants being equal to the sum of demand for each product over its process yield times the binary variable, ensuring that exists flow from the warehouse to the plant only when plant is open and also that the necessary biomass for the process is available. Equation (8) describes the restriction of the flow from the warehouses to the recycling plants that will have to be less than or equal to the maximum capacity of each warehouse, ensuring that the capacity of the warehouses is not exceeded. Equation (9) describes the restriction of the flow from the factory to the market that will have to be less than or equal to the maximum capacity of each factory, if it is open, ensuring that the capacity of the factories is not exceeded. Equation (10) defines that the flow from factories to markets should be equal to the demand, ensuring that all demand is satisfied. Equation (11) defines the existence and the location of the recycling plants between both scenarios. Finally, equation (12) defines the existence of a process with certain yield taking place in each recycling plant. By saying this, it is obvious that the mass that goes in is different from the mass that goes out, since what is been considering is that the inflow is biomass (cigarette butts) and outflow is Bio-oil, meaning that the flow from factories to markets is equal to the flow from the warehouses to the plants times the yield, remaining sub-products of the reaction.

Conclusions

This chapter presents the model considering its Indices, parameters, variables, objective functions, and imposed restrictions.

Thus, the model described consists of a MILP, which includes an objective function that aim to analyse the performance of the supply chain considering its economic dimensions. The economic function minimizes the total cost associated with the implementation and activity of the supply chain. The model aims at the proper definition of the supply chain configuration, intending to support decision making regarding the flow from each warehouse to each plant, flow from each plant to each market and the existence and location of the plants.

4.3.3 Data collection

Plants capacity

According to Biofuels Canada, 2010, 50,000 hectares worth of biomass is processed annually, in both the first and second-generation biofuel production plants, meaning 200362 m3 bio-oil production annually. The average liquid density (measured at 293 K) of bio-oil is around 1020 kg/m^3, Bharath et. al, 2020. Considering this information, it is possible to assume that a bio-oil plant capacity is 204 ton/ year.

Fixed Costs of Implementing Bio-oil production Plants

Financing and set-up costs of commercial second-generation biofuel plants is between $125-250 million, averaged out to $187.5 million (161.02 million €) which includes both domestic funding and foreign direct investment according to sustainable production of second-generation biofuels potential and perspectives in major economies and developing countries, 2010. According to INE, land values in the Lisbon metropolitan area are around 40% higher than in the Porto metropolitan area. Considering that the land acquisition costs represent 30% of the total value of implementation costs, it is assumed that the final impact will then be 12%. That said, it is assumed that the cost of implementing the plant in Porto will be the average mentioned above (161 million €) and in Lisbon 12% higher (180 million €).

Distance

Distances between warehouses-plants and plants-markets were calculated using the travel optimisation programme, Viamichelin.

Warehouses- Plants

Table 7- Warehouse- Plants Distances

Distance km	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda
1)Lisbon	255	176	366	488	226	206	132	277	318
2)Porto	2314	446	56	208	255	117	363	547	198

Distance km	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu
1)Lisbon	146	10	227	314	82	50	385	378	291
2)Porto	181	314	290	10	243	347	75	94	125

Plants-Markets

Table 8- Plants- Markets Distances

Distance km	1 Spain	2 France	3 Germany	4 U. Kingdom
1)Lisbon	628	1739	2418	2180
2)Porto	554	1552	2232	1993

Price of the biomass-Cigarette butts (€/ton)

In this model it was assumed that the biomass available in each warehouse in each district is sold to the recycling company at a certain value. Since there is no integrated system in Portugal for cigarette butts' collection it is not possible to define a specific value for the cost of its management. Therefore, based on the figure presented, a value in euros/tonne will be estimated.

	Collection and transport	Sorting	Composting	Anaerobic digestion with energy recovery	Landfilling	Landfilling with energy recovery	Incineration with energy recovery
MoE/UNDP/ECODIT (2011); CDR (2010)	33	23	25	–	46	–	–
Maalouf and El-Fadel (2017)	20–250	26–28	5–90	20–150	10–100	13–67	–
Assamoi and Lawryshyn (2012)	–	–	–	–	18	–	38
Dijkgraaf and Vollebergh (2004)	–	–	–	–	45	–	97
European Commission (2002)	–	–	–	80	62	58	88
Jamasb and Nepal (2010)	–	26	–	–	15	13	70
Rabl et al. (2008)	–	–	–	–	45	40	92
Tsilemou and Panagiotakopoulos (2006)	–	–	17–73	22–67	12–50	–	117
World Bank (2012)	20–250	–	5–90	20–150	10–100	–	120
WRAP (2016)	–	28	27	44	21	–	94
Range (US$/tonne)	20–250	23–28	5–90	20–150	10–100	13–67	38–120
Adopted average (US$/tonne)	33[a]	23[a]	25[a]	85[b]	46[a]	57[c]	90[d]

Figure 22-Average cost of municipal solid waste management ($/ton of waste) Maalouf et. al., 2019 .

As it is a new and very specific collection proposal, the highest value for collection, transport and sorting of municipal waste will be considered. Consequently:

Collection and transport = 250 $/ton = 215 €/ton

Sorting = 28 $/ton = 24 €/ton

Total cost = 239 €/ton

It is therefore assumed that each district will sell the biomass to the recycling company at its estimated management cost (239 €/ton). The model implemented in excel is made so that different values can be applied in different districts.

Warehouse capacities

To define the capacity of each warehouse for cigarette butts' storage some results were collected, and some approximations were considered. Thus, it was considered a value of 4 cigarettes smoked per person per day in Portugal, in average, considering figure number 23. The age groups in Portugal are split at 15% under the age of 15, 40% between the ages of 25 and 54, and 20% over 65 years of age (World Population review, 2021). Considering a percentage of 65% active smokers (age groups 15-24 + 25-54) it is possible to estimate the total number of active smokers, by doing:

- Total Population (10.30 M) x 65%= 6.695 M active smokers
- 6.695 M x 4 cigarettes smoked/day/person x 365 days/year= 9774.7 M cigarettes consumed/year
- Considering a linear consumption of cigarette butts among 18 Portuguese districts : 543M cigarette butts consumed/year/District
- Assuming a 50% successful collection rate in an integrated waste collection chain: 271M Cigarette butts collected/district.
- According to Qamar, 2020, a cigarette butt weight is approximately 0.27 g. Meaning: 73 tons of cigarette butts collected/District.
- Predicting, 80% of the biomass is in good quality to sell to the recycling company:58.4M
- Assuming a 20% variation of this quantity, the interval of the total amount of cigarette butts collected per district considered is 46 ton- 70 ton
- Finally, in this model were assigned random values to each district of total biomass collected in ton, between 46 ton-70 ton- defining the warehouse capacities in this way.

Table 9- Warehouse capacities

	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda
Capacity ton	46	48	56	45	60	54	49	46	54

	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu
Capacity ton	50	59	68	63	65	47	49	51	53

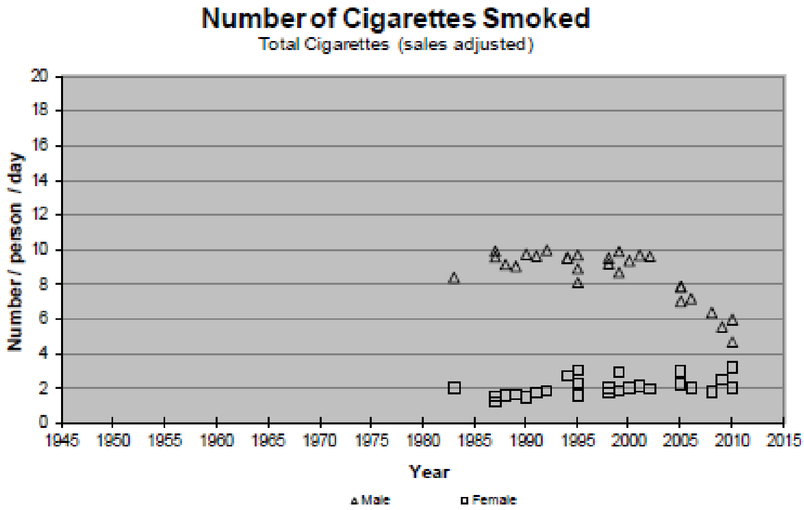

Figure 23-Estimated number of total cigarettes smoked per person per dayin Portugal, sales-adjusted; by year of survey. Males and females aged 15 years and over (Forey et.al., 2015)

Production Costs

Solvent and Catalyst costs

It is intended to calculate the solvent costs per tonne of bio-oil production. Thus, and considering the reaction used in the laboratory it is found that to produce one ton of bio-oil, 5 tons of solvent will be needed and 0.18 tons of catalyst (3% 6 Ton- Solvent + biomass). The following suppliers sell the following compounds at their respective prices:

- Shandong Aojin Chemical Technology Co., Ltd - ***2-Ethylhexanol*** (Solvent)- 1050 $/Ton
- Weifang Ocean Trading Co., Ltd- ***p*-Toluenesulfonic acid** (catalyst)- 550 $/Ton

Total Costs= 5350 $/Ton = 4620 €/Ton

Labour Costs

To estimate labour costs, the paper published by Rogers and Brammer, 2012 was followed. In this article costs are estimated for the implementation of a pyrolysis plant. Considering:

- All sizes of pyrolysis plant would require a control room operator and one plant attendant while they were running.
- Small plants that used forklift trucks or front-end loaders for biomass handling would require two materials handling plant operators for shifts when the plant is receiving deliveries.
- Larger plants with automated materials handling plants will require one materials operator for shifts when the plant is receiving deliveries.
- There would be a day team to cover routine maintenance and commercial maters. The team would have 3 members for the small plant increasing to 6 on the larger plants.
- A staff member works 206, 8 h shifts a year once allowances are made for holidays, training, and sickness

Based on these propositions, a value of 45 K euros per worker was calculated, which includes: national insurance cost, employers pension contributions, anti-social hours payments, training, and administration charges.

Total Cost (12 employees)= 540 K€ to produce annual capacity (204 ton) , meaning a new **Total cost of 2600€/Ton**

Electricity and Operating costs

Due to some difficulty in estimating these costs it was assumed that they represent 20% of the total costs of solvent, catalyst, and labour. Resulting in **1444 €/Ton**

Total Production costs= 8664 €/Ton, value used in the excel file.

5 Results and Discussion

5.1- Overview

In this section the results are presented along with its discussion for better readability. The results are presented following the same order as the methodology for better interpretation. Only the more relevant data from experimentation is shown.

5.1 Laboratory Research

5.1.1 Biomass conversion (Process Yield)

In order to obtain optimized results, three biomass liquefaction trials were performed. Between trials a substantial variation in yield was observed which indicated that the pre-treatment of cigarette butts is critical for the success of the liquefaction process. The results of all analyses will be studied considering the conversion results.

- For the **first** experiment the following masses were obtained (**Bio-oil 1**):

Petri dish- 107,64 g

Filter 1- 0,54 g and **Filter 2**-0,49g

Total mass-111,60 g

$$Liquefaction\ Yield\ (\%) = \left(1 - \frac{(111{,}6 - 107{,}64 - 0{,}54 - 0{,}49)}{25{,}05}\right) \times 100 = 88{,}3\%$$

- For the **second** experiment the following masses were obtained (**Bio-oil 2**):

Petri dish- 107,67 g

Filter- 0,49 g

Total mass-119,20 g

$$Liquefaction\ Yield\ (\%) = \left(1 - \frac{(119{,}2 - 107{,}67 - 0{,}49)}{25{,}17}\right) \times 100 = 56{,}1\ \%$$

- For the **third** experiment the following masses were obtained (**Bio-oil 3**):

Petri dish- 107,66 g

Filter- 0,49 g

Total mass-108,62 g

$$Liquefaction\ Yield\ (\%) = \left(1 - \frac{(108{,}62 - 107{,}66 - 0{,}49)}{25{,}35}\right) \times 100 = 98{,}15\ \%$$

With these results it is possible to say that the pre-treatment of the cigarette butts is crucial since, using the same type of biomass and the same experimental conditions, completely different yields were obtained: 98.15% for bio-oil 3, which underwent a more aggressive pre-treatment (removal of the paper around the filter) and 56.1% for bio-oil 2, which had a pre-treatment that only involved cutting the filter into smaller pieces.

5.1.2 Cigarette Butts Characterization

FTIR

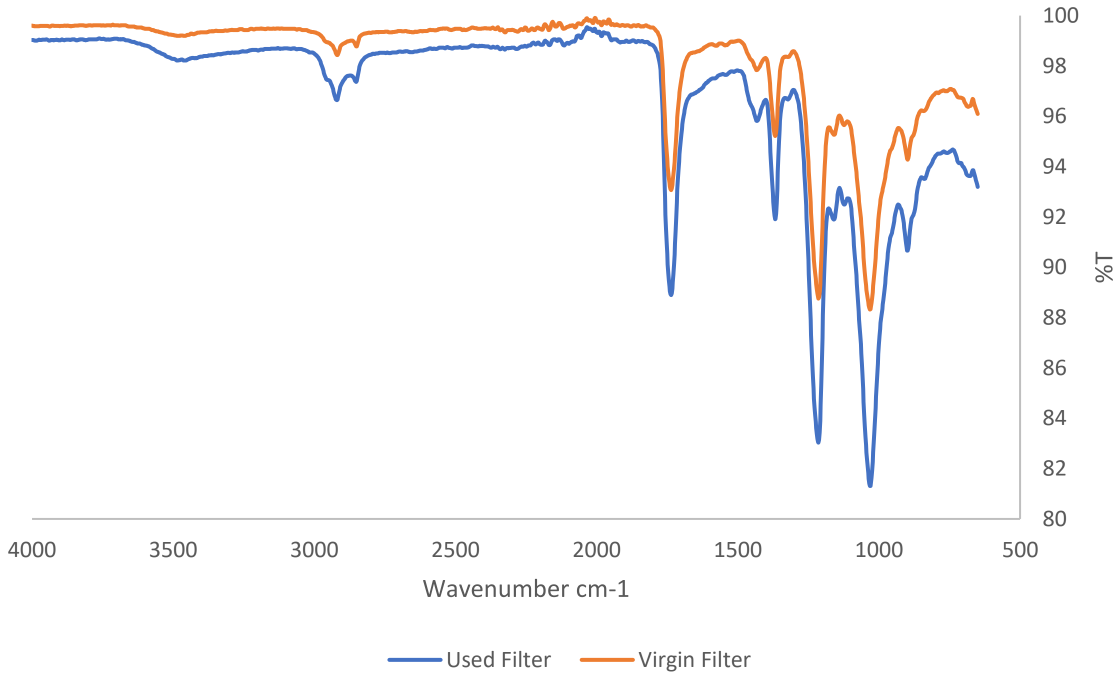

Figure 24- Transmittance vs wavenumber in Used and Virgin filters

Used and virgin filters were analysed through FTIR technique to compare and evaluate possible changes in their chemical structures. Figure 24 shows the FTIR spectra for the tested samples. In this figure, the cellulose acetate (CA) composition of the cigarette filters can be identified by the acetyl groups characteristic bands at 1240, 1370, and 1750 cm^{-1} wavenumbers. Hence, it can be observed that the FTIR spectra of the virgin filters and used filters are practically identical. Besides, no difference was found between used and virgin filters, which indicates that the smoking process does not change the chemical structure of the filter.

It is important to note that the FTIR results indicate that the contaminants in the cigarette butts are in trace amounts and therefore there are no major changes in the FTIR of the used and virgin filters.

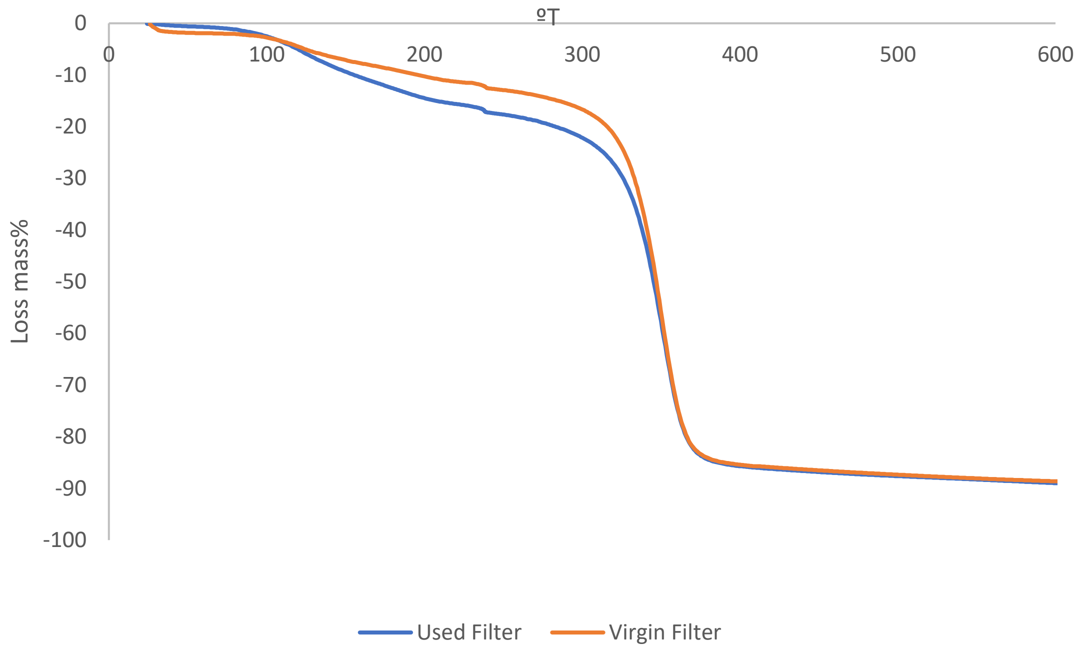

Figure 25- TGA Curves For virgin and used filters

A heating rate of 5 ºC/min was used to clearly distinguish the main thermal behaviour regions of the materials because faster heating tends to suppress smaller thermal events (Baker, 1976). An additional 5-min holding time at 240 ºC was included to simulate the average heating session experienced by the filters, and a combination of temperature ramping and isothermal holding is typical in temperature management. As figure 25 shows, the initial mass loss up to 100 ºC was mainly due to water and solvent evaporation (Banyasz, 1999). The second mass loss region, between 100 ºC and the 240 ºC holding temperature, resulted in a further mass loss of ca.15%. This region may be accounted for by the evaporation of glycerol, nicotine, and some volatile chemicals from the tobacco. The initial thermal decomposition of some biopolymers such as sugars and pectin might also contribute to mass loss in this temperature range (Wang et al., 2009). Isothermal holding at 240 ºC continued to reduce the mass to a small extent. Up to approximately 350 ºC. In the temperature region above 240 ºC, there was a slightly faster rate of mass loss. The capability of TGA to assess the major thermal breakdown behaviour of common biopolymers qualitatively and quantitatively (e.g., cellulose, hemicellulose, pectin, and lignin) is well established (Yang et al., 2006). The three main components of common biomass e hemicellulose, cellulose, and lignin- each display a well-defined thermal decomposition region: hemicellulose starts to decompose between 220 and 315 ºC, followed by cellulose at temperatures close to 400 ºC, and lignin at temperatures above 400 ºC. Once again, in this analysis it is possible to conclude that the contaminants present in the used filter are in trace amounts and for this reason the difference between the TGA curves are minimal. The difference between the two curves, more noticeable between 100ºC and 240ºC, is probably due to the degradation of nicotine, present in the used filter.

GPC

By this analysis it is possible to obtain the average molecular weight distribution of each filter sample. Figure 26 shows the results for used and virgin samples.

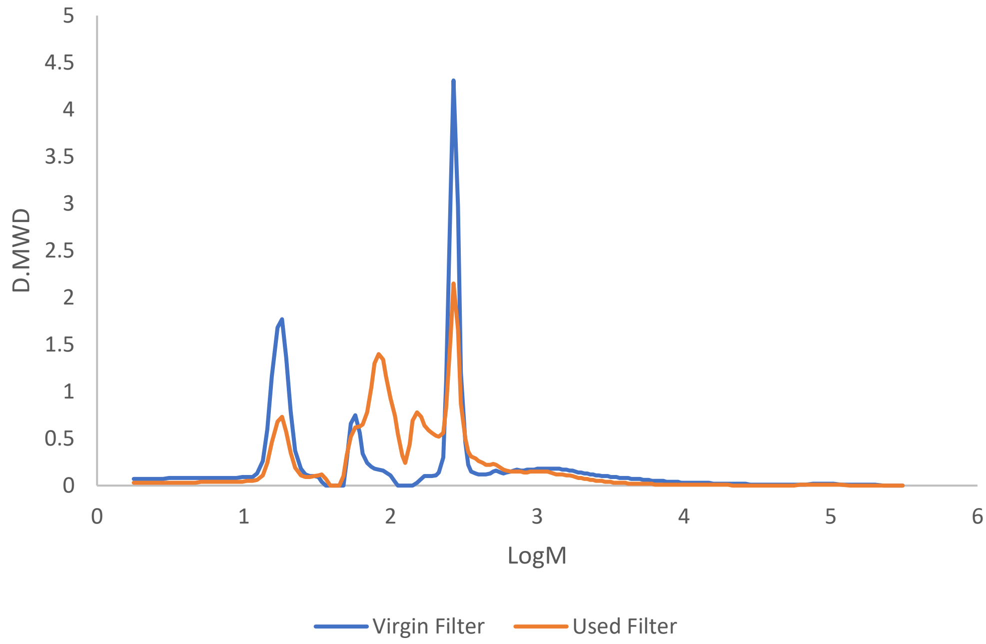

Figure 26- Distribution of the average molecular weight of the filter samples

It was also possible to extract from the software the data concerning the average numerical and mass molecular weights (Mn and Mw respectively) as well as their polydispersity index, which can be seen in the following table.

Table 10-GPC Results for filter samples

Sample	**Mn (g/mol)**	**Mw(g/mol)**	**PDI**
Virgin Filter	1263.3	49505.8	39.2
Used Filter	538.7	29370.8	54.5

The value of Mw varies between 29370.8 g/mol for the used filter and 49505.8 g/mol for the virgin filter, while Mn varies between 538.7 g/mol and 1263.3 g/mol, respectively. These values obtained in this characterisation phase will be very important for the interpretation of the bio-oil results. As they were used as the biomass for their production. More detailed analysis will be done in the next chapter.

5.1.3 Liquefaction products characterisation

FTIR

The samples processed in the infrared spectrum analysis were the products resulting from the liquefaction reactions, i.e., the liquid bio-oil and the solid residues. These products, as mentioned above, are mostly composed of small-sized fragments of polysaccharides in the form of cellulose, hemicellulose, and lignin. Through the analysis of the IR spectra, it is possible to observe the transmittance level of various organic groups that constitute these fragments in the form of bands. Next in Figure 27 is represented the spectra corresponding to all the bio-oils produced, for a better perception of the results.

Theoretically, the liquid phase (bio-oil) should have a higher concentration of functional groups compared to the solid waste phase and consequently higher liquefaction conversions result in more extensive bands of the functional groups of the bio-oils. The opposite occurs for the solid phase with less extensive bands. Generally, this correlation was verified for the spectra of the bio-oils, although with minimal differences between the samples with high and low conversion, a fact which reflects an ambiguity of both the type of functional groups and their content in the bio-oils.

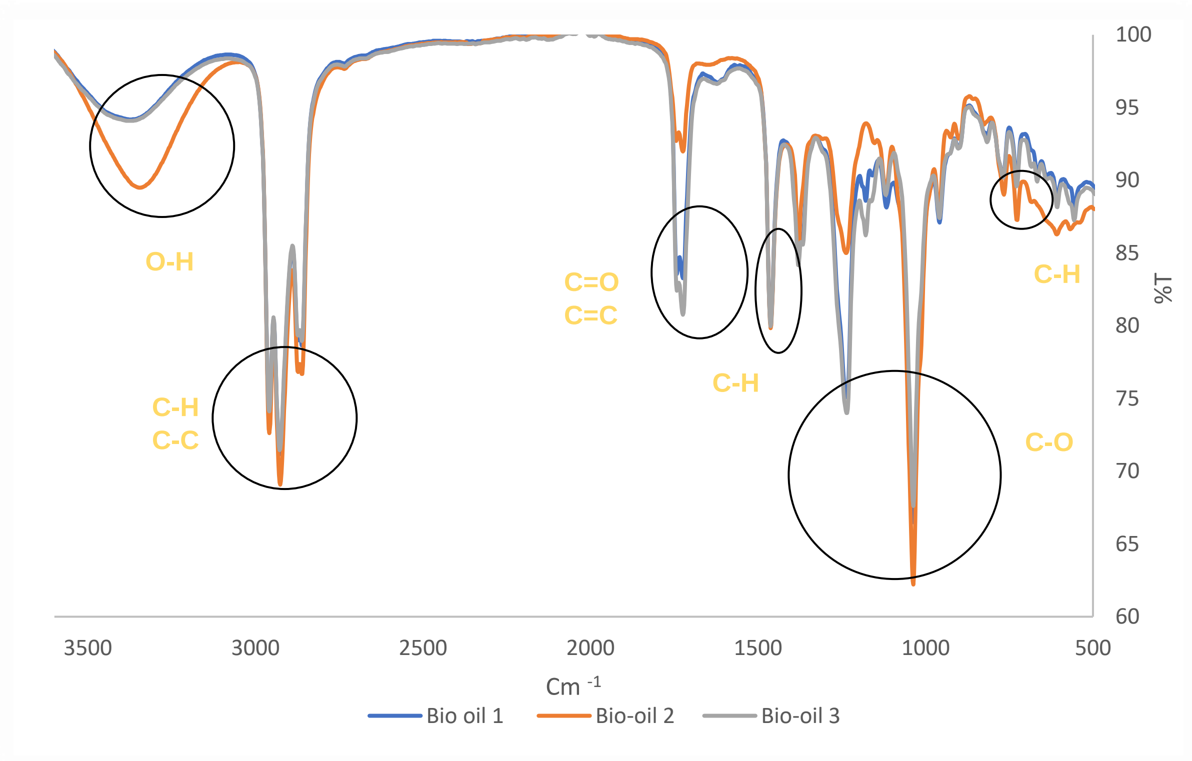

Figure 27-FTIR transmittance spectrum Of Bio-oils

As for the bands themselves, it is interesting to note a band with transmittance at 3400 cm^{-1} corresponding to O-H bonds, this due not only to the presence of water in the sample but also phenolic groups and alcohols. The bio-oils 1 and 3 present higher conversion rates (88.5% and 98.15%) and therefore the transmittances are identical at this wave number (3400 cm^{-1}), in contrast with the bio-oil 2 that presents a more intense band, indicating a greater presence of water, phenols and alcohols, something that is in accordance with the low conversion that had, about 56.1%. Considering then the wavenumbers of the order of 3000 cm $^{-1}$, a broad band of considerable transmittance was detected corresponding to alkane molecules derived from the fragmentation of polysaccharide constituents. Between 1600 cm^{-1} and 1730 cm^{-1} two peaks equivalent to the stretching of C=O and C=C bonds were noted, with bio-oil 3 showing the longest bands, resulting from higher concentrations of ketones, aldehydes, carboxylic acids and olefins. The C-H bond transmittance bands, located approximately at 1460 cm-1, prove that a more efficient liquefaction results in a better fragmentation of the lignin polymer chain and consequently in a higher concentration of aromatic compounds in the liquid phase.

Finally, it is important to highlight the peaks referring to the minimum values of transmittance at about 1030 cm-1, equivalent to C-O bonds indicating a large influx of aromatic compounds and alcohols in the composition of the bio-oils. It is worth mentioning that the highest band at this wave number and adjacent (660-800 cm-1) does not belong to the bio-oil corresponding to the liquefaction with the highest conversion, but rather relative to bio-oil 2, which recorded low conversion value (56.1%).

Similarly, the infrared spectrum of the solid residues was obtained (Figure 26).

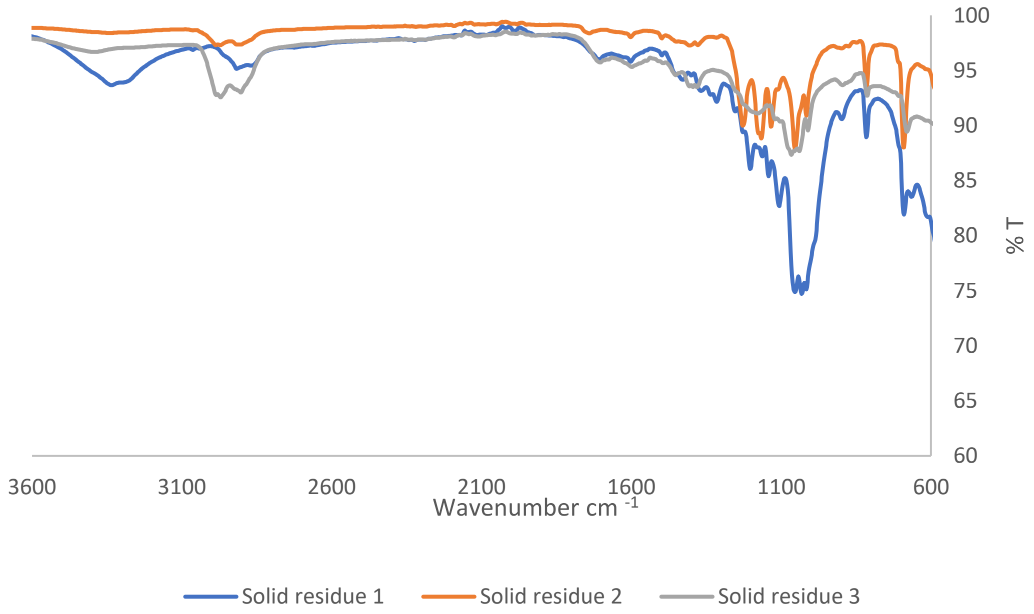

Figure 28-FTIR transmittance spectrum of the solid residues

Comparing the spectrum for bio-oils, the bands are in approximately the same wavenumber ranges, indicating, as would be expected, much lower transmittance values. Again, higher conversions provide in general higher transmittance peaks.

Some C=O are found (ketones, carboxylic groups, and aldehydes) but the great predominance resides, as before in the C-O bonds, indicative of the presence of aromatic groups resulting from the depolymerization of lignin, with the maximum and minimum representations for the products of Bio-oil 1 (88% conversion), and 2 (56%), respectively.

It will be interesting to point out the fact that the solid residues that have the most similar bands are not the ones with highest yields. It should be noted that solid residues 2 and 3 show similar bands and both are the result of a reaction with used filters despite the large difference between yields (56% and 98%) respectively.

GPC

With this technique it was possible to obtain the average molecular weight distribution of each bio-oil sample. Figure 29 shows the results for the three bio-oil samples.

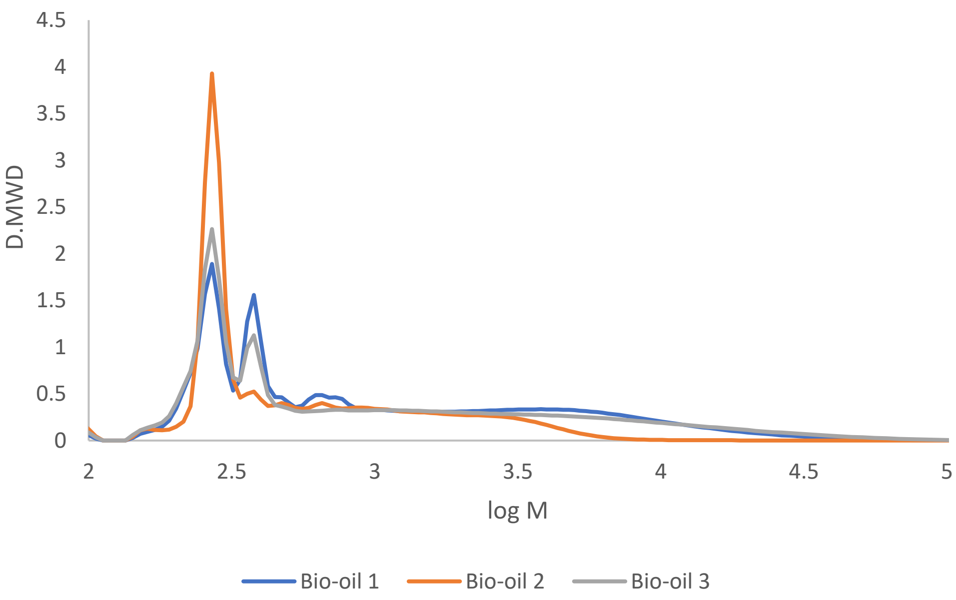

Figure 29-Distribution of the average molecular weight of the bio-oil samples

It was also possible to extract from the software the data concerning the average numerical and mass molecular weights (Mn and Mw respectively) as well as their polydispersity index, which can be seen in the following table.

Table 11- GPC results for bio-oil samples

Sample	**Mn (g/mol)**	**Mw(g/mol)**	**PDI**	**Yield**
Bio-oil 1	2574.7	13632.0	5.3	88.3%
Bio-oil 2	805.1	4566.5	5.7	56.1%
Bio-oil 3	2790.8	17543.6	6.3	98.15%

Based on these results it is possible to state that the value of Mw and Mn for bio-oil 2 is negligible, having been obtained because of some experimental error. In the production of bio-oil 2 the same biomass was used as in bio-oil 3 and for this reason the order of magnitude of Mw should be the same as of bio-oils 1 and 3. Moreover, given its low yield the Mw value should be the highest, indicating that there were not as many bond breaks as in the other bio-oils, and therefore the presence of compounds with higher values of Mw.

For the bio-oil 1 there is a substantial reduction of the Mw (13632.0 g/mol) when compared with the biomass used for its production (49505.8 g/mol) about 1/4 of reduction of the value, something expected, due to the breaking of bonds of larger compounds during the process of liquefaction, thus giving rise to compounds of smaller dimensions and therefore with lower Mw. The same happens and for the same reason with the bio-oil 3, there is a reduction of about half of the Mw of the biomass used (29370.8 g/mol) when compared with the Mw of the bio-oil (17543.6 g/mo), something also expectable due to the explanation given above.

The greater reduction of Mw observed in bio-oil 3 (about half) when compared with the reduction in bio-oil 1 (about a quarter), is explained by the difference in yield, being this in bio-oil 3 of 98.15% and 88.3% in bio-oil 1. This means that the greater the yield, the greater the number of breaks in the bonds of the compounds and therefore greater presence of compounds with lower Mw.

<u>TGA</u>

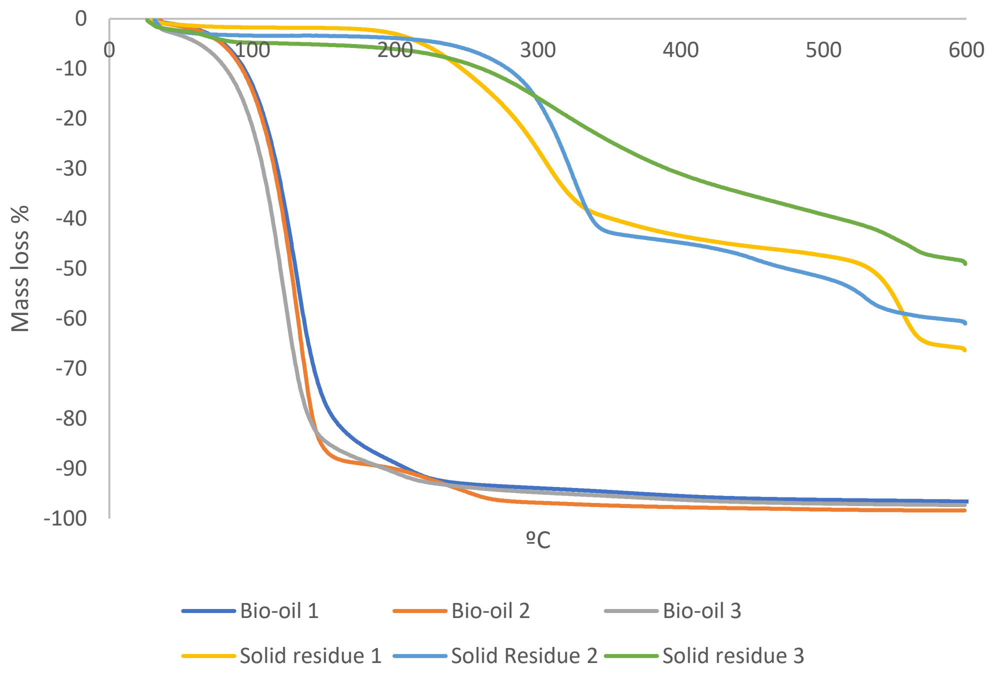

Figure 30- TGA results for the bio-oils and solid residues

The TG and DTG results of the pyrolysis (in N_2 atmosphere) of bio-oils using a heating rate of 5°C/min are shown in figure 30 and 31, respectively. The bio-oil undergoes thermal decomposition due to the absence of oxygen and a notable mass loss is observed between 70

°C and 140 °C. This region is characteristic of the elimination of water - which forms a major portion of the bio-oil - and removal of acids, alcohols, and other aromatic oxygenate such as mono-phenols and furans (Stankovikj et. al., 2017). DTG peaks of bio-oils 1,2 and 3 are observed in this region at temperatures of 134 ºC, 136ºC and 123 ºC, respectively. At temperatures between 200 °C and 350 °C, the decomposition of mono-sugars such as levoglucosan and poly-sugars such as cellobiose takes place as reported (Perez et. al., 2007). The remaining bio-oil that underwent dehydration and crosslinking reactions (Xiong et. al., 2019) now forms carbonaceous structures that correspond to about 10% of the initial mass and are a result of the decomposition of pyro-lignin, which is the heaviest fraction of the bio-oil (Sholze and Meier, 2001). The rate of mass loss continues to fall steadily beyond 350 °C as the volatile content is depleted and the residue left at the end is mostly carbonaceous char that does not decompose further.

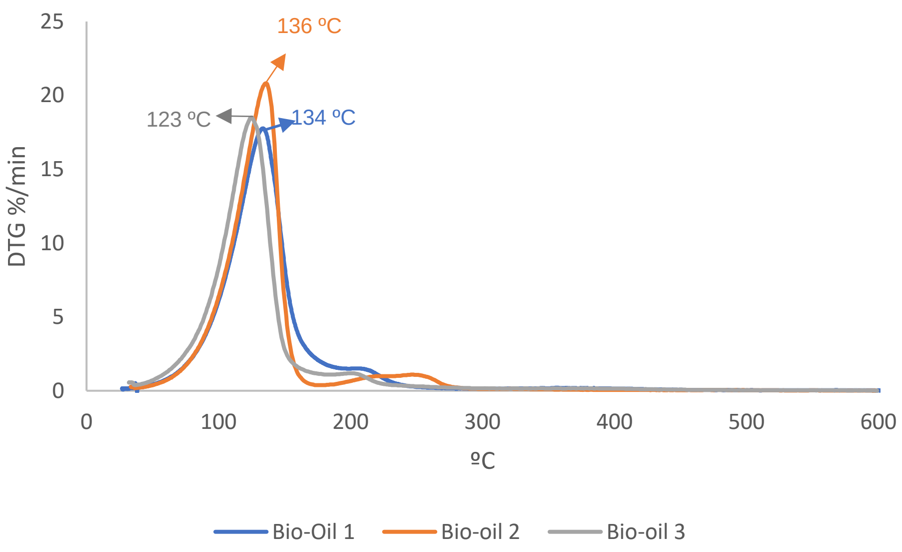

Figure 31- DTG Results for bio-oils

Overall, it is possible to note a major difference between the TGA performed on the biomass used to produce these bio-oils, the great loss of mass in bio-oils occurs at much lower temperatures which is indicative of the presence of much more volatile components, something which is desired in a fuel.

Higher heating value

The higher heating values were obtained through an external laboratory. The results received were as shown in the table below:

Table 12- Higher Heating value of Bio-oils

Sample	HHV (MJ/KG)	Yield
Bio-oil 1	32.644	**88.3%**
Bio-oil 2	26.454	**56.1%**
Bio-oil 3	33.287	**98.15%**

It is possible to notice a correlation between the HHV value and the yield. The bio-oil that presented the highest yield in its liquefaction process presents the highest HHV value.

Considering the literature, the results obtained were compared with those of an article containing 52 samples of bio-oil produced through liquefaction process (Mateus et. al., 2021).

In this article the HHV values of the 52 samples are in between 14.44 MJ/KG and 45.11 MJ/KG. Based on these results, it is possible to state that the values of HHV obtained in this investigation were quite acceptable, with the bio-oils and 1 and 3 being in the upper half of the best results obtained in this paper.

5.2 Logistic Process

In this chapter is described the different scenarios to be analysed and the consequent results obtained with the application of the optimisation model developed in section 4.3.2.

5.2.1 Scenarios

Two scenarios were considered in order to compare the results of the model developed. Scenarios only depend on the demand for bio-oil in four countries to which the company will export the final product.

Table 13. Demand for Bio-oil in scenario 1 and 2

Demand (Ton)	1 Spain	2 France	3 Germany	4 U.Kingdom
Scenario 1	58	107	124	84
Scenario 2	45	76	36	45

Based on demand the model will optimise costs by defining the flows of biomass between warehouses and plants and the flow between plants and markets. It will also decide the opening and location of plants. The considered probability of each scenario occurring is as follows:

Table 14- Scenarios Probability

Scenarios Probability	
Scenario 1	0.3
Scenario 2	0.7

The results obtained for each scenario of each set of demand will be presented, firstly explaining the configuration obtained in terms of flows and locations and then the results in terms of cost performance.

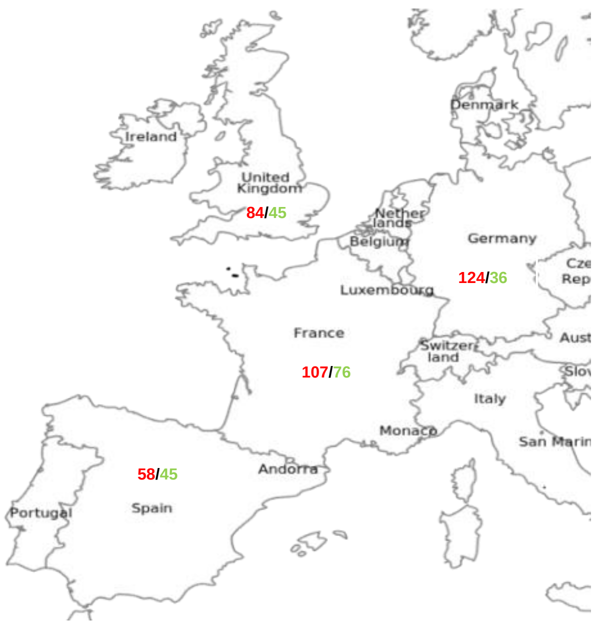

Figure 32- Demand by market country in ton

5.2.2 Results-Flows and locations of plants

Scenario 1

Given the demand presented above for scenario 1 the model concludes that the two plants should be opened to meet the needs of the market and therefore variables $Y_{1,1}=1$ and $Y_{2,1}=1$.

The optimal flows of biomass from warehouses to plants are:

Table 15- Optimal flows in ton between warehouses and Plants

Flow Ton	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda
Plant 1 (Lisbon)	0	0	0	0	0	0	19	0	0
Plant 2 (Porto)	46	0	56	0	0	0	0	0	0

Flow Ton	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu
Plant 1 (Lisbon)	0	59	0	0	65	47	0	0	0
Plant 2 (Porto)	0	0	0	63	0	0	49	13	0

The optimal flows of biomass from plants to markets are:

Table 16- Optimal flows in ton between plants and markets scenario 1

Flow Ton	1 Spain	2 France	3 Germany	4 U. Kingdom
Plant 1 (Lisbon)	58	0	111	0
Plant 2 (Porto)	0	107	13	84

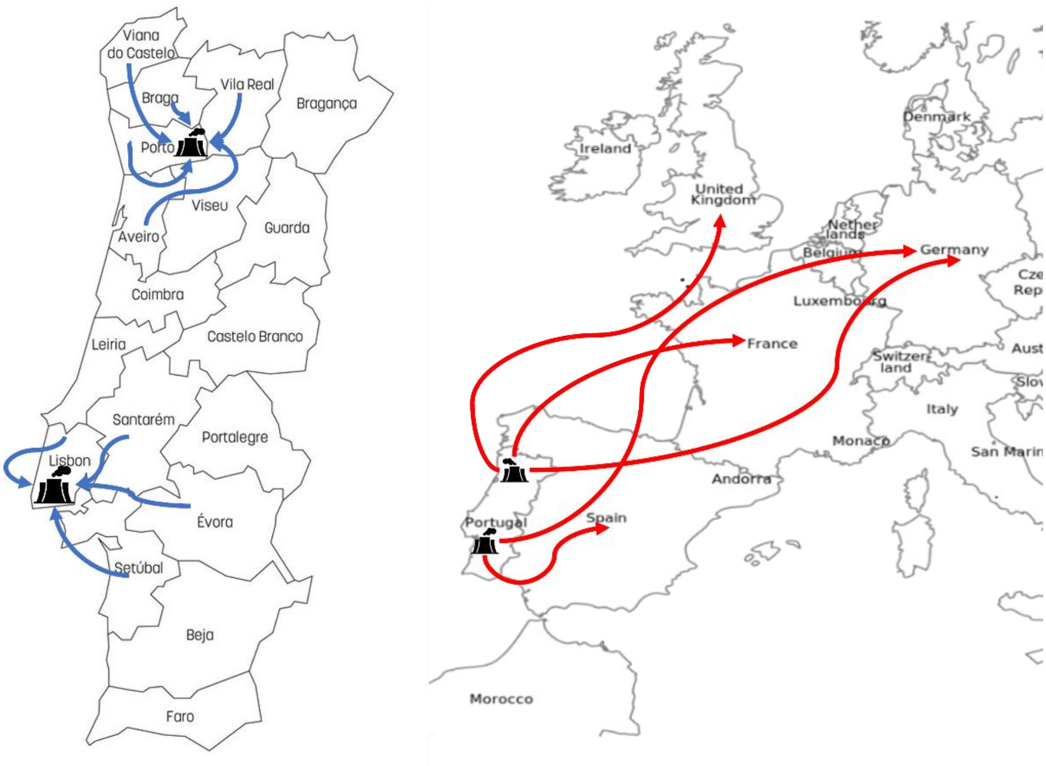

Figure 33- Scenario 1 map

<u>Scenario 2</u>

Given the demand presented above for scenario 2 the model concludes that only plant 2 (Porto) will be open, and therefore variables: $Y_{1,2}$=0 and $Y_{2,2}$=1.

The optimal flows of biomass from warehouses to plants are:

Table 17- Optimal flows in ton between warehouses and Plants scenario 2

Flow Ton	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda
Plant 1 (Lisbon)	0	0	0	0	0	0	0	0	0
Plant 2 (Porto)	46	0	56	0	0	0	0	0	0

Flow Ton	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu
Plant 1 (Lisbon)	0	0	0	0	0	0	0	0	0
Plant 2 (Porto)	0	0	0	63	0	0	49	13	0

The optimal flows of biomass from plants to markets are:

Table 18- Optimal flows in ton between plants and markets scenario 2

Flow Ton	1 Spain	2 France	3 Germany	4 U. Kingdom

Plant 1 (Lisbon)	0	0	0	0
Plant 2 (Porto)	45	76	36	45

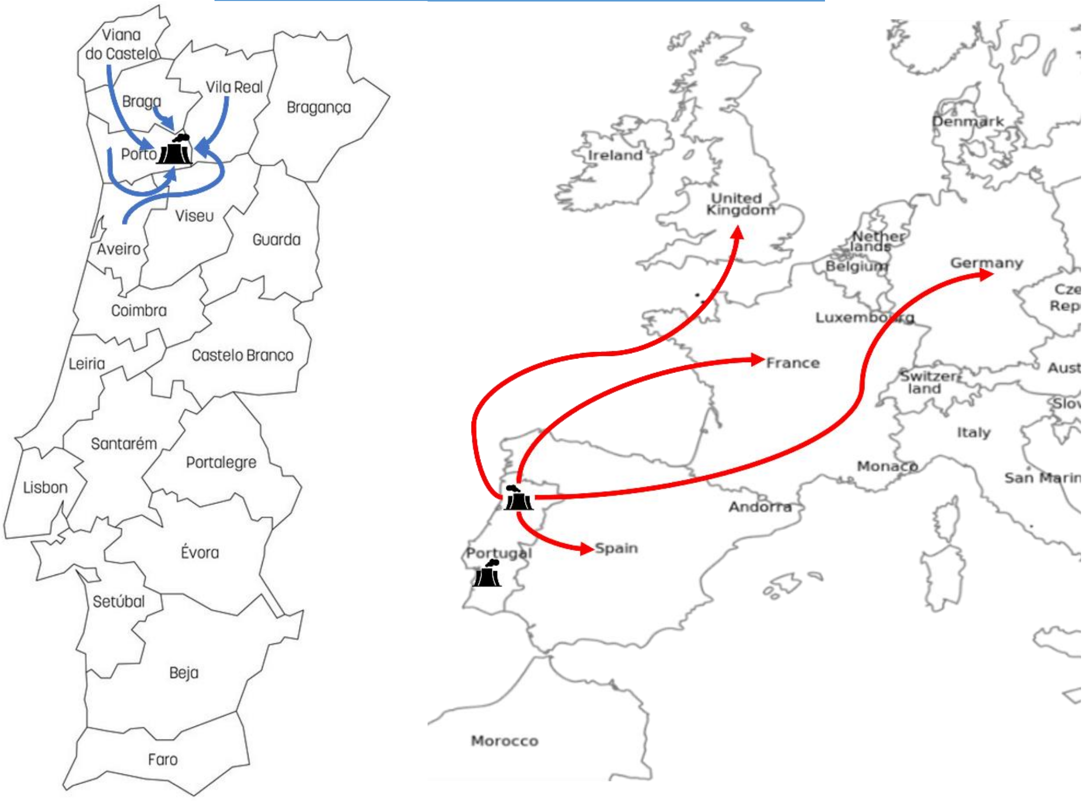

Figure 34- Scenario 2 Map

5.2.3 Results-Costs

The economic dimension is the main objective of the development of the optimisation model. The objective function aims to minimise the costs involving the supply chain that integrates the movement of cigarette butts and bio-oil as a final product.

Two different scenarios were considered, and for this reason the results will have significant differences at the level of Variable costs (transportation costs, biomass cost and production costs) and fixed costs.

<u>Fixed Costs</u>

Given the fixed costs of plant implementation described above, the model presents the following results for each scenario:

Table 19- Fixed costs

	Scenario 1	Scenario 2
Fixed Costs M€	340	160

Given the difference in scenarios, more specifically the difference in demand, it was expected that fixed costs would vary. As the demand in scenario 1 is substantially higher than the demand in scenario 2 there is the need to open two plants in the first scenario in contrast to the second where only one plant is opened. Consequently, the fixed costs of the scenario 1 are considerably higher (a little more than double) due to the implementation costs of two plants in different locations.

Variable Costs

Taking into account all the data collection to estimate the capacity of the plants, the distances between warehouses and plants and between plants and markets, the price of biomass, the capacity of the warehouses, and the production costs of bio-oil, it was obtained the optimal values for the following variable costs: total transportation costs between warehouses and plants and between plants and markets, total production costs and finally total biomass costs. Thus, the following table 21 presents all the results obtained.

Table 20- Variable Costs

	Scenario 1		**Scenario 2**	
	€	**%**	**€**	**%**
Transportation Costs W-P	11542	0%	6055	0%
Transportation Costs P-M	333657	9%	156460	8%
Biomass Costs	100165	3%	54245	3%
Production Costs	3231672	88%	1750128	89%
Total Costs	3677036		1966887	

Overall, the difference in variable costs between the first and second scenario is striking. Once again, given the higher demand in the first scenario it is expected that the transport costs for both inflow and outflow of the factories will be higher given the significant difference in quantities to be transported. The same is true for biomass and production costs.

It is important to note that production costs represent the highest percentage of the variable costs considered, between 88% and 89%. The transportation costs between plants and markets are much higher than the transportation costs between warehouses and plants due to the great difference between the distances covered, differences in the order of 10 times in average.

Once the mechanism for calculating the fixed and variable costs for each scenario had been stipulated, all the restrictions necessary for implementing the model had been applied and the probabilities of each scenario had been defined, the optimised result for the objective function was obtained using Excel's Solver function (Figure 35).

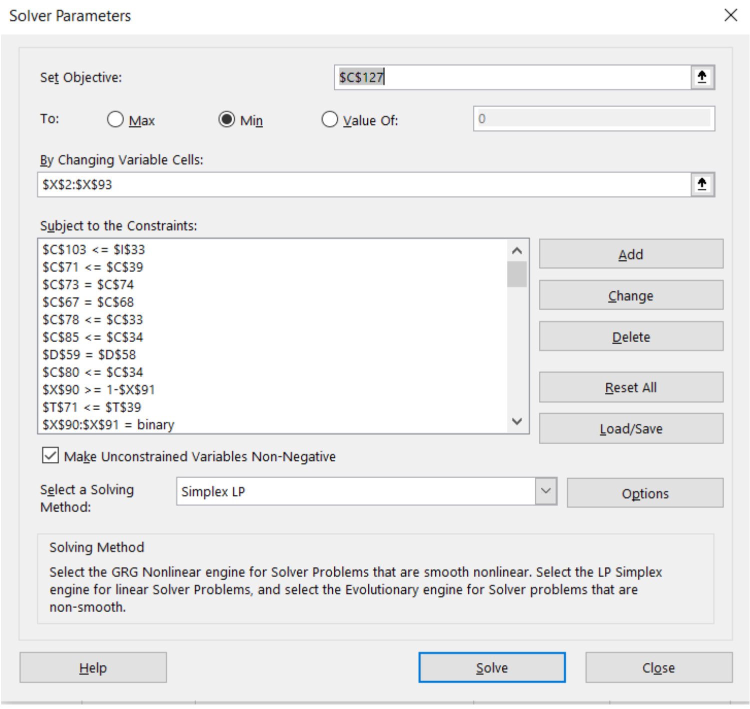

Figure 35- Excel´s Solver Function

The optimised result obtained for the objective function was **289163992 €.**

5.2.4 Sensitivity analysis

This section presents the sensitivity analysis performed on the factor with the greatest uncertainty considered and on which the model depends. In this case study, the factor analysed was the demand.

Demand

The present analysis was carried out with the objective of verifying the impact of demand on the configuration of the supply chain and consequent performance, with pessimistic scenarios being modelled, contemplating a decrease of 5 and 10% in demand, and optimistic scenarios, with an increase of 5 and 10% in demand. As expected, as the model is based on the movement of flows, triggered by market demand for bio-oil, the scenarios present variations in performance in each dimension, variations which correspond to that modelled for demand. Thus, in Table 22 it is seen a worsening of the economic impact in response to increased demand.

Table 21- Costs with demand variation

Demand	**-10%**		**-5%**		**0%**		**5%**		**10%**	
Scenarios	1	2	1	2	1	2	1	2	1	2
Transportation Costs W-P	9352	5249	10211	5627	11542	6055	12925	6195	***	***
Transportation Costs P-M	298394	143918	316026	150189	333657	156460	351288	163298	***	***
Biomass Costs	90149	49895	95157	52070	100165	54245	105173	56420	***	***
Production Costs	2908504	160977 1	3070088	1679949	3231672	1750128	3393255	1820306	***	***
Variable Costs	3306399	180883 3	3491482	1887835	3677036	1966887	3862643	2046219	***	***
Fixed Costs	**340M**	**160 M**	**340M**	**160 M**	**340M**	**160 M**	**340M**	**160 M**	***	***

***- Plant capacity exceeded

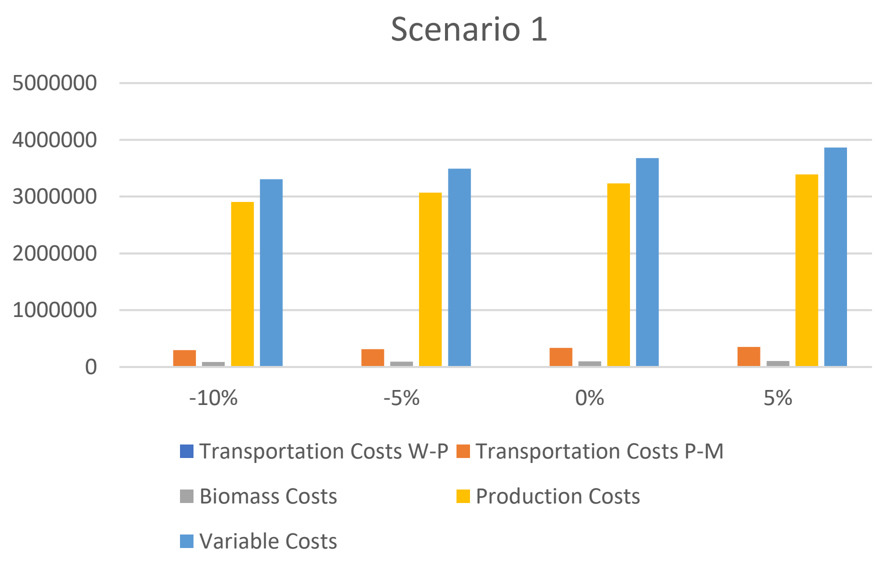

Figure 36- Variation of the costs according to variation of the demand-Scenario 1

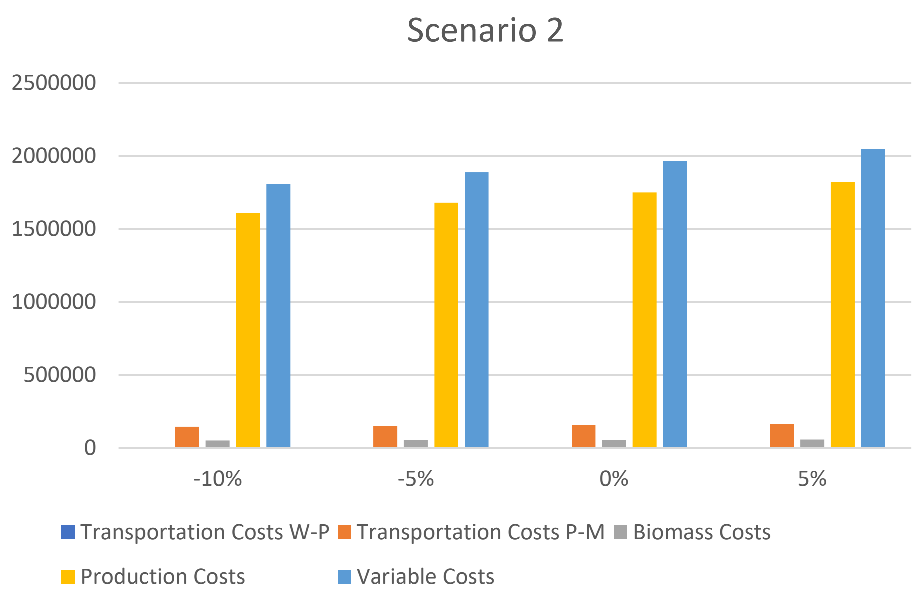

Figure 37-Variation of the costs according to variation of the demand-Scenario 2

The analysis performed in this section shows that there are no changes in the configuration of the supply chain in terms of the number of factories and their locations, being only visible variations in the flows between warehouses and plants and between plants and markets. Thus, with the growth in demand, there is a proportional increase in transportation, biomass, and production costs, which naturally increase variable costs. Therefore, focusing on economic performance, we conclude that the variation in demand causes a variation in the economic performance of the supply chain, being then naturally proportional to the variation in demand.

5. Conclusions and Future Work

Cigarette consumption is not expected to decrease, and it is also not expected that consumer behaviour will change in the coming years, cigarette butts will remain as one of the waste products with the greatest impact on the environment. The increasing development of the population will put increased pressure on natural resources and will inevitably create social imbalances. To deal with the coming future it is necessary to change the paradigm of business strategy and for that, circular economy could play a key role in creating a sustainable economic system. Cigarette Butts waste management is almost non-existent worldwide, and this represents a serious problem for the environment, since plastic, the constituent of the cigarette filter, takes many years to degrade and the chemicals are highly toxic. After problem characterization, it is concluded that this type of waste deserves more attention so that management and reuse solutions can be developed to deal with the excessive and unwanted amount of cigarette butts.

The literature review shows that there is some work on the reuse of cigarette butts through chemical, physical or chemical-physical processes. However, the solutions presented in the reviewed papers are underdeveloped, as there are few analyses to understand if the material recovery process is viable in economic and environmental terms and if it is actually feasible on an industrial scale. Moreover, it is almost inexistent the work of sustainable logistics of this waste. Authors suggest that it is critical to analyse the effective management of supply chains towards the improvement of operational efficiency and enhancing sustainable competitive advantage in circular economy. This means that in the literature the practical solution is often developed with direct re-use of cigarette butts with good operational results. However, how to efficiently obtain the cigarette butts to create a solution based on a structured supply chain to enable scaling up the process, is rarely addressed.

Two main literature gaps have been identified, first the lack of research on an integrated process of cigarette butt's collection for the creation of a structured supply chain and second, the lack of studies on the feasibility of cigarette butts reuse solutions, i.e., whether they are economically viable on an industrial scale and sustainable.

The development of this research shows, even if in an embryonic stage, it is possible to have a viable solution for value creation through cigarette butts. The laboratory results of the bio-oils produced are very encouraging, insofar as the yield of the most optimised process was around 98.15% and the higher heating value of 33.287 MJ/KG is, within the literature, well above the average of the bio-oils produced worldwide. However, it is necessary to stress once more that the valorisation solution will only have an impact if a different management of the cigarette butts is done, and a valid proposal was also presented during the development of this work. This research may represent great advances in the resolution of the problem characterised and contributes fully to sustainability and circular economy.

This project aims to fill the gap not only in literature but also in the world. The truth is that this entire study was developed in order to present a complete solution, which both presents solutions for the management of this very complicated waste but also a practical solution, most likely scalable and future-proof. The world is going through an industrial and energy revolution and alternatives to fossil fuels are increasing dramatically. The production of bio-oil from cigarette butts proves to be a perfect solution, since at the same time it minimises environmental pollution from one of the most toxic types of waste, it produces a biofuel, thus helping to reduce carbon emissions.

In the future, it is important to continue to invest in this solution, which may play a key role in society and, at the same time, may lead to the creation of a business. For that, it is necessary to carry out a pilot project, allowing a more robust economic analysis and further optimization of the process to prove that its application at an industrial level is profitable and sustainable. The theme of the project is very urgent, and the solution developed contributes to the objective defined by the European Union, reduction of greenhouse gas emissions by 2050. For this reason, I believe it is of common interest to finance this project, and therefore the next steps should involve an application to a European project.

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Appendix 1- Mathematical model optimization model

Scenarios Probability	
Scenario 1	0.7
Scenario 2	0.3

Fixed Costs of implementing each infrastructure

Plant	1)Lisbon	180000000
	2)Porto	160000000

Transportation Cost (€ ton) =	0.5

Distance (km)

Warehouses to Plants

	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu
1)Lisbon	255	176	366	488	226	206	132	277	318	146	10	227	314	82	50	385	378	291
2)Porto	75	446	56	208	255	117	363	547	198	181	314	290	10	243	347	75	94	125

Plants to Markets

	1 Spain	2 France	3 Germany	4 U. Kingdom
1)Lisbon	628	1739	2418	2180
2)Porto	554	1552	2232	1993

Plant Capacities

scenario 1	Capacity (ton)	CxY	Sum Capacities
1 Lisbon	204	204	408
2 Porto	204	204	

scenario 2	Capacity (ton)	CxY	Sum Capacities
1 Lisbon	200	0	250
2 Porto	250	250	

Warehouse Capacities Sheet "Warehouses"

	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu
Capacity	46	48	56	45	60	54	49	46	54	50	59	68	63	65	47	49	51	53

	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu
P_k (€ ton) CB's Cost	239	239	239	239	239	239	239	239	239	239	239	239	239	239	239	239	239	239

Process	Yield	Production cost
Bio-oil	89%	8664

Figure 38-Estimated Costs, distances,Yield and Capacities

Scenario 1	Demand Bio-oil (ton)	58	107	124	84	373.00
	Flow	58.00	107.00	124.00	84.00	
	Total Flow from Plant 1	169.00	Total Flow 1+2	373.00		
	Total Flow from Plant 2	204.00				
Scenario 2	Demand Bio-oil (ton)	45	76	36	45	202.000
	Flow	45.000	76.000	36.000	45.000	
	Total Flow from Plant 1	0.00	Total Flow 1+2	202.00		
	Total Flow from Plant 2	202.00				

	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu	Total
Flow Scenario 1	46	0	56	0	0	0	19	0	0	0	59	0	63	65	47	49	15	0	419

Total Flow	419
Demand/yield	419

	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu	Total
Flow Scenario 2	46	0	56	0	0	0	0	0	0	0	0	0	63	0	0	49	13	0	227

Total Flow	227
Demand/yield	227

Scenario 1	Total Inflow P1=	189.89	Inflow P1*Yield	169	419.1011236
Scenario 1	Total Outflow P1=	169.00			
Scenario 1	Total Inflow P2=	229.21	Inflow P2*Yield	204	
Scenario 1	Total OutflowP 2=	204.00			
Scenario 2	Total Inflow P1=	0.00	Inflow P1*Yield	1.13829E-13	226.9662921
Scenario 2	Total Outflow P1=	0.00			
Scenario 2	Total Inflow P2=	227	Inflow P2*Yield	202	
Scenario 2	Total OutflowP 2=	202.00			

	Flow	1 Aveiro	2 Beja	3 Braga	4 Bragança	5 Castelo Branco	6 Coimbra	7 Évora	8 Faro	9 Guarda	10 Leiria	11 Lisbon	12 Portalegre	13 Porto	14 Santarém	15 Setúbal	16 Viana do Castelo	17 Vila Real	18 Viseu
Scenario 1	Plant 1	0	0	0	0	0	0	19	0	0	0	59	0	0	65	47	0	0	0
	Plant 2	46	0	56	0	0	0	0	0	0	0	0	0	63	0	0	49	15	0
Scenario 2	Plant 1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Plant 2	46	0	56	0	0	0	0	0	0	0	0	0	63	0	0	49	13	0

	Flow	1 Spain	2 France	3 Germany	4 U. Kingdom
Scenario 1	Plant 1	58	0	111	0
	Plant 2	0	107	13	84
Scenario 2	Plant 1	0	0	0	0
	Plant 2	45	76	36	45

Figure 39-Flow Results

	Scenario 1	Scenario 2
Transportation Costs Warehouse- Plant 1	5382	0
Transportation Costs Warehouse- Plant 2	6161	6055
Transportation Costs Plant 1- Markets	152411	0
Transportation Costs Plant 2- Markets	181246	156459.5

Transportatin Cost	Scenario 1	Scenario 2
W-P	11542	6055
P-M	333657	156460

	Scenario 1	Scenario 2
Fixed Costs	340000000	160000000
Variable Cost	345199	162514

Biomass costs scenario 1	100165
Biomass costs scenario 2	54245
Production Costs Scenario 1	3231672
Production Costs Scenario 2	1750128
Objective Function	289163992
	289 MI

	Scenario 1		Scenario 2	
	I	%	I	%
Transportation Costs W-P	**11542**	0.3%	6055	0.3%
Transportation Costs P-M	**333657**	9.1%	156460	8.0%
Biomass Costs	**100165**	2.7%	54245	2.8%
Production Costs	**3231672**	87.9%	1750128	89.0%
Total Costs	**3677036**		1966887	

Figure 40-Costs Results

Variables	
XW1,1,1	0.00
XW2,1,1	0.00
XW3,1,1	0.00
XW4,1,1	0.00
XW5,1,1	0.00
XW6,1,1	0.00
XW7,1,1	18.89
XW8,1,1	0.00
XW9,1,1	0.00
XW10,1,1	0.00
XW11,1,1	59.00
XW12,1,1	0.00
XW13,1,1	0.00
XW14,1,1	65.00
XW15,1,1	47.00
XW16,1,1	0.00
XW17,1,1	0.00
XW18,1,1	0.00
XW1,2,1	46.00
XW2,2,1	0.00
XW3,2,1	56.00
XW4,2,1	0.00
XW5,2,1	0.00
XW6,2,1	0.00
XW7,2,1	0.00
XW8,2,1	0.00
XW9,2,1	0.00
XW10,2,1	0.00
XW11,2,1	0.00
XW12,2,1	0.00
XW13,2,1	63.00
XW14,2,1	0.00
XW15,2,1	0.00
XW16,2,1	49.00
XW17,2,1	15.21
XW18,2,1	0.00
XW1,1,2	0.00
XW2,1,2	0.00
XW3,1,2	0.00
XW4,1,2	0.00
XW5,1,2	0.00
XW6,1,2	0.00
XW7,1,2	0.00
XW8,1,2	0.00

XW8,1,2	0.00
XW9,1,2	0.00
XW10,1,2	0.00
XW11,1,2	0.00
XW12,1,2	0.00
XW13,1,2	0.00
XW14,1,2	0.00
XW15,1,2	0.00
XW16,1,2	0.00
XW17,1,2	0.00
XW18,1,2	0.00
XW1,2,2	46.00
XW2,2,2	0.00
XW3,2,2	56.00
XW4,2,2	0.00
XW5,2,2	0.00
XW6,2,2	0.00
XW7,2,2	0.00
XW8,2,2	0.00
XW9,2,2	0.00
XW10,2,2	0.00
XW11,2,2	0.00
XW12,2,2	0.00
XW13,2,2	63.00
XW14,2,2	0.00
XW15,2,2	0.00
XW16,2,2	49.00
XW17,2,2	12.97
XW18,2,2	0.00
XP1,1,1	58.00
XP1,2,1	0.00
XP1,3,1	111.00
XP1,4,1	0.00
XP2,1,1	0.00
XP2,2,1	107.00
XP2,3,1	13.00
XP2,4,1	84.00
XP1,1,2	0.00
XP1,2,2	0.00
XP1,3,2	0.00
XP1,4,2	0.00
XP2,1,2	45.00
XP2,2,2	76.00
XP2,3,2	36.00
XP2,4,2	45.00

Y2,1	1.00
Y1,2	0.00
Y2,2	1.00

Figure 41- Decision Variables