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Master's Degree Thesis:

Pyrolysis of plastics for the production of sustainable alternative fuels for the marine sector

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Chapter 1

Introduction

Plastics are a versatile and widely used material which possess distinctive and unique features such as durability, lightness, chemical resistance, and low costs. These qualities enable plastics to be consumed in large quantities in different industries such as packaging, building and construction, textiles, transportation, industrial and consumer goods, electrical and electronic devices, and industrial machinery. The global production of plastics has increased substantially in the past decade, rising from 270 million metric tons (MMT) to 367 MMT in 2020 and it is predicted to become 590 MMT in 2050. In Europe, plastics production exceeded 60 million ton in 2018. Packaging is the dominant end-use market for plastics in Europe, with a share of 40%. The other two main sectors are the construction with 20% and automotive with 10% [8, 20, 57].

A serious issue regarding plastics is the lack of post-consumption treatments. A large portion of manufactured plastics are used as single used packaging material, and often have a relatively short service life, which leads to generation of huge amount of plastic wastes. It is estimated that around 300 Mt of plastic waste is generated annually, creating a significant impact on the environment. The majority of monomers used in plastics production such as ethylene and propylene have fossil hydrocarbons origin. In addition to using non-renewable resources, these types of plastics are not biodegradable, thus they accumulate instead of decomposing in the landfills or natural environment. From year 1950 to 2015, the accumulative production of plastics reached 8.3 billion metric tons of which 7.2% have undergone recycling processes and 9.6% were incinerated and the remaining plastics were disposed of in the lands, rivers, and seas [22, 25, 47, 57].

The plastics left in the environment due to irresponsible waste disposal gradually enter the oceans. It is estimated that 10 to 20 million tons of plastic waste annually ends up in the oceans resulting in over 5 trillion plastic wastes of varying sizes and shapes weighing over 250,000 tons, currently floating in the ocean. Additionally, due to the recent COVID-19 pandemic, the demand for single use plastics such as personal protective equipment and online-shopping packaging material increased substantially, which generated 8 million tons of pandemic related waste plastic worldwide, with $>$25,000 tons entering the oceans. In Europe, according to an updated analysis, the input of plastics into the Mediterranean Sea amounted to 229,000 tons per year or approximately 627 tons per day and over 1 million tons of plastics is currently present within the basin. Plastic accumulation in deep sea is particularly concerning, since plastic longevity increases in deep waters. It is estimated that approximately 500 million litter items are currently scattered across the Mediterranean Sea floor [17, 20, 106].

In marine environment plastic waste is a great environmental issue. It is fundamentally altering both marine and terrestrial ecosystems. The presence of plastic pollution in marine environment presents substantial threats to human livelihoods that relies on the integrity of such environments, such as tourism and fishing, additionally it carries significant economic loss. It is estimated that the potential negative impacts on fishing and tourism are around 3300 USD (approximately 3000 €) per ton of marine plastic per year. Furthermore, in European countries the expenses associated with beach cleaning may reach 3,800 € per ton per year. Addressing floating litter, it was indicated that removal was equal to a unit cost of 2,200 € per ton per year per km^2. In the case of the fishing industry an annual economic loss of EUR 61.7 million has been estimated in European waters with a total cost for all sectors reaching EUR 263 million [35, 105].

As previously stated, landfilling is the common method of dealing with plastics. However, this method of management has negative impacts on environment and human health. The chemicals present in waste plastic can reduce soil fertility and may pollute groundwater. Additionally, the rising costs and decreasing availability of suitable sites have contributed to plastic waste becoming a significant global environmental issue. Incineration is another way for processing plastic waste. The practice while enables energy recovery is extremely harmful for the environment, since during combustion harmful gases such as dioxins, polychlorinated biphenyls, mercury, furans, halogenated and volatile organic compounds are emitted and must be treated. In addition, incineration which only recovers heat/ electricity, while chemical and monomers are lost is not preferable in waste management hierarchy. Recycling is the third and the preferred option for end-of-life management of plastic waste, since it can avoid disposal and replace the use of virgin materials. Despite that, just 14% of plastic packaging is collected today and only 2% is closed loop recycled into same quality material. Currently in Europe, only one-third of post-consumer plastic waste is collected for recycling, with the majority (43%) incinerated in waste-to-energy facilities, while the remaining portion landfilled. Nearly all commercial plastic recycling plants utilize mechanical recycling routes. The main drawback is that it can degrade the mechanical properties of plastic materials due to loss in polymer quality during recycling process, 'downcycling' the plastics into secondary and less valuable products. Furthermore, such process's efficiency is hindered in recovering large amounts of targeted plastic from mixed municipal solid waste, multilayered or heterogeneous plastics and plastics with high contamination levels [57, 66, 69, 85].

Another option for plastic recycling, besides mechanical recycling is chemical recycling. Chemical recycling encompasses a group of advanced recycling technologies that convert plastic waste into valuable feedstocks such as monomer, oligomers, and higher hydrocarbons, which subsequently can be used in chemical industry. One of the most mature and important chemical recycling technologies is pyrolysis. Pyrolysis is a process which involves the thermal decomposition of materials at high temperatures without the presence of oxidants which causes the breakdown of polymers into monomers or shorter chain hydrocarbons, and the production of oil, fuel gas, and other by-products. The advantage of pyrolysis process lies in its ability to recycle plastics contaminated with other organic materials and mixed waste plastics, thus eliminating washing and carful sorting steps, lowering pre-treatment costs. Moreover, pyrolysis is more environmentally friendly than incineration and landfilling, and has considerably lower carbon footprint compared to direct incineration. The main products of waste pyrolysis plastics are gas, liquid oil, and char, which can be utilized in different industries. Among the main products, plastic oil exhibits a high heating value (HHV) comparable to conventional gasoline and diesel fuels. Additionally, it possesses lower acidity and higher stability in comparison to pyrolysis oil derived from biomass, therefore it can be utilized as fuel in diesel engines, boilers, furnaces, and turbines [57, 66, 69, 72, 85].

Considering these factors, using marine plastic waste as feedstock for a pyrolysis process to produce fuel for maritime shipping presents a compelling opportunity. Large quantities of plastic waste currently pollute the oceans, posing significant threats to both the environment and human health. Conventional methods of dealing with marine plastics often exacerbate environmental harm, while pyrolysis has proven effective in managing complex plastic waste streams, producing oil that can be refined into fuel. This approach offers the dual benefit of creating cleaner fuels for shipping and contributing to the cleanup of our oceans.

The objective of this project is to assess the feasibility of using marine plastic waste as feedstock for a pyrolysis process to produce fuel for marine sector. To achieve this, relevant policies on ocean cleanup and marine fuel standards were reviewed. An analysis of marine litter quantity, types, and composition was conducted to estimate the potential product distribution from pyrolysis. Based on these findings, two potential processing capacities were proposed, each with multiple feedstock case studies, and corresponding mass and energy balance calculations were performed. Building on these calculations, an industrial-scale plant was designed, and the mass and energy balances were adjusted to reflect realistic operational conditions. Finally, a basic economic analysis was carried out to evaluate profitability and key economic factors.

Chapter 2

Possibility of Marine Litter Plastic Oil for Shipping

The chapter explores the possibility of utilizing oil derived from pyrolyzing marine plastic waste as a sustainable fuel alternative for the maritime industry. It begins by analyzing existing policies and initiatives aimed at the collection of marine litter, highlighting the potential for a consistent supply of plastic feedstock from European seas. It then delves into the characteristics of the oil produced through plastic pyrolysis, drawing on literature reviews to assess its suitability for use in shipping. Finally, this chapter broadly examines the marine transportation sector, focusing on current decarbonization efforts and the challenges faced by other sustainable fuel options, ultimately arguing that plastic-derived oil offers distinct advantages that address many of these challenges. Through this analysis, the chapter provides a comprehensive overview of the potential for integrating marine plastic waste into a circular economy that supports the decarbonization of maritime transport.

2.1 Policy Framework

It is clear that marine litter, specifically plastics, poses a great threat to ocean's ecosystems. Throughout the years policies have been introduced to tackle this persistent and widespread issue.

The London Convention, also known as the "Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter 1972" was one of the earliest conventions established to safeguard the marine environment from human activities and it has been in effect since 1975. It implements practical measures to prevent the dumping of waste and other substances into the sea. The "London

Protocol" further modernized the Convention in 1996 and eventually replaced it. The Protocol, being more restrictive than Convention, adopts a "reverse list" approach which prohibits all dumping activities, except when explicitly permitted. In 1982, United Nations Convention on the Law of the Sea (UNCLOS) was adopted. It is a global treaty, which establishes a legal structure for all marine and maritime activities. UNCLOS article 194 specifies that states should take necessary measures to prevent, reduce, and control marine environment pollution from any source, by using practical methods available to them and aligning their policies to this objective [51, 104].

The International Convention for the Prevention of Pollution from Ships (MARPOL) is a global agreement adopted by the International Maritime Organization (IMO) that encompasses measures to prevent pollution of the marine environment by ships from operational activities and accidental occurrences. It includes six technical Annexes. Annex V of MARPOL main objective is to eliminate and reduce the pollution by garbage discharged by ships except in cases where explicit permission under the Annex is granted. Under MARPOL Annex V, garbage includes all types of food, domestic and operational waste, all plastics, cargo residues, incinerator ashes, cooking oil, fishing gear, and animal carcasses generated during the regular operation of the ship and are subject to continuous or periodic disposal. Fresh fish and its parts, resulting from fishing activities conducted during the voyage or aquaculture operations, are excluded from the definition of garbage. Regulation 7 outlines limited exceptions to these regulations in emergency and non-routine situations. In General, discharge is restricted to food wastes, identified cargo residues, animal carcasses, identified cleaning agents and additives, and cargo residue entrained in wash water which poses no harm to marine environment. It is advised that ships use Port Reception Facilities (PRF) as the primary method of discharge for all types of garbage [51, 70, 76].

Under Annex V, multiple sea areas were designated as Special Areas, due to particular oceanographic, ecological and traffic characteristics, such as heavy maritime traffic, low water exchange, extreme ice states, endangered marine species, etc. These areas are Mediterranean Sea area, Baltic Sea area, Black Sea area, Red Sea area, the Gulfs area, North Sea area, Wider Caribbean Region, and the Antarctic area. Stricter measures are required in these areas to prevent marine pollution caused by garbage, and they are provided with a higher level of protection. Ships navigating in Special Areas may be unable to meet the stricter discharge criteria for waste, thus be required to deliver their waste to PRF. The effectiveness of ships to meet the discharge requirements of MARPOL primarily relies upon the availability of adequate PRF, especially within Special Areas. Regulation 8 of MARPOL Annex V provides that governments must ensure the provision of sufficient PRFs for garbage from ships and should facilitate and encourage their utilization. MARPOL parties with coastlines border the respective Special Areas have an obligation to provide adequate PRF [51, 70, 76].

Moreover, Annex V provides guidance and instructions regarding various aspects of waste management on board ships, information, and education, PRFs, inspection and more. It mandates that all ships weighing 400 gross tonnage or more and every ship which is certified to carry 15 persons or more engaged in voyages to ports and offshore terminals under the jurisdiction of another Party to the Convention and every fixed or floating platform to provide a Garbage Record Book and to document all disposal and incineration operations. Additionally, it requires every ship measuring 12 meters in length or over along with every fixed or floating platform to display placards notifying passengers and crew of the disposal requirements of the Annex, written in the working language of ship's crew and also in English, French or Spanish for ships travelling to other States' ports or offshore terminals [51, 76].

At European level several additional directives exist to ensure the safety of marine ecosystem, enhance the ports waste management and overall address the plastic pollution issue. To combat marine litter, damage of seabed, biodiversity loss and ocean warming, the European Union (EU) has implemented Marine Strategy Framework Directive (MSFD) as a holistic policy to protect the marine environment in European seas while enabling the sustainable utilization of marine resources. MSFD was adopted by EU in 2008 with the goal of maintaining healthy and resilient marine ecosystems while securing a more sustainable use of marine resources. This directive serves as one of the most ambitious international marine protection legal frameworks, bringing together 23 coastal and 5 landlocked states to implement ecosystem-based management and achieve good environmental status in approximately 5,720,000 km^2 of sea surface across four sea regions. Member States are required to develop national marine strategies to attain or maintain 'good environmental status', which was expected to be achieved by 2020, to effectively protect and conserve the oceans and coasts. Base on the directive the definition of Good Environmental Status (GES) is "The environmental status of marine waters where these provide ecologically diverse and dynamic oceans and seas which are clean, healthy and productive". Moreover, Annex I of the directive outlines eleven qualitative descriptors to assist the member states in understanding the characteristics of the environment when GES has been achieved [28, 30].

Based on the implementation report adopted in 2020, marine litter, particularly plastic items, has gained significant attention. This report reveals that plastic items are the most prevalent type of marine litter. For example, single-use plastics make up 50% of the total count of litter items on European beaches, and fishing gear containing plastics accounts for an additional 27% . These findings, alongside assessments conducted through the MSFD and regional sea conventions, have led to swift legislative actions at the EU level. The actions specifically target single-use plastics, fishery-related litter, as well as the revision of PRFs to facilitate the proper disposal of waste from ships which is Directive (EU) 2019/883. In European ports, the development and usage of Port Waste Management Plans (PWMPs) is already commonplace, since the initial EU PRF Directive 2000/59/EC, was implemented in 2000, required the establishment of Waste Reception and Handling Plans for all ports receiving seagoing vessels, regardless of vessel type or port size. Directive (EU) 2019/883 on PRFs for the delivery of waste from ships, which amended Directive 2010/65/EU and repealed Directive 2000/59/EC, introduced even more detailed guidelines for the development, usage, approval, and renewal of PWMPs. Furthermore, European Green Deal and EU Circular Economy framework tackle plastic waste issue (both in marine and terrestrial environment) in a comprehensive approach, contributing more to the reduction and recycling of the waste plastics [30, 70].

During fishing operations, fishers often encounter waste that has caught in their nets, which is known as "passively fished waste". As a result, several international non-governmental organizations have developed the Fishing for Litter scheme. The main idea is to encourage fishers to gather waste caught in their nets instead of discarding it at sea. Participating vessels are given especially designed bags to collect marine litter that is encountered. The filled bags are then delivered free of charge to designated PRFs, where they are moved by staff to a dedicated skip for disposal. It is important to note that waste generated on board during the operation is the responsibility of the vessel, and it continues to go through established port waste management systems. The Fishing for Litter program was initiated in March 2000 by the North Sea Directorate of the Dutch Government, in collaboration with a Dutch Fisheries Association and the active involvement of KIMO. The primary aim of the initiative was to clear marine litter from the North Sea. The simplicity and efficient nature of the scheme led to its swift adoption by fishers and ports in various European countries and measures have been included in several regional action plans on marine litter to address Fishing for Litter. Furthermore, policy making is beginning to address passively fished waste. On the latest document of Annex V which is resolution MEPC.295(71), adopted on 7 July 2017, it is encouraged that seafarers recover persistent garbage from the sea during routine operations as opportunities arise and prudent practice permits and to retain the material for discharge to port reception facilities. In resolution MEPC.310(73) which is an action plan addressing directly plastic waste originated from ships, has introduced measures including incentives for fishing vessels to retrieve used fishing gear and deliver it to port reception facilities, and to consider the issue of waste collected during fishing operations, building on experience gathered from established projects. These measures were also included in resolution MEPC.341(77) and were considered as mid-term actions. Additionally, Directive (EU) 2019/883 contains regulations related to the handling of passively fished waste, which was included in the definition of "waste from ships". EU Member States must ensure the availability of adequate PRFs capable of receiving such waste. To avoid placing the costs of collection and treatment of passively fished waste solely on port users, Member States are expected to cover relevant expenses using revenues generated from alternative financing systems such as extended producer responsibility schemes, and by EU, national or regional funding [51, 68, 71, 76–78].

2.2 Plastic Oil as Maritime Fuel

2.2.1 Literature Review

Plastic components decompose across a broad temperature range and produce a variety of products in liquid, gas, and solid form. The composition and yield of these products depend not only on process parameters such as temperature, and residence time but also on the specific composition of the waste plastic itself. To determine the expected outputs and assess whether the resulting pyrolysis oil is suitable for marine applications, it is essential to analyze a wide range of studies on plastic pyrolysis. While numerous studies have investigated the pyrolysis of single plastic types and documented their behavior during the process, these findings, though insightful, do not fully represent the conversion of marine litter into pyrolysis oil. Marine litter typically consists of a complex mixture of multiple plastic types, often contaminated with foreign materials. Therefore, this literature review will focus exclusively on the pyrolysis of mixed plastics under various conditions. The composition of the feedstock will be discussed in greater detail in subsequent chapters.

In a study conducted by Gerardo Martinez-Narro et al., the chemical recycling of mixed waste plastics was investigated. The composition of plastic feedstock loosely resembled European plastic demand and was consisted of PE, PP, PET, and PS. The study explored both thermal and catalytic decomposition processes with biochar and Zeolite HY serving as catalyst separately and temperature range of 500°C to 800°C. In most of the cases the wax faction (both in reactor and condenser) was the dominant product with a yield of 50% to 70%, followed by gas faction and char faction. Increasing temperature led to the increase in gas faction and in the case of thermal pyrolysis and biochar, temperature of 800°C led to gas being the dominant product. In the wax fraction, 36 components were detected with components having lower carbon than C9 being the dominant group. Despite being mostly made of long chain hydrocarbon feedstock, considerable amount of aromatics was detected, with styrene which is formed due to presence of PS, being the dominant aromatic compound. Benzoic acid which forms due to PET, and other types of aromatics were also detected. Catalysts mostly affected gas faction. Biochar, activated at 800°C, led to almost 80% of gas production, while it removed benzoic acid from wax. On the other hand, Zeolite HY was activated at lower temperature of 600 °C, it increased the light hydrocarbons in the gas faction and somewhat lowered CO_2 without any dramatic effect on wax yield [69].

In a similar study, Jude A. Onwudili et al. analyzed mixed plastic pyrolysis with multiple catalysts in a two-stage reactor. The plastic feedstock composition consisted of PE, PP, PS, and PET. Four catalysts were used for this study including spent FCC, two types of zeolite Y (ZY-1and ZY-2), and one ZSM-5. Moreover, quartz sand was used in the second stage to simulate a non- catalytic situation. At 500°C, oil yield was as high as 70% for all the settings, with sand bed having the highest yield of close to 80% followed by spent FCC and ZY-2, while ZSM-5 and ZY-1 showed stronger conversion to the gas fraction. Increasing temperature to 600°C, led to an increase in the gas fraction in expense of oil. The effect of temperature was much more dramatic for ZY-1 and ZSM-5, with ZSM-5 having over 50% of gas yield. Using catalyst improved the oil by increasing hydrocarbons within fuel range for all the cases. The increment of fuel range hydrocarbons was observed when the temperature increased to 600°C for all the cases aside spent FCC, however the amount of oil was reduced. Aliphatic compounds were dominating in all of the cases, consisting close to 60% of all the compounds within the oil, aside for ZY-1 catalyst which produced more aromatic content. In other cases, temperature had more effect on the formation of aromatics than the catalyst type. Increasing the temperature to 600°C led to slight reduction in aliphatic compounds and increase of the aromatic content [75].

Mohammed Al-asadi et al. conducted a pyrolysis-gasification study on real waste plastic at 550°C and 850°C using a single-stage tubular reactor. The research focused on examining the effects of various bimetallic catalysts combined with dolomite, as well as the impact of two different carrier gases (N_2 and CO_2). The feedstock was obtained from municipal waste containers, and was consisted of PE, PP, PET, and other plastic groups. The share of PET was noticeably higher in this study at 45%. Six different bimetallic catalysts were synthesized using neat ZSM-5 as the base. The findings revealed that both the catalysts and the elevated temperatures increased gas yields. In the absence of any catalyst, the process produced nearly 60%

liquid oil. However, with the use of catalysts, the oil yield dropped to around 40%, with Ni/ZSM-5 yielding the lowest oil output at 30%. Dolomite slightly reduced the oil yield, an effect that was most pronounced at 850°C when used in conjunction with bimetallic catalysts, which also helped reduce carbon deposition on the catalysts. The resulting oil contained a significant amount of n-paraffins and n-olefins, attributed to the high polyethylene content in the feedstock. Catalysts promoted the formation of branched aliphatic compounds, while the presence of CO_2 in the atmosphere further increased the n-paraffin and n-olefin content. Regarding the single ring aromatics, use of catalysts leads to increase the amount of such compounds, which encourages aromatization reactions though this effect was different for each catalyst. Presence of CO_2 and high temperature slightly decreased the aromatic compounds in the oil. Oxygenated compounds, primarily phenol, benzoic acid, and terephthalic acid, were also detected. Under an N_2 atmosphere, the levels of phenol and terephthalic acid increased with temperature, whereas the opposite trend was observed under a CO_2 atmosphere. The use of catalysts reduced the concentrations of phenol and benzoic acid at both temperatures. However, catalysts with a second metal incorporation resulted in higher concentrations of terephthalic acid at 850°C [3].

In another study done by A. Lopez et al. four real samples from the reject stream of a waste separation plant in the north of Spain have been pyrolyzed and their product characteristics have been reported. Sample 1 was mainly made of main groups of plastics with low levels of other packaging materials and ABS. Sample 2 was also similar to sample 1, but it had a high amount of PE films. Unlike the other two samples, sample 3 had a considerable amount of foreign materials with papers being the dominant material after plastics, while in sample 4, the amount of glass was high after the plastics. The pyrolysis results revealed that sample 1 and sample 2 achieved the highest conversions to liquids and gas, exceeding 90%. The solid fraction constituted the minority in all of the cases. Sample 3 yielded the highest amount of char due to presence of paper which encourages char formation, however other samples produced 3% to 5% of char, attributed to plastics with a tendency to form char, such as PET and PVC. Sample 3 also produced a significant amount of aqueous liquid phase, a result of the pyrolysis of cellulose-rich samples. GC-MS analysis of the pyrolysis oil from the four samples indicated that the liquid is a mixture of organic compounds of 6 to 21 carbons. A short summary of the results has been provided in the table below:

	Sample 1	Sample 2	Sample 3	Sample 4
Total Aromatics	74.9	36.5	96.6	93.4
Total unsaturated compounds	21	38.9	3.4	4.7
Total saturated compounds	0	24.6	0	1.93
Not identifies	4.1	0	0	0

Table 2.1: Fractions of interest in pyrolysis liquids (percent area) [67]

High levels of aromatics were attributed to Diels-Alder mechanism. Furthermore, it was pointed out in the study that despite sample 1 and sample 4 having a similar polyolefin content, sample 4 produced much higher proportions of aromatics. This was attributed to higher metal content of Sample 4, and it was noted that other research groups have found that metal-containing catalysts lead to formation of aromatic compounds in plastic pyrolysis. Additionally, gross calorific and elemental composition of liquid oils have been examined. Calorific value for sample 1 and 2 was 41.2 MJ/kg and 41.8 MJ/kg showcasing their potential to be used as a fuel. Sample 4 calorific value was 36.6 MJ/kg, indicating that with slight adjustment its oil can also be used as fuel for most applications [67].

Finally, A. Adrados et al. compared plastic pyrolysis processes of plastic residue from a material recovery facility, which was the same as sample 4 of A. Lopez et al. study with a simulated plastic waste stream consisting solely of plastics. The waste sampled from the recovering facility (sample 4) comprised 59.98% of main group plastics, 5.34% other packaging materials such as metals, and 34.68% inappropriate materials such as other plastic groups, paper, wood, and glass. In contrast, the simulated sample consisted exclusively of main plastic groups with PE and PP being the dominant factions. The study indicated that the plastic stream contaminated with other materials showed a higher char formation due to presence of materials with functional groups such as -OH and =O, which are typical in wood, paper, Acrylonitrile Butadiene Styrene (ABS), and Polycarbonate (PC). Furthermore, this sample had a lower liquid to gas ratio than the sample with only plastics. This was attributed to metal and glass possibly acting as a catalyst, increasing the gas yield. The pyrolysis oil from material recovery plant sample had a lower molecular weight compared to simulated sample and it consisted of over 90% aromatic compounds. Both being lighter weight and high aromatic content were attributed to presence of inorganic materials, which seems to facilitate cracking, and formation of aromatics [2].

A summary of the literature review is provided at the table below:

Temperature [°C]	Plastic Mixture	Catalysts Used	Remarks	References
500°C-800°C	PS: 10%, PP: 30%, PET: 13%, HDPE: 20%, LDPE: 27%	No Catalyst, Biochar, Zeolite HY	Wax (liquid) fraction was the dominant product in all temperatures aside 800°C. 40% to 70% of wax can be expected. Catalysts led mostly to gas production and, in some cases, removed Benzoic acid.	Martinez [69]
500°C & 600°C	PS: 15%, PP: 8%, PET: 15%, HDPE: 19%, LDPE: 43%	No Catalyst, Zeolite from FCC, ZSM-5, Zeolite Y-1, Zeolite Y-2	At 500°C with no catalyst, oil yield was 80%. Catalysts improved oil production by increasing hydrocarbons within the fuel range but also increased gas yield. ZY-1 produced more aromatics. Higher temperature led to more aromatic formation.	Onwudili [75]
550°C & 850°C	PP: 19%, PET: 45%, HDPE: 14%, LDPE: 17%, Other plastics: 5%	No Catalyst, Ni/ZSM-5, Ca/Ni/ZSM-5, Ce/Ni/ZSM-5, La/Ni/ZSM-5, Mg/Ni/ZSM-5, Mn/Ni/ZSM-5	Without any catalyst at 550°C, oil yield was 60%. With catalysts, it dropped to around 40%. Catalysts encouraged single-ring aromatic formation and reduced oxygenated compounds.	Al-Asadi [3]
500°C	Sample 1: Plastic with 3% foreign material, Sample 2: Film (PE) rich, Sample 3: Paper rich, Sample 4: Glass and metal rich	No Catalyst	Samples 1 and 2 had oil yields over 90%. Sample 3 had the highest char content and produced an aqueous liquid phase. Glass and metal in Sample 4 encouraged Diels-Alder reactions, producing aromatics. Oil's gross calorific value was close to conventional fuels.	A. Lopez [67]
500°C	Simulated Sample, Real Sample with glass and metal	No Catalyst, Red mud	Feedstock contaminated with foreign materials produced more char. Glass and metal in the feedstock encouraged gas production and aromatic formation.	A. Adrados [2]

Table 2.2: Summary of literature review

From these studies, it can be deduced that achieving a relatively high plastic oil yield, in the order of 70%, is possible in most settings. Furthermore, the byproduct of the pyrolysis is often rich in light hydrocarbons and depending on the feedstock and operational conditions its heating value is in the range of 25 to 45 MJ/kg. Thus, it has the potential to be used as a heating source for the pyrolysis process itself. The composition of the oil exhibited high variability, influenced by multiple factors. Nonetheless, it was abundant in high-value hydrocarbons, highlighting its potential as an alternative source of fuel. Despite the feedstock being mostly made of polyolefins, aromatic content of the pyrolysis oil was relatively high. A mechanism known as Diels-Alder of alkenes has been suggested as the main reason for high yields of aromatic compounds. Finally, the presence of foreign materials, usually leads to the pyrolysis yields to be somewhat lower than an optimum situation, where the feedstock consists solely of plastics, with more char formation due to the presence of certain materials and more gas production because of metal and glass acting similar to a catalyst. Metal and glass contamination also encourages Diels-Alder mechanism and further breaking of molecular chains, creating a light oil product with extremely high levels of aromatics [2, 67, 69, 75, 85].

2.2.2 Plastic Oil Possibility and Challenges

A crucial property of a fuel is its calorific value which indicates the energy content of a fuel. In the table below the calorific value of some conventional and alternative fuels used in maritime sector has been provided.

Fuel	Gasoline	Diesel	LPG	MGO	FAME	HVO	DME
Calorific Value (MJ/kg)	46.8	43	46.1	42-44	37-38	34-44	28

Table 2.3: : Calorific value of several fossil fuels and alternative fuels in maritime sector [63, 72].

Depending on the operational conditions and the plastic feedstock calorific value for the plastic oil is within the range of 18 to 49 MJ/kg. Plastic oil with high content of HDPE, LDPE, PE, and PS can easily substitute conventional fossil fuels in terms of energy. On the other hand, PVC, and PET with a calorific content in the magnitude of 18 to 25 MJ/kg are unsuitable for marine applications. Subsequently, physio-chemical properties of the plastic oil should fall within the specified range set by the marine diesel standard ISO 8217. A summary of ISO 8217 values for marine distillate fuels is provided below [72].

Characteristics	Units	Marine distilate fuels
Kinematic viscosity at 40 °C	mm^2 /s	1.4 - 11
Density at 15 °C	kg/m^3	<900
Cetane index	-	>35
Sulfur	mass (percent)	<1.5
Flash point	°C	>43
Hydrogen sulfide	mg/kg	<2
Acid number	mg KOH/g	<0.5
Oxidation stability	g/m^3	<25
Fatty acid methyl ester (FAME)	volume (percent)	<7
Carbon residue – Micro method	mass (percent)	<0.3
Cloud point	°C	Summer: <-16 Winter: <-16
Pour point (upper)	°C	Summer: <6 Winter: <0
Water	volume (percent)	<0.3
Ash	mass (percent)	<0.01

Table 2.4: ISO 8217 [91].

A recent study by S.M.R. Mirkarimi et al. indicated that from among 19 plastic oils, almost all of them can be used as a fuel for marine diesel engine with some modifications done on their flash point. Moreover, plastic oil Sulphur content is negligible, which is in line with new IMO regulation regarding Sulphur content [20, 72].

However, there are challenges, which prevent plastic oil to become a drop-in fuel within the marine transportation industry. A major issue is the inconsistent plastic quality, which leads to variations in the characteristics of the resulting pyrolysis oil. Various types of plastics, yield distinct types of liquid oil with specific traits, and as different sources of mixed waste plastics possess varying plastic compositions, the quality of the produced pyrolysis oil differs accordingly. In one of the studies examined in literature review, it was evident that even different foreign materials can significantly alter the plastic oil composition. Another significant challenge is regarding the aromatic content of plastic oil. Current marine fuels such as HFO, are mostly composed of long chains of hydrocarbons, on the other hand plastic oil from the pyrolysis process tends to yield large quantities of aromatic compounds. Even in case of plastic feedstocks mostly consisted of polyolefins such as PE and PP, aromatic compounds can be found in significant quantities due to Diels- Alder mechanism, while in some cases the aromatic content can reach to above 90% . While there are no values or restrictions for aromatic content for marine fuels, it is safe to say that such high levels of aromatic content will certainly leads to inefficient engine performance by more NO_x emissions, higher levels of unburned hydrocarbon, CO emissions, and greater amount of smoke than conventional diesel oil since aromatic contents tend to lead to higher engine temperature. More studies should be done regarding the effect of plastic pyrolysis oil on ship engines [2, 67, 72, 75].

2.3 A Look into Marine Transportation Sector

In previous sections, it was established that that existing policies and programs support the collection of plastic waste at PRFs and the removal of marine litter from the seas, ensuring a steady supply of mixed waste plastics. Through literature review it was demonstrated that pyrolysis of these plastics can possibly produce substantial yields of oil that are significantly compatible with marine fuel standards. To determine whether plastic oils can truly serve as a viable alternative to conventional marine fuels, it is essential to examine the broader context of maritime transport. This includes an analysis of sustainability goals, current challenges in the sector, and the existence of alternative fuels in the effort to decarbonize maritime operations.

The global economy heavily relies on maritime trade, which accounts for over 80% of global trade by volume and 70% by value. With more than 85,000 registered vessels, the maritime sector serves as a vital asset, facilitating the majority of international trade. In the European Union (EU), maritime trade plays a crucial role, accounting for approximately 75% of external and 31% of internal trade volumes. Moreover, in 2019, around 400 million passengers embarked or disembarked in EU ports. Heavy Fuel Oil (HFO) is the primary energy carrier of maritime shipping industry because of its low cost, being abundant, and developed infrastructure. HFO is a low-quality fuel which is obtained through the refining and distillation of crude oil, and often contains high concentrations of mineral pollutants like sulfur, vanadium, and nickel. Consequently, HFO combustion emits high pollutant emissions such as CO_2, Nitrogen oxides ($NO_{x,}$) and Sulphur oxides (SO_x). Approximately 14% to 31% of global NO_x emissions and 4 to 9% of SO_x originate from marine vessels. Additionally, maritime shipping is the leading source of black carbon within the Artic Circle and serves as a significant source of anthropogenic particulate matter (PM) and CO_2 emission [44, 84, 88].

In line with the objectives of Paris Agreement, the IMO adopted "Initial Strategy for the Reduction of GHG emissions from Shipping" in 2018, which sets forth a goal to reduce GHG emissions by 50% by 2050 compared to 2008 as initial step, and ultimately, the complete decarbonization of maritime transport. In 2023 this strategy was revised to enhance the IMO's efforts in reducing GHG emissions from the shipping industry. In this new and more ambitious strategy, IMO aims to achieve zero GHG emissions from international shipping by the year 2050. To facilitate progress towards this target, the IMO has also introduced indicative checkpoints. By 2030, IMO aims to achieve a total annual GHG emissions reduction of at least 20%, with a striving goal of 30% compared to the levels in 2008. Looking further ahead, the plan is to reduce the total annual GHG emissions from international shipping by at least 70% by 2040, with a striving goal of 80%, in comparison to 2008 emissions. Additionally, to ensure the successful achievement of these ambitious targets, the revised strategy introduced actions and measures mainly to prevent a burden on developing States while also mitigating the risk of emissions being shifted to other sectors of the economy. The revised strategy of the IMO strongly highlights the pressing need for the maritime sector to shift to alternative fuels and energy sources in order to achieve climate neutrality. Moreover, the establishment of the emission control areas (ECA) in 2005 was another of the sector's significant measures to reduce environmental impacts. This strategy was implemented to reduce emission of SO_x, NO_x, and PM. In October 2016, IMO's Marine Environment Protection Committee (MEPC) made a decision to lower the Sulphur content of marine fuels to 0.50% starting from 1 January 2020, aligning with the European standards (IMO, 2020). This resolution is expected to bring about a notable impact on the types of fuels employed in the maritime industry [24, 52, 84].

At the European level, the 'Fit for 55' package, which refers to the EU's target of net GHG by at least 55% by 2030, seeks to achieve the 'European Green Deal' aim of climate neutrality in Europe by 2050. The 'Fit for 55' package introduces a range of regulatory policies, including two significant measures. First, is the incorporation of shipping into the EU Emissions Trading System (EU ETS). Additionally, it puts forward the adoption of the FuelEU Maritime Initiative, which establishes specific limits on greenhouse gas (GHG) intensity for the energy used onboard ships, starting from 2025. It applies to ships with a gross tonnage exceeding 5000, that visit European ports, except for fishing vessels. It encompasses approximately 55% of all ships and accounts for about 90% of CO_2 emissions generated by the maritime sector. According to this initiative, each vessel will need to adopt alternative fuels or energy sources to ensure compliance with GHG intensity limits which will become tighter over the years. A summary of FuelEU Maritime targets is provided in the below table [24].

Year	Carbon Reduction compared to 2020
2025	-2%
2030	-6%
2035	-14.5%
2040	-31%
2045	-62%
2050	-80%

Table 2.5: Annual average carbon intensity reduction compared to the average in 2020.

By 2050, the aim is to achieve a reduction of 75% in GHG emissions from energy usage compared to 2020 levels. In order to achieve these ambitious objectives, based on the policy scenarios outlined in the Climate Target Plan (CTP), the utilization of renewable and low carbon fuels in international maritime transport should be from 6% to 9% by 2030, and reach as high as 88% by 2050 [24, 88].

Types	**Names**
Biodiesel	Fatty Acid Methyl Ester (FAME)
	Hydrotreated Vegetable Oil (HVO)
	Fischer-Tropsch (FT) diesel
	Dimethyl Ether (DME)
Bioalchols	Methanol
	Ethanol
Biocrudes	Straight Vegetable Oil (SVO)
	Pyrolysis oil
	Hydrothermal Liquefaction (HTL)
	Solvolysis oil
Gaseous biofuels	Bio-LNG
	LNG
Others	Ammonia
	Hydrogen

Table 2.6: Possible Alternative fuels [63].

From a technical viewpoint, shipping exhibits greater flexibility in terms of fuel supply when compared to other modes of transportation such as aviation. However, the current alternative fuel uptake is almost negligible on commercial scale. Marine fuels are one of the cheapest fuels on the market which makes transition to alternative fuels more challenging. Multiple other factors are also influencing alternative fuel penetration such as: specific engine requirements, regulatory drivers, supply availability, volume requirements based on ship size and industry's expertise, etc. Important factors are presented in the Figure below [84].

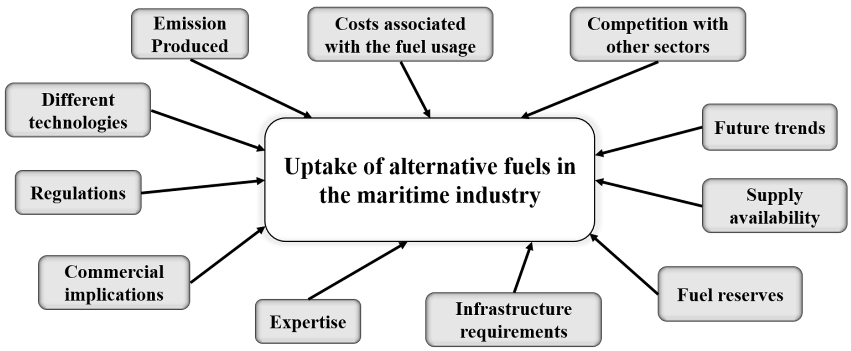

Figure 2.1: Framework of the uptake of alternative fuels [84].

While a comprehensive analysis is needed to fully assess the suitability of plastic-derived oil for maritime use, several clear advantages can already be seen. The carbon range of plastic oil is predominantly C13-C20, which makes it well-suited for diesel engine applications. Additionally, its calorific value is comparable to conventional fuels used in the maritime sector. These characteristics suggest that plastic oil could serve as a near-equivalent replacement for traditional marine fuels, requiring minimal modifications to existing infrastructure, ship engines, and fuel handling regulations. Furthermore, the vast amounts of plastic waste currently polluting both land and sea represent a largely untapped resource. Pyrolysis offers an effective solution to convert this waste into a valuable fuel, helping to mitigate environmental damage. As a well-established and mature technology, pyrolysis has been extensively researched and proven viable. Taken together, these factors make plastic oil a promising alternative to more polluting fuels, offering both environmental and operational benefits for the maritime transportation sector [72].

Chapter 3

Assessment of Marine Litter as Feedstock for Pyrolysis

As the issue of marine litter continues to persist and grow, evaluating its potential as a feedstock for energy recovery processes like pyrolysis becomes increasingly important. In this chapter, the scope and characteristics of marine plastic waste are explored, with a particular focus on European seas. By examining the availability of this waste and its varied composition, we can assess the potential yield of pyrolysis oil and its general characteristics, as well as quantify its contribution to a sustainable solution. Additionally, the capacity of existing initiatives, such as the Fishing for Litter (FFL) program, will be analyzed. Based on its recovery data and the amount of marine litter in the seas, various capacity and composition scenarios are introduced to inform further heat and mass balance analysis.

3.1 Plastic Waste Availability in Marine Environment

The plastics left in the environment due to irresponsible waste disposal gradually enter the oceans, where they either sink to the bottom, float on the surface, or accumulate at shorelines. It is estimated that 10 to 20 million tons of plastic waste end up in the oceans annually, resulting in over 5 trillion plastic pieces of varying sizes and shapes, weighing over 250,000 tons, currently floating on the ocean's surface. Additionally, due to the COVID-19 pandemic, the demand for single-use plastics, such as personal protective equipment and online shopping packaging, increased substantially, generating 8 million tons of pandemic-related plastic waste worldwide, with more than 25,000 tons entering the oceans. Globally, the majority of plastic waste is concentrated in five oceanic hotspots, known as "plastic islands." These hotspots are distributed across two areas in the Pacific Ocean, two in the Atlantic, and one in the Indian Ocean. However, the Mediterranean Sea, though smaller, has become another significant plastic waste accumulation zone, often referred to as the sixth "garbage patch" [17, 20, 54].

Since the focus of this analysis is primarily on European seas, it is essential to consider European waters in more detail. Plastics are reported to represent over 70% of marine litter items in the European marine regions. Mediterranean Sea situation can be considered more noteworthy. Despite containing only 1% of the world's water, the Mediterranean holds 7% of all global microplastics. Microplastic concentration on the surface of the Mediterranean far exceeds 100,000 particles per km^2, reaching a peak of more than 64 million floating particles per km^2. The total weight of microplastics in the Mediterranean is estimated to exceed 1,000 tons. According to recent analysis, the input of plastics into the Mediterranean Sea amounts to 229,000 tons per year, or approximately 627 tons per day, with over 1 million tons of plastic currently present in the basin. Plastics account for up to 95-100% of total floating marine litter due to their high floatability. Plastic accumulation in the deep sea is particularly concerning, as the longevity of plastics increases in deeper waters [17, 56, 58, 105, 106].

Plastic waste levels are highly location-dependent, and Mediterranean sites tend to show some of the highest levels of plastic pollution. This is due to a combination of factors: a densely populated coastline, intense coastal shipping activity, limited tidal flows, and the fact that the Mediterranean is a relatively closed basin. Based on 7 surveys and 295 samples in Mediterranean Sea and Black Sea, the average density of 179 plastic items per km^2 found in all compartments such as shelves, slopes, canyons, and deep-sea plains, it can be estimated that approximately 500 million litter items are currently scattered across the Mediterranean Sea floor [106].

The table below summarizes the findings from various studies on marine litter density across several European marine regions. In the table, 'Surface Observation' refers to litter observed floating on the sea surface, while 'Bottom Trawl' denotes samples collected from the seabed using trawling techniques.

Sea	**Type of sampling**	**Density (item/km²)**	**Description**	**Source**
Eastern Med. Sea	Surface observation	232±325	Plastic pieces were dominant then bags and bottles.	[33]
Central Med. Near Malta	Surface observation	1321±688	91% were plastics and 4% woods. Mostly plastic fragments.	[34]
Adriatic Sea	Surface observation	251±601	91.4% were plastics. Mostly packaging materials. Bags and plastic pieces were dominant.	[110]
Black Sea	Surface observation	93.6±128.3	96% were plastic made. Mostly plastic pieces.	[49]
Central Adriatic sea	Surface observation	175.3±180.6	95% were made from plastics, and the rest were wood and paper.	[79]
Baltic and North Sea	Bottom Trawl	16.8 (NS), 5.07 (BS)	Plastics consisted 80% of items caught.	[58]
Baltic and North Sea	Bottom Trawl	70.7 (NS), 9.6 (BS)	Plastic was found in 91.3% of all samples.	[54]
Antalya Bay, East Med. Sea	Bottom Trawl	13.3-651.1	Plastic is the most abundant, but weightwise rubber is the most abundant material.	[74]

Table 3.1: Plastic debris densities and composition in different European seas.

The studies referenced above clearly demonstrate the significant presence of marine litter on both the surface and seabed of European seas. A substantial portion of this litter is plastic waste, often exceeding 90% of the total. However, these studies typically focus on the number of plastic items rather than their mass. For the purpose of utilizing this waste plastic as a feedstock for pyrolysis, estimating the potential mass of plastic waste in marine environments is essential. Research on the mass of plastic waste is considerably more limited compared to studies on the quantity of litter, largely because measuring mass is more complex than simply counting items. Nevertheless, several studies have reported the density of marine litter in terms of mass per km^2, though these studies focus exclusively on seabed litter.

Sea	**Type of sampling**	**Density (kg/km^2)**	**Description**	**Source**
Northern and central Adriatic Sea	Bottom Trawl	82 ± 34	Plastics are 80% in terms of number, and 62% in terms of weight, dominant waste.	[82]
Greek gulf, East Med.	Bottom Trawl	6.7-47.4	Plastic was the dominant item (56%).	[60]
Southern Black Sea	Bottom Trawl	80.68 ± 48.06	Number-wise, plastics were the most dominant waste type (69.03%). Weight-wise, it was 16.37%. 62.01% of the overall weight was for rubber which only had 2% of items.	[38]
Catalan Coast, NW Med. Sea	Bottom Trawl	–	Plastic removal rate 0.74 ± 0.11 kg, accounting for 64.2% of marine litter in nets. Wood was second with 21.5%.	[9]

Table 3.2: Marine litter densities and composition in different seas.

As indicated by these limited studies, plastic does not always dominate in terms of mass, unlike its prevalence in terms of item count. This is primarily because materials such as glass and metal are generally heavier than plastics. Additionally, materials like cloth and rubber can absorb water, increasing their weight and complicating precise mass measurements. However, based on these studies, it can be reasonably estimated that approximately 60% of marine litter, by mass, consists of plastic.

Regarding waste plastics laying on the beaches, these plastics originates from litter on the shorelines of seas and oceans and is collected through beach clean-ups and other similar activities. Its quantities and composition are highly dependent on factors such as beach topography, meteorological events, periodical or seasonal beach usage, etc. Plastic litters constitute the predominant form of litter found on beaches. In 2016, approximately 85% of the litter on European beaches was comprised of plastics. Additionally a summary of International Coastal Cleanup in 2021 for several European countries is provided in the below table [1, 27].

Country	Kilogram Collected	Kilometers	Total Items Collected
France	949	34.6	15,158
Germany	1,603	47.8	32,245
Greece	8,338	57.4	103,917
Italy	4,223	19.5	15,101
Netherlands	185	52.1	6,309
Spain	6,455	110.9	78,325
Turkey	2,834	41	8,500
United Kingdom	6,499	102	130,610

Table 3.3: Summary of beach clean-ups in 2021 for several European countries [27].

Additionally, a recent study analyzing the number and weight of beached macro-litter from various publications reported that, on average, plastics accounted for 80% of the total litter by number and 51% by weight globally. The findings for Europe, the Mediterranean, and the Black Sea are summarized in the table below [5].

Location	Percent by number	Percent by weight
Europe	91%	64%
Mediterranean	81%	53%
Black Sea	80%	57%

Table 3.4: Percentage of plastic waste by number and weight in different locations [5].

All these reports and studies indicates that considerable amount of plastic waste in forms of marine litter exist in both seas and shorelines. These plastic wastes can be a potential feedstock for plastic pyrolysis.

3.2 Composition of Marine Litter

Understanding the polymer composition of the waste is crucial for the plastic pyrolysis process. As highlighted in the literature review, even small variations in polymer types or the presence of foreign materials like glass or metal can significantly change the composition of the resulting pyrolysis oil. Marine litter is highly diverse in composition. In addition to plastics, it contains foreign materials such as glass, wood, metal, rubber, and cloth. Furthermore, exposure to saltwater, UV radiation, and biofouling alters the structure of plastics, leading to fragmentation and changes in their physico-chemical properties. To better understand the overall composition of marine litter, this waste has been categorized into three groups: plastic waste found on beaches, floating marine plastics, and plastics on the seabed. It is estimated that from all the litters entering the sea, 15% reaches the shores, 15% remains floating on the surface and 70% sinks to the seabed. Each of these categories will be analyzed in the following sections [10, 50, 55].

3.2.1 Plastic Laying on Beaches

Various factors, as mentioned earlier, contribute to the distinct plastic waste found on each beach, thus it is not possible to identify a single polymer composition that would be precise for all beaches. There are numerous reports and surveys attempt on identifying the primary litter items present on beaches. OSPAR has undertaken the most advanced research at the marine region scale, on marine litter within the North-East Atlantic region. OSPAR Commission released in 2017, presents data from 76 survey sites and provides insights into the top litter items observed between 2014 and 2015. Base on OSPAR report, the majority of plastics found on beaches are packaging of food and beverages. The main polymers for such products are mostly PE, PP, PS and PET. Fishing gears can also be found on beaches, which their main building blocks are PE, PP, and PA. It is speculated that the amount of PVC is negligible, since this type of polymer is mostly found in construction materials [1].

The amount of foreign materials in marine litter found on beaches is generally negligible. Since this waste stream is typically collected through physical beach cleaning, non-plastic materials can be separated during the collection process, provided the operation is carried out properly. A challenge lies in the potential for disposed cigarette filters to enter the main waste plastic stream. Cigarette filters are mostly made of cellulose acetate and in a pyrolysis condition they will degrade and form acetic acid as their primary constituent in pyrolytic oil [23].

3.2.2 Plastic Floating on Seas

On the sea surface, polymers constitute the predominant portion of floating derbies and in some cases the figures can reach up to 100% . These floating plastics undergo physical degradation overtime and transform into microplastics. The exact composition of surface plastic litter can also be easily determined through density analysis. Litters made from polymers lighter than sea water will remain afloat, while those comprised of denser polymers will sink beneath the surface. In the table below the density of some of the widely used polymers have been provided [106].

Material	Density (g/cm^3)
PVC	1.406
PP	0.92
PET	1.37
PS	1.04-1.13
PE	0.9745
Seawater	1.28

Table 3.5: Density values of seawater and main polymers.

Based on the above table, it can be expected that the majority of the wastes floating on the sea surface are consist of PP, PS, and PE polymers. This claim is supported by multiple studies on micro plastics composition. A summary of these studies is provided in the table below.

Sea	PE	PP	PS	Other	Source
Eastern and Southern Atlantic	63%	32%	1%	4%	[97]
Med. Sea	67.30%	20.80%	–	11.90%	[83]
North Pacific	53.70%	39.90%	–	6.40%	[73]
NW Med. Sea (Protected Area)	63.30%	24.90%	3.30%	8.50%	[41]
NW Med. Sea (Mallorca Island)	69%	–	–	31%	[31]
Cornish Coast, UK	31.10%	8.40%	3.40%	NI	[26]
Adriatic Sea	67%	18%	–	12%	[110]

Table 3.6: Composite and density of micro plastics in several regions.

3.2.3 Plastic on the Seabed

Determining plastic composition of sea bottom is much more challenging. Almost any type of polymer can be expected within this sample pool, given that plastics lighter than seawater tend to accumulate on objects or sink due to the attachment of biomass to their surfaces. Furthermore, other materials, such as metals and glasses can also be expected within a catch. The accumulation of plastic in the deep sea is particularly concerning, given the prolonged longevity of plastics and their slow degradation in environments lacking light and with lower oxygen content. At the bottom of the sea, as it was mentioned in previous sections, waste plastics remain the predominant form of marine litter. Studies regarding polymer composition of sea bottom are notably scarce due to inherent difficulties. Nevertheless, a study conducted in the Baltic Sea and North Sea provides valuable insights into the plastic composition of the deep sea [54, 106].

Location	HDPE	LDPE	PP	PS	PA	PVC	PET	Other
North Sea	46.08%	23.52%	20.67%	–	6.65%	–	0.95%	1.90%
Baltic Sea	14.29%	10.71%	21.43%	3.57%	21.43%	3.57%	17.86%	7.14%

Table 3.7: Composition of plastics on the sea bottom

On the sea bottom, similar to surface PE and PP are the dominant polymer types, though high variations depending on the location exists. As anticipated the amount of PVC is generally low or nonexistent, since this polymer is mostly used in construction applications. PET can also be expected and at times, they may be found in significant quantities. PET serves as the main polymer used for drinking bottles and wet wipes. Waste containing this polymer often originates from populated areas and can easily make its way into the sea. Given that its density is higher than seawater it sinks below the surface. Consequently, it is expected that this polymer will be more prevalent near coastal areas. This aligns with findings from other studies, which indicate that near-shore marine litter on the seabed consists of approximately 70% general plastics and 30% fishing gear waste. In deeper waters, these proportions are often reversed, with fishing gear becoming the dominant component [13, 32, 43, 110].

A significant portion of seabed waste consists of abandoned, lost, or discarded fishing gear (ALDFG). These items are primarily made from plastic polymers with long lifespans, and they can continue to trap marine organisms for decades, making them one of the most hazardous waste for marine life. Most fishing gear is made from PE, PP, and PA, with PA, particularly in the form of nylon-6 and nylon-66, commonly used in fishing nets and lines. Each year, large quantities of fishing gear are lost at sea, adding to the accumulation of PA within the plastic waste on the seabed [36, 80, 96].

3.3 Marine Litter Recovering Rate

As established in previous sections, large quantities of plastic exist in the form of marine litter in the seas. To assess the potential of utilizing this waste as a pyrolysis feedstock for producing marine fuel, it is essential to understand the recovery rates of marine litter. Recovering marine litter is a challenging task, contributing to the persistence of this environmental issue. Data on recovery rates are scarce and often localized. However, information on the quantities of passively collected waste through initiatives like FFL scheme can serve as a useful benchmark for estimating the amount of waste that could be removed from the seas. Originally FFL program was implemented for North Sea and only recently pilot schemes were carried out in a number of other countries including Italy, Slovenia, Croatia, Montenegro, and Greece. In table below the performance of Fishing for Litter initiatives organized through OSPAR is reported [29, 68].

Countries	**No. Harbours**	**No. Vessels**	**Tonnes**	**Tonnes per vessel**
Germany	3	60	1.2	0.02
Netherlands	12	91	285.2	3.13
Sweden	2	33	491	14.88
UK	25	474	142.7	0.3
Total	**42**	**658**	**920.1**	**1.4**

Table 3.8: Performance of fishing for litter programs (OSPARP) [29].

Moreover, specific information was found for Netherlands. During the period of 2020-21, the scheme saw the highest-ever participation of fishing vessels, with a total of 137 joining it, while 756 tons of litter were collected, which was the largest quantity of annual litter. Between the years 2011 and 2021, the annual collection of litter amounted to an average of 381 tons, resulting in a total quantity of 4189 tons over the 11-year period [68].

Finally, in a study aimed at estimating the potential of bottom trawl fleets to remove marine litter from the seabed along the Catalan Coast, it was determined that the fleet could potentially remove 237 $\pm$ 36 tonnes of marine litter annually. The maximum recorded value was 308 tonnes in 2020, while the minimum was 187 tonnes in 2019 [9].

It is important to note that the figures above represent only the FFL scheme. Other methods of marine litter recovery, such as beach cleanups, riverine barriers, and sea-cleaning vessels, also contribute to the removal of marine litters. The recovery rates for these methods vary depending on factors like seasonal fluctuations and cleanup capacity. Nevertheless, available data exist for these methods, often reported as the mass of litter collected or the area cleaned per unit of financial investment. These figures will be explored in more detail in the economic evaluation chapter.

3.4 Capacity and Composition for Modeled Pyrolysis Process

To begin the calculations for the modeled pyrolysis process, it is essential to define both an accurate capacity and composition for the feedstock. Two capacity classes were selected for this study. The first is 360 tonnes per year, equivalent to 1 tonne of marine litter per day. This figure was based on current data from the FFL scheme. However, relying solely on the FFL scheme was insufficient, as it does not account for beach or ocean cleanup operations and only considers litter collected by fishers, which operate in specific areas. To address this limitation, a second capacity of 3600 tonnes per year, or 10 tonnes per day, was introduced for analysis. Although estimates from various reports suggest the actual volume of marine litter is significantly higher, this capacity was chosen to align with current plastic pyrolysis plant capacities, facilitating a smoother transition toward utilizing marine litter as a fuel source.

The composition of marine litter is highly diverse, comprising various polymers and materials. While plastics dominate in terms of the number of items, the weight distribution can vary significantly depending on what is recovered. Based on available studies and reports, it is estimated that plastics constitute between 50% and 65% of the total mass of marine litter, while the rest can be other materials such as metals, glass, wood, and rubber [5, 9, 38].

It is speculated that most of these foreign items are big and visible and they can be removed easily, without any intensive presorting even on boats themselves. Thus they can be eliminated before entering the process. It is assumed that 40% of the mass of marine litter will be separated, so in reality the marine litter that is comprised mostly from plastics and is going to be used for the modeled pyrolysis process is 180 and 1800 ton per year.

Chapter 4

Heat and Mass Balance Analysis of a Modeled Pyrolysis Process

In this chapter, a comprehensive heat and mass balance analysis for a modeled pyrolysis process will be conducted. The analysis builds on insights from previous studies of pyrolysis processes that use feedstock similar to marine litter, with the most suitable one selected as a reference model. By introducing multiple feedstock case studies, the diversity and variability of marine litter composition are considered in the context of process efficiency and product yield. The selected pyrolysis process is described in detail, followed by a breakdown of the heat and mass balance calculations. Finally, the results are discussed, offering key insights into the potential of marine litter as a sustainable feedstock for pyrolysis-based energy recovery.

4.1 Process Selection

When selecting a reference study for plastic pyrolysis, the abundance of research in this field makes the task challenging. It is essential to choose a study that closely aligns with the conditions of the modeled process, as this study will form the basis for subsequent heat and mass balance calculations. To make the search an easier task, two constraints were introduced, which accurately represent the conditions of the process. The first constraint is that the study should use a plastic mixture as its feedstock, reflecting the composition of marine litter, which typically consists of various polymer types rather than a single or two distinct polymers. Studies with feedstock compositions similar to marine litter will be prioritized. The second constraint is the study should focus on pyrolysis oil production. Since the objective of this project is to produce oil from waste plastics that can serve as fuel for the maritime sector, thus the emphasis is placed on the oil fraction of the pyrolysis process. With these criteria in place, ten studies were identified as potential reference points for this work. The names and brief descriptions of these studies are summarized in the table below.

Author	**Description**
A. Lodh [65]	Creating a plastic sample based on marine litters on the beach and pyrolyzing it in a lab-scale reactor.
A. Lopez [67]	Pyrolysis of 4 samples from a recycling center reject stream in an autoclave reactor.
A. Adrados [2]	Pyrolysis of a simulated plastic sample and comparing results with A. Lopez's work.
G. Yadav [109]	Simulation of mixed plastic pyrolysis on a scale of 240 ton/day.
H. Almohamadi [4]	Simulation of mixed plastic pyrolysis on a scale of 1000 ton/day.
J. HEE [50]	Pyrolysis and gasification of surface marine litter in a retort furnace.
M. Ghodrat [48]	Simulation of mixed plastic pyrolysis on a scale of 40 ton/day.
Stalkamp [95]	Pyrolysis of car plastics using a heated screw reactor on a scale of 1kg/h.
G. Faussonne [43]	Pyrolysis of marine litter without any pretreatment to obtain fuel on a scale of 10kg/cycle.

Table 4.1: Summary of different studies, which can be used as reference studies.

Among the selected studies, G. Yadav, H. Almohamadi, and A. Adrados employed simulation tools, while the others utilized experimental setups with real data. Notably, A. Lodh, J. Hee, and G. Faussonne used marine litter samples or simulated plastic mixtures representative of marine litter, making their studies more relevant compared to the others. For instance, A. Lopez's study did not include PA in the plastic waste samples, while Stalkamp's study contained significant amounts of polycarbonate (PC), a polymer commonly used in cars but negligible in marine litter. Of the three studies that used marine litter as feedstock, G. Faussone's study stands out as the most suitable candidate. It was conducted on a bench scale, offering greater operational relevance compared to the lab-scale conditions of the other studies. Furthermore, this study utilized untreated marine litter directly sourced from the sea, while the others either used beached marine litter or created simulated samples based on it.

Additionally, it is crucial to consider both oil and gas yields when selecting a reference study. Choosing a study with yields that deviate significantly from typical values, either abnormally high or low,could compromise the accuracy of the modeled process. The graph below compares the oil and gas yields across the ten selected studies. It should be noted that several studies reported results from multiple test runs using different samples. In such cases, the average values have been used for comparison purposes.

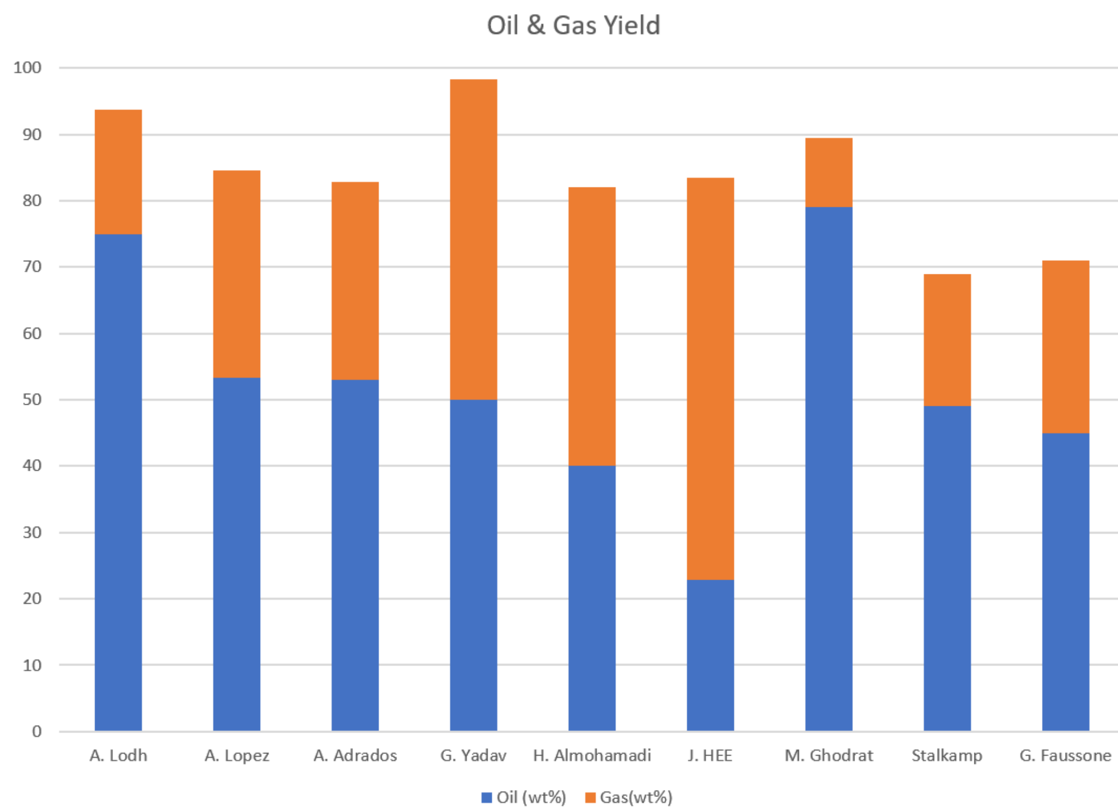

Figure 4.1: Oil and Gas yield for different studies

The graph illustrates that the data reported by G. Faussone aligns more or less with the average values observed in the other studies. Taking this into account, along with the previously mentioned factors, G. Faussone's study has been selected as the reference for the analysis in this work.

4.2 Reference Process Description

Marine litter collected by scuba divers from the Venice Lagoon was used as the pyrolysis feedstock. The litter underwent minimal pretreatment, consisting only of an 8-hour natural drying process and the removal of obvious non-plastic macroscopic items. Due to the complexity of the waste, determining the exact composition of the marine litter was not possible, and no chemical characterization was performed. The collected litter was divided into multiple samples weighing between 4 kg and 11.5 kg, which were then pyrolyzed. To prevent the formation of acidic compounds, a fixed amount of CaO-based inorganic additives was added to each sample [43].

The reactor temperature was maintained at 450 ± 20°C, and the pyrolysis cycle lasted 4 hours, a duration considered longer than most other studies. This extended time was reported because no condensed liquids were observed after the 4-hour mark. Additionally, another study analyzing a real-world plastic pyrolysis plant reported similarly long cycle times [42, 43].

Volatile compounds produced during pyrolysis were directed through a condenser system, where they were cooled to ambient temperature. The resulting pyrolysis oil was separated from non-condensable gases and collected in a storage tank. The gas was first passed through an alkaline water gurgle box, followed by a polymer-engineered granular sorbent material designed to remove any remaining acidic or harmful components. The treated gas was then flared [43].

After the pyrolysis of all samples, the collected plastic oil was processed in a distillation tower. The tower separated the oil into three fractions: Virgin Naphtha (VN) with a boiling point of up to 170°C, Marine Gas Oil (MGO) boiling up to 320°C, and Intermediate Fuel Oil (IFO), which had a boiling point higher than 320°C and was collected as residue at the bottom of the tower. A schematic of the process is shown in the figure below [43].

Five products were obtained from the pyrolysis process. The gas product contained a significant amount of combustible gases, making it a potential energy source for sustaining the process or for power generation. However, the gas also contained detectable quantities of ammonia and hydrogen cyanide, and it is speculated that other harmful compounds could be present. This highlights the importance of having a filtration system. A substantial amount of solid residue was also produced during pyrolysis. Proximate and elemental analyses were performed on the solids, revealing that 15 wt% consisted of volatile matter, likely due to incomplete evaporation of the pyrolysis oil. Additionally, the concentration of pollutants in the solid products exceeded the thresholds for material recovery and non-hazardous disposal. To mitigate this, the concentration of pollutants were reduced through stabilization by cementation [43].

The liquid products from the distillation tower were analyzed at various levels. The MGO was evaluated for compliance with ISO8217:2017, DMA distillate fuel classification, with the exception of oxidation stability. The results showed that

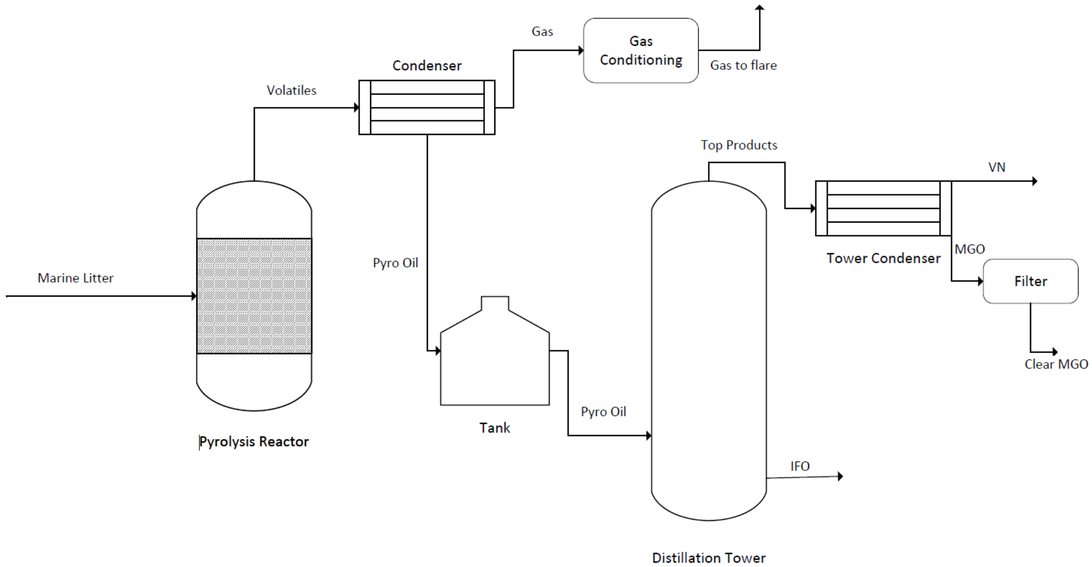

Figure 4.2: Reference study process schematic

all parameters, except for the flash point, were within the standard limits. It was suggested that improvements in the separation process and column design could bring the flash point up to the required value. The evaluation also revealed a higher cetane index than the standard, low sulfur content qualifying the MGO as Ultra Low Sulfur Fuel Oil (ULSFO), and a low acid value, highlighting its potential as a viable alternative to conventional fossil fuels. The IFO was assessed according to the ISO8217:2017 residual fuel classification. The results indicated that the pour point, ash content, and water content exceeded the DMB classification limits, while the pour point and water content were slightly above the threshold for ISO-F residual marine fuels. The most significant issues were the sodium and aluminum-silicon content, which disqualified the fuel from being classified as residual marine fuel. However, the extremely low sulfur content and high cetane index present the possibility of using this fuel as a blend with traditional residual fuels or as a low-cost option for heating applications [41].

In this study, VN was considered as a potential feedstock for steam cracking to produce plastic monomers, offering a pathway toward a circular economy for plastics. An in-depth analysis revealed that, compared to naphtha derived from fossil fuels,which primarily consists of paraffins and iso-paraffins with some naphthenes,naphtha from marine litter exhibits a more diverse mixture of hydrocarbons, including olefins, aromatics, along with paraffins. Additionally, the marine litter naphtha contained higher concentrations of nitrogen, oxygenated, and halogen compounds. Metal analysis also showed elevated levels of calcium and silicon, exceeding standard thresholds. Despite these issues, marine litter naphtha performed reasonably well in steam cracking, with coke formation higher than that of fossil-derived naphtha but not significantly so. The study concluded that marine litter naphtha, when blended with fossil naphtha, would not cause substantial coke formation at an industrial scale, indicating its potential as a valuable product [43].

4.3 Feedstock Case Studies

G. Faussone's study offers extensive detail on the characteristics and composition of the product oils, as well as valuable technical information that can aid in scaling up and economic analysis. However, a notable limitation is the absence of a detailed feedstock composition or elemental analysis of the marine litter used. The only description provided regarding the feedstock is that it mostly consists of plastics, with a mixture of general packaging and fishing-related plastics present, though no exact breakdown is given.

The primary focus of this study is conducting heat and mass balance calculations, and the lack of detailed feedstock composition in reference study presents a significant challenge for this analysis. Without an accurate breakdown of the marine litter feedstock, it becomes difficult to estimate the energy and mass flow within the pyrolysis process, potentially leading to inaccuracies in the calculations. To address this issue, several possible marine litter feedstock compositions were estimated based on available data from literature. These estimates allow us to proceed with the heat and mass balance analysis despite the lack of detailed information from the reference study. Given the substantial variation in marine litter composition across different regions and collection methods, multiple feedstock case studies were created to account for these variations and ensure that the analysis reflects a range of possible conditions. Four distinct feedstock case studies were developed to account for the variability in marine litter sources. These include one for beach litter, one for floating marine debris, and two for seabed litter. The composition of each case study is illustrated in the pie charts below.

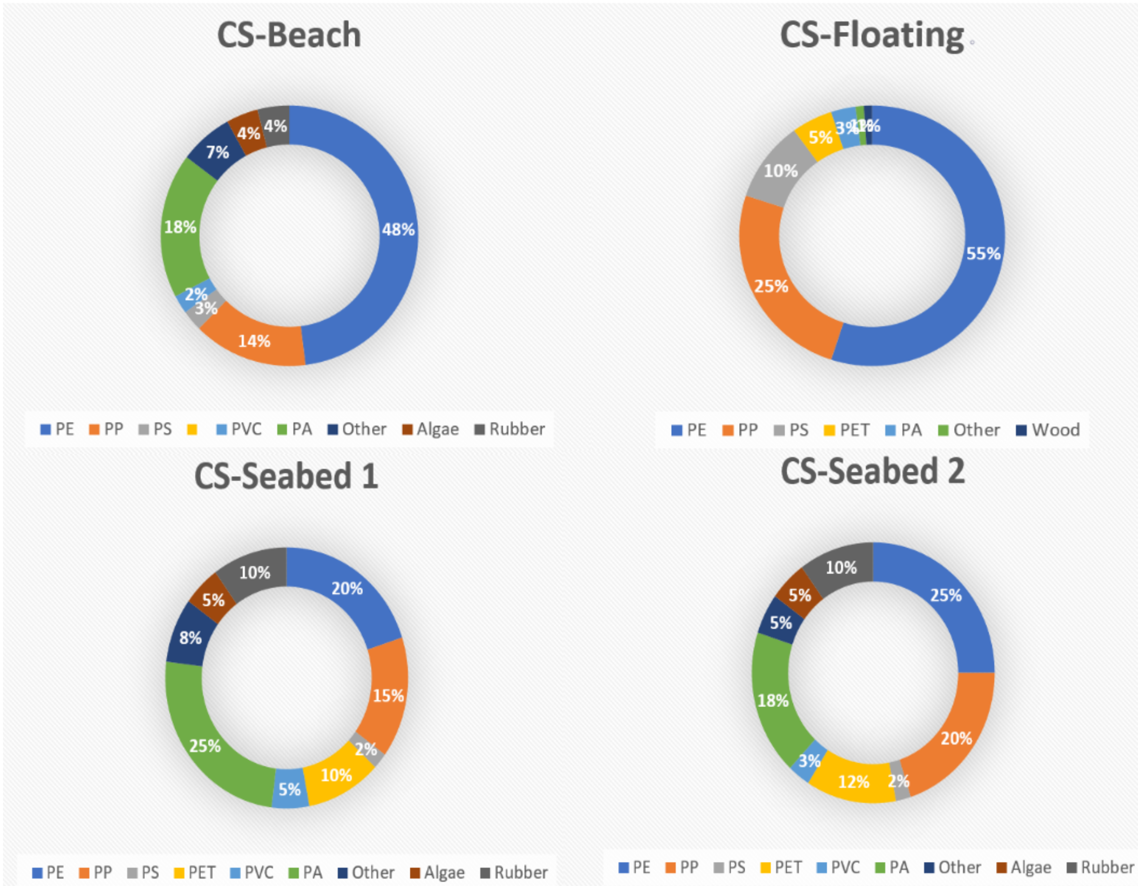

Figure 4.3: Case studies detailed composition.

The composition of these case studies is broadly based on published researches that reports on marine litter composition and is aligned with the key points discussed in Chapter 3. While the data is not exact, it reflects general trends observed in the literature, providing a representative basis for the subsequent analysis.

4.3.1 Correlating Case Studies to Reference Studies Yields

In G. Faussone's study, 14 marine litter samples were pyrolyzed, and their product yields were reported. With the exception of Trial 14, which indicated the use of floating marine litter, and three other trials involving mostly non-plastic materials, the remaining trials provide minimal or no information on the feedstock composition. Therefore, it is essential to establish a method for correlating the case studies on beach and seabed marine litter with the corresponding trial yields.

The correlation was done by determining the oil yield for each polymer group present in the feedstock, based on data from single-plastic pyrolysis experiments. Using this approach, the overall oil yield for each case study was calculated by aggregating the individual yields of the polymers in the composition. The calculated yields were then compared with the trial yields reported in the reference study. The table below presents the oil yield values for different plastics and other components present in marine litter when pyrolyzed individually, along with references to their corresponding studies.

Plastic	**Oil Yield (wt%)**	**Source**
PE	75%	[20, 72, 94]
PP	80%	[20, 72]
PS	90%	[20, 72]
PET	23%	[72]
PVC	12.3%	[72]
PA	60%	[80, 89, 107]
Seaweed	30%	[62]
Rubber	43%	[81]

Table 4.2: Oil yield of different plastics and other materials.

The estimated oil yields were 64%, 66%, 56%, and 52% for Beach, Floating, Seabed 2, Seabed 1 case studies respectively. Comparison of the estimated oil yield for the Floating case study with the actual yield reported in the reference study for floating litter revealed around 6% higher calculated value. This discrepancy may be due to differences in feedstock composition, but it is also likely that oil yields from single-polymer pyrolysis are generally higher than those from mixed-plastic pyrolysis. Pyrolyzing a single plastic typically occurs under optimum conditions that prioritize high oil yield, whereas marine litter is far from ideal situation. In addition to being a mixture of different plastics, the polymers have likely undergone structural changes due to prolonged exposure to sunlight and salt, and the feedstock may also contain foreign materials. Taking these factors into account, the estimated oil yields for the case studies were adjusted downward by 5% to 7% [55, 72].

Case Studies	Oil (wt%)	Gas (wt%)	Solid (wt%)
CS-Beach	62.60%	20%	17.40%
CS-Floating	60%	27.50%	12.50%
CS-Seabed 1	47.30%	31.80%	20.90%
CS-Seabed 2	52%	28%	20%

Table 4.3: Yields of pyrolysis products for each of case studies based on the reference study.

4.4 Modeled Process

Heat and mass balance calculations are important in the design and optimization of chemical processes, providing insights into energy requirements and material flows. These balances are particularly valuable when developing new processes or enhancing existing ones, as they help to ensure efficiency, safety, and scalability.

The modeled process in this study is similar to the reference study and its schematic diagram is shown in the below figure.

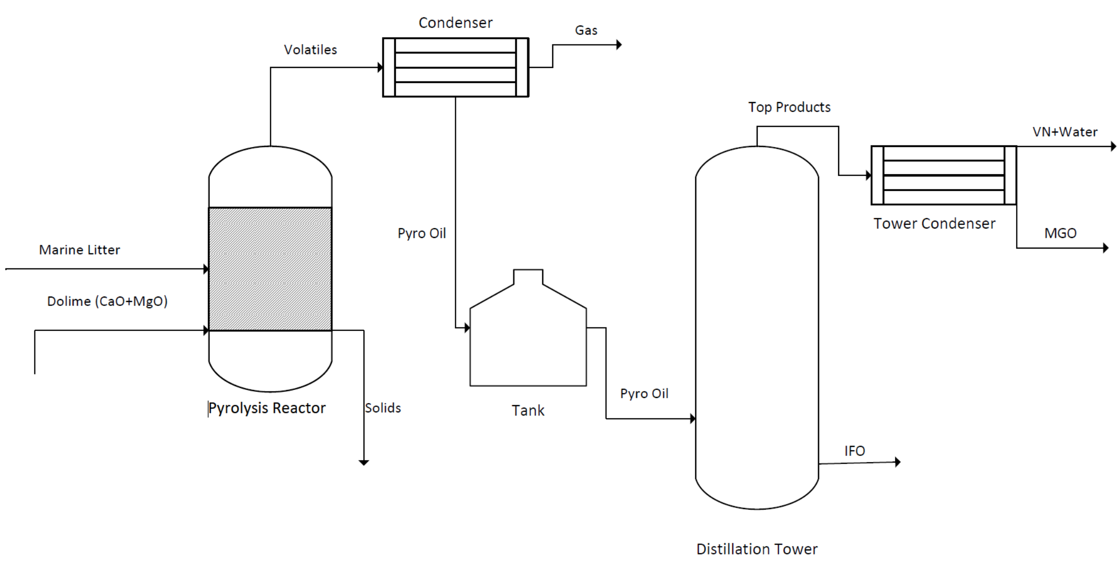

Figure 4.4: Modeled Process Schematic

The First Law of Thermodynamics is represented by the equation below:

$$\Delta U = Q - W \tag{4.1}$$

where Q is the heat added to the system, W is the work done by the system, and ΔU term represents changes in internal energy. To simplify the calculations and align them with the reference study, the following assumptions and constraints were applied:

No Shaft Work : There is no shaft work performed by or on the system, as this study focuses solely on thermal processing without any mechanical work.

Batch Operation: The process operates entirely in batch mode, consistent with the reference study conditions.

Ambient Conditions: Ambient pressure and temperature are set at 1 atm and 20°C, respectively.

Isobaric Process: The process conditions are maintained at a constant pressure throughout.

No Secondary Reactions In the Distillation Tower: It is assumed that no secondary reactions occur in the distillation tower, simplifying the separation process for product analysis.

Taking to account these conditions, and the existence of multiple streams, The First Law of Thermodynamic can be written in this form:

$$Q = \sum_{\text{outlets}} m_{\text{out}} h_{\text{out}} - \sum_{\text{inlets}} m_{\text{in}} h_{\text{in}} \tag{4.2}$$

where m is the mass of inlet and outlet streams and h is their respective enthalpy.

Under the conditions of the process, total enthalpy of chemical components consists of three thermodynamic properties, which are heat of reaction, sensible heat, and latent heat. In subsequent sections, the calculation for each of these properties for the plastic pyrolysis process is explained in detail.

4.4.1 Heat of Reaction

When chemical components react with each other, a certain amount of heat is either released to environment or absorbed from it in line with the First Law of Thermodynamics, which is heat of reaction or heat of formation. The heat of reaction is the difference between the total enthalpy of the reaction products and the total enthalpy of the reactants. The plastic pyrolysis process involves numerous complex reactions, making it impractical and unnecessary to calculate the heat of reaction for each individual reaction. The overall heat of reaction for the pyrolysis process can be estimated by determining the difference between heating value of the feed stream and total heating value of the products. This approach provides a practical estimation of the thermal demands of the entire process [59].

$$Q_{\text{Reaction}} = HV_{\text{Products}} - HV_{\text{Reactants}} \tag{4.3}$$

The majority of the feedstock is consists of plastic components which generally have high heating values comparable to fuels. From the literature the heating values of different plastics can be found and these values are reported in the table below. In

Material	**HV (MJ/kg)**	**Source**
PE (mix)	35.72	[6]
PP	42.43	[6]
PET	21.28	[6]
PS	39.14	[6]
PVC	19	[21]
PA (mix)	30	[37, 92]
Rubber	36.84	[64]
Seaweed	16.51	[37]
Wood	18.43	[64]

Table 4.4: LHV of materials found within marine litter.

above table PE is the mixture of HDPE and LDPE with ratio of 2:1 respectively. Moreover, PA has multiple types. The value provided is the avrage of heating values of fishing nets which is mainly made from nylon6 and another type of PA, in order to provide a more accurate value.

Another key factor to consider is the effect of seawater exposure on the properties of plastics. Although data on specific impacts for all individual plastics are limited, studies have explored the effects of seawater aging on fishing nets, which primarily composed of polyethylene (PE) and polyamide (nylon-6). Research indicates that seawater aging increases the ash content while reducing volatile content in these plastics. Structural analysis further reveals that seawater aging leads to partial oxidation and decomposition. While direct measurements of heating values for aged plastics were not provided, ultimate analysis (in wt.%) suggested a decrease in heating values of approximately 1.5 to 4 MJ/kg. Therefore, an average reduction of 2.5 MJ/kg was applied to the plastics' LHVs to account for seawater aging. Rubber was excluded from this adjustment, since no relevant information on seawater effects was available [55]. The enthalpy of the feedstock for each case study has been calculated and reported in the table below.

Case Study	Beach	Floating	Seabed-1	Seabed-2
Heating Value (MJ/kg)	32.27	34.21	29.84	30.77

Table 4.5: Heating Values of Different Case Studies

To verify the accuracy of the calculated heating values, the results were compared with those reported by J. Hee et al., which provided calorific values for beached marine litter. This study included two samples with calorific values of 33.43 MJ/kg and 35.97 MJ/kg, respectively, both of which fall within the range of heating values calculated for each of the case studies. This consistency supports the validity of the calculated values for our feedstock samples [50].

The pyrolysis reactor produces three main output streams: pyrolysis oil, solid residue, and gas. The heating value of the solid residue has been documented by G. Faussone, who reported it to be 10.58 MJ/kg. For the gas stream, a heating value of 34.5 MJ/kg was noted in the supplementary data of the same study. However, no specific heating value was provided for the pyrolysis oil, which is central to this study. To address this, each product fraction from the distillation tower was analyzed. Heating values of 43 MJ/kg and 40 MJ/kg were assigned to MGO and IFO fractions, respectively, based on marine distillate and residual fuel standards. For the Virgin Naphtha fraction, results from SPME-GC-MS analysis were used to model the stream in Aspen HYSYS, and its calculated heating value was applied in subsequent calculations [43, 63].

With the heating values of MGO, Virgin Naphtha, and IFO, it is possible to calculate the heating value of the pyrolysis oil. Since the quantity of the streams from distillation tower is different in each case studies, the heating value of the pyrolysis oil is slightly different in each case study. The values for the case studies are reported in the table below. To further validate the heating values of the pyrolysis

Case Study	Beach	Floating	Seabed-1	Seabed-2
Oil HV (MJ/kg)	39.07	42.47	36.47	36.49

Table 4.6: Oil Heating Values for Different Case Studies

oil, heating values reported in several relevant studies where presented in table below for comparison.

The calculated values for marine litter pyrolysis oil is comparable to other similar studies. Additionally, expected trends can also be seen in the values. Waste plastics found floating on the sea surface are typically composed of PE and PP, which yield oils with higher heating values. In contrast, seabed marine litter contains a more

Study	Oil HV (MJ/kg)	Description
Stallkamp	38.4	Waste car plastic
J. Hee	41.5 & 37.2	Beached marine litter
A. Lodh	40.8	Simulated marine litter
A. Lopez	41.2 & 41.8 & 36.6	Recycling reject stream

Table 4.7: Oil Heating Values from Various Studies

diverse polymer composition, resulting in oils with lower heating values similar to those derived from waste automotive plastics.

With all the heating values calculated for both feedstock and products it is now possible to calculate the heat of reaction for each case study and both scales.

4.4.2 Sensible Heat

Sensible heat refers to the thermal energy required to change a substance's temperature without causing a phase change. This form of heat can be quantified based on temperature changes within the material and is essential in calculating energy requirements for heating and cooling in pyrolysis processes. The equation for sensible heat is expressed below:

$$Q_{\text{sensible}} = \int_{T_\text{i}}^{T_\text{f}} m\, C_p(T)\, dT$$

where m is the mass of the material being heated or cooled, $C_p(T)$ is the specific heat capacity of the substance, which can vary with temperature, T_i, and T_f are the initial and final temperatures respectively.

To calculate the feedstock C_p, the components where categorized into two groups. The first group which are consisted of MgO, CaO, Others, and Rubber have a straightforward procedure. MgO, and CaO are only present in solid form and their specific heat of capacity equations are well known, thus they can be easily calculated. Others faction includes inert materials, wood, and seaweed. Due to their unknown precise composition or in case of wood and seaweed their thermodynamic behavior, a constant value based on the average of several material was selected for their C_p. Rubber exists both in solid and liquid form within the reactor, however rubber has many types with distinct behaviors. Since no information was available on the types of rubber, constant value of vehicle tire was assumed for both solid and liquid form of the rubber. The table below summarize the value of C_p, temperature range and type of calculation for the first group.

Material	T_i (K)	T_f (K)	Calculation Type	$C_p[T]$ (J/g)	C_p (J/g.K)
MgO	293	723	Empirical Eq.	475.03	-
CaO	293	723	Empirical Eq.	367.38	-
Rubber	293	600	Average	-	1.476
Others	293	723	Average	-	0.9

Table 4.8: Specific heat coefficient for the first group materials

Calculating C_p(T) for the second group which are plastics are more challenging. This group exists in three phase of solid, liquid, and vapor in the pyrolysis reactor and in order to have a precise calculation of sensible heat, it is necessary to calculate C_p(T) in all of three phases. Additionally, the structure of most plastics is a combination of crystalline and amorphous regions, which complicates specific heat capacity calculations. The distinct thermal behaviors of these regions, contribute to a variable specific heat capacity across temperature ranges. For this reason studies either report the plastic heat of capacity either for complete crystalline or complete amorphous structure. Furthermore, in several cases there is no single equation to accurately model the specific heat capacity of complex polymers across different temperatures. Instead, experimentally measured data points are often used alongside numerical methods to approximate specific heat capacity over the relevant temperature ranges. The two tables below summarize the results of specific heat capacity for the polymers present in the case studies in solid and liquid phase.

Material	T_i (K)	T_f (K)	Calculation Type	Structure	$C_p[T]$ (J/g)
PE	293	410	Table data [45]	Crystalline	228.26
PP	293	460	Empirical Eq. [46]	Crystalline	363.99
PS	293	373	Empirical Eq. [108]	Amorphous	110.23
PET	293	340	Empirical Eq. [103]	Amorphous	48.82
PVC	293	360	Empirical Eq. [19]	Amorphous	68.83
Nylon 6	293	313	Table data [103]	Amorphous	17.53
Nylon 6,6	293	323	Table data [103]	Amorphous	41.79

Table 4.9: Sensible heat data for plastics in solid phase

Material	T_i (K)	T_f (K)	**Calculation Type**	**Structure**	$C_p[T]$ (J/g)	C_p (J/kg.g)
PE	410	600	Empirical Eq. [45]	Crystalline	269.32	-
PP	460	600	Empirical Eq. [46]	Crystalline	409.68	-
PS	373	600	Empirical Eq. [108]	Amorphous	488.68	-
PET	340	590	Empirical Eq. [103]	Amorphous	403.24	-
PVC	360	400	Average [19]	Amorphous	-	1.56
Nylon 6	313	600	Empirical Eq. [103]	Amorphous	375.71	-
Nylon 6,6	323	600	Table data [103]	Amorphous	628.67	-

Table 4.10: Sensible heat data for plastics in liquid phase

In both tables T_i and T_f are the temperature range of the plastic phase. For this study PE and PP were assumed to have crystalline structure while other types of plastic having an amorphous structure. It was further assumed that PA components within the plastic fraction consist of an equal mixture of Nylon 6 and Nylon 6,6. Both polymer types are widely used in fishing nets and are therefore likely to be present in the marine litter waste pool.

As for the vapor phase of the plastics within the reactor, in this phase the reactions occur and it is impossible to have a separate specific heat capacity for each of the plastics. In the reference study supplementary data section value of 1.8 KJ/kg.K was assumed for the vapors leaving the reactor, thus such value will be used for the calculations.

For the specific heat capacity of the pyrolysis products and distillation oil cuts, exact compositions are not available, as these hydrocarbon mixtures vary in each setting. Consequently, a constant specific heat capacity value was adopted from online sources and petrochemical specification sheets. These values are reported in the table below.

Material	C_p **(kJ/kg.K)**	**Description**
Char	1	Value for ash
Volatile-liquid	2.04	Average value between gasoline and paraffin
Volatile-gas	1.63	Value for Propane
IFO	1.97	Value for HFO
MGO	2.22	Value for Diesel oil
VN	2.1	Value for petroleum Naphtha

Table 4.11: Specific heat capacities of product streams

With all the specific heat capacities for both feedstock and product streams determined, it is possible to calculate the sensible heat for all the streams within the system.

4.4.3 Latent Heat

Latent heat is the amount of energy absorbed or released by a substance during a phase change, such as melting, freezing, vaporization, or condensation, without a change in its temperature. During these transitions, energy is used to alter the internal structure of the substance like breaking or forming bonds.

In the pyrolysis reactor, two phase change happens for the feedstock, which are melting and vaporization. Only PE and PP components of the feedstock undergo melting since it was assumed that their structure is crystalline. Other plastics with amorphous structure will not undergo melting phase change and instead they have a specific temperature called glass transition temperature, which the polymer transition from having solid form to a liquid state. With the increase of temperature all the polymers in their liquid form will eventually vaporized. The reference study reported the value of 400 KJ/kg for the latent heat of condensation in supplementary data. This value was also used for the latent heat of vaporization for the polymers in liquid state [11, 12].

Two additional phase changes occur within the distillation tower for the MGO and VN cuts. The latent heats of vaporization and condensation for these cuts were selected from petrochemical specification sheets, with diesel oil representing MGO and petroleum naphtha representing VN. The specific values for latent heat are provided in the table below.

Transition Type	**Latent Heat (kJ/kg)**
Solid to Liquid (PE)	550
Solid to Liquid (PP)	250
Liquid to Vapor (All)	400
Vapor Condensation	400
MGO Vaporization	250
VN Vaporization	320

Table 4.12: Latent heat values for different phase transitions of pyrolysis system

The following section will present and discuss the results obtained from these calculations, providing insight into the energy balances and efficiencies within the pyrolysis and distillation processes.

4.5 Mass and Energy Balance Results

4.5.1 Mass Balance

As outlined in Chapter 3, two processing scenarios have been established: one for 300 tons per year and another for 3000 tons per year of marine litter collected from marine environment. This corresponds to approximately 180 tons and 1800 tons of marine plastic waste per year processed through pyrolysis. Given that each pyrolysis cycle has a duration of 4 hours, the system can operate for 6 cycles per day if run continuously. Assuming 300 operational days per year, these parameters yield an estimated batch size of 100 kg per cycle for the 180 ton scenario and 1000 kg per cycle for the 1800 ton scenario.

ML collected (ton/year)	**Waste Plastics** (ton/year)	**Pyrolysis Input** (ton/day)	**Pyrolysis Input** (kg/cycle)
300	180	0.6	100
3000	1800	6	1000

Table 4.13: Pyrolysis Process Overall Numbers

Using the pyrolysis feed rate per cycle and the associated product yields, the quantities of pyrolysis oil, gas, and solids produced were estimated. Product yields from the distillation tower were provided in the reference study in terms of volume percent. To convert these values to weight percent, density data for each product at specific temperatures were required. The densities of the IFO and MGO cuts were reported in the reference study at 15°C as 841.2 kg/m^3 and 802.9 kg/m^3, respectively. The VN cut density was reported at 20°C as 772 kg/m^3. Further, the VN stream was modeled in Aspen HYSYS, and, after checking with petroleum naphtha density data at various temperatures, a final density value of 775 kg/m^3 was used for VN. This density information allowed conversion of the results from vol% to wt% [43].

In the reference study, a single distillation run was conducted on all the pyrolysis oil. The resulting yields were applied to all four case studies. However, for the Beach and Floating marine litter case studies, the amount of water produced was unexpectedly high. Water typically forms during the pyrolysis of Nylon 6,6, though some studies suggest that even this polymer does not always yield water upon pyrolysis. For the Floating marine litter case, only 3% of the polymer composition consists of PA, which includes Nylon 6,6. Similarly, in the Beach marine litter case, while PA make up 18% of the polymer pool, distillation yields suggested that almost half of the PA were converted to water, which seems unlikely. Therefore, for these two case studies, water yields were adjusted to better represent the actual feedstock composition. For the Seabed 1 and Seabed 2 case studies, while the water yield reported in reference study was still somewhat high, it remained within a reasonable range and were thus used as reported in the reference study [43].

Case Study	**Beach**	**Floating**	**Seabed-1**	**Seabed-2**
IFO (wt%)	7.03	7.46	6.5	6.5
MGO (wt%)	54.57	58.04	50.5	50.5
VN (wt%)	23.8	25.3	22	22
Water (wt%)	6	0	13	13
Loss (wt%)	8.6	9.2	8	8

Table 4.14: Distillation tower product yields for different case studies

With the distillation tower product yields established, the mass balance calculations for both processing capacities can be finalized. The results for a single pyrolysis cycle at each of the capacities are presented in the tables below.

Streams	**Beach(kg)**	**Floating(kg)**	**Seabed-1(kg)**	**Seabed-2(kg)**
Marine Litter	100	100	100	100
Dolime	10	10	10	10
Volatiles	82.6	87.5	79.1	80
Gas	20	27.5	31.8	28
Solids	27.4	22.5	30.9	30
Pyro oil	62.6	60	47.3	52
IFO	4.39	4.48	3.07	3.38
MGO	34.15	34.82	23.88	26.26
VN	14.88	15.17	10.41	11.44
Water	3.75	0	6.15	6.76

Table 4.15: 100 kg per cycle (180 ton/year) Scale

Streams	Beach (kg)	Floating (kg)	Seabed-1(kg)	Seabed-2(kg)
Marine Litter	1000	1000	1000	1000
Dolime	100	100	100	100
Volatiles	826	875	791	800
Gas	200	275	318	280
Solids	274	225	309	300
Pyro oil	626	600	473	520
IFO	43.94	44.76	30.74	33.8
MGO	341.54	348.24	238.86	262.6
VN	148.8	151.74	104.1	114.4
Water	37.56	0	61.5	67.6

Table 4.16: 1000 kg per cycle (1800 ton/year) Scale

The total production of products in a single day is also reported in the charts below for both of the capacities.

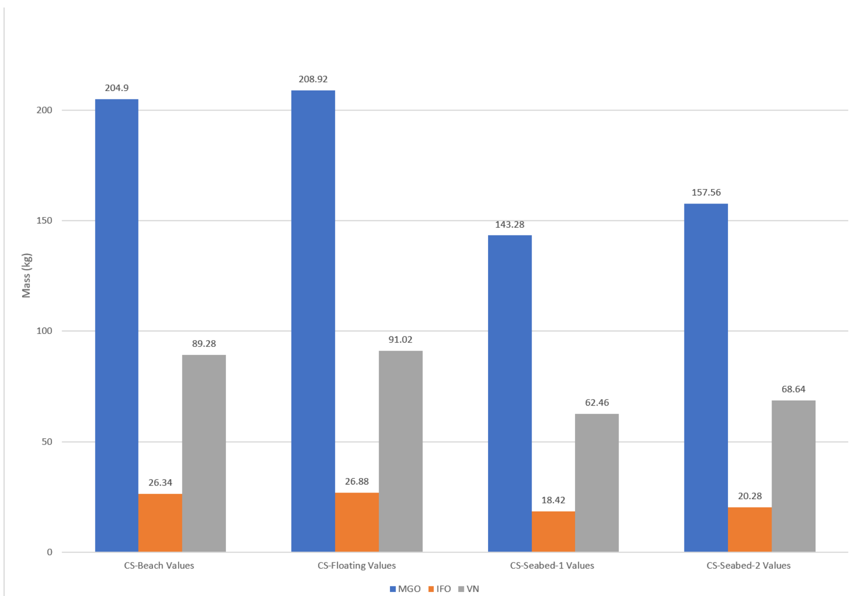

Figure 4.5: Oil products for 1 day (scale 180 ton/year)

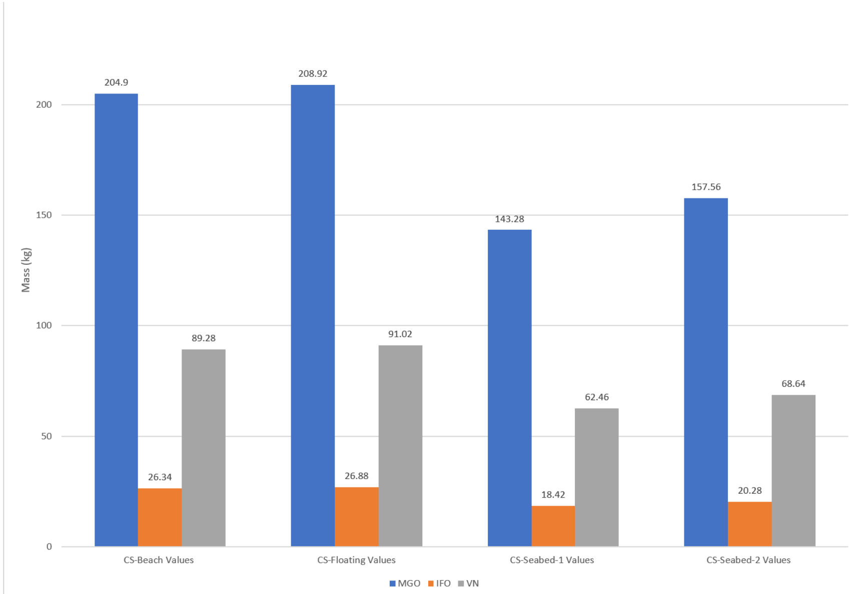

Figure 4.6: Oil products for 1 day (scale 1800 ton/year)

Another key factor to consider is the oil product yield relative to the total feedstock, as it provides insight into the conversion efficiency of the feedstock to product. Given the linear scale up for both capacities, these yield values are identical for each scenario; thus, a single chart is used to represent them.

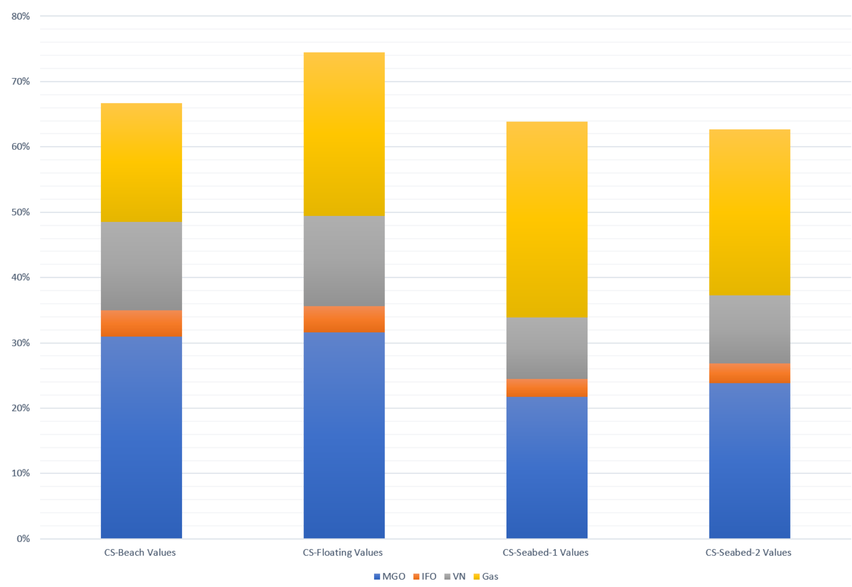

Figure 4.7: Oil Product Yield Relative to Total Feedstock Mass

The chart above demonstrates that, across all case studies, over 60% of the total feedstock is recoverable as products. It is worth noting that the yield for plastic waste alone would likely be even higher, as the calculation includes both the inert fraction and Dolime added to mitigate acidic compound formation. MGO, which is the primary product of this process, stands out with yields ranging from 20% to 35% depending on the case study. In the Beach and Floating scenarios, MGO yield is the highest among products, while in the seabed-focused cases, gas yield surpasses MGO, making it the dominant product.

With the completion of the mass balance calculations, the results serve as a basis for further process analysis, including energy balance and economic assessment, which will be discussed in the subsequent sections.

4.5.2 Energy Balance

The energy balance results are presented in the tables below. To better illustrate the energy flow, Sankey diagrams of the pyrolysis reactor and distillation tower have been provided. The Beach case study represents the 100 kg per cycle capacity, while the Seabed-2 case study represents the 1000 kg per cycle capacity.

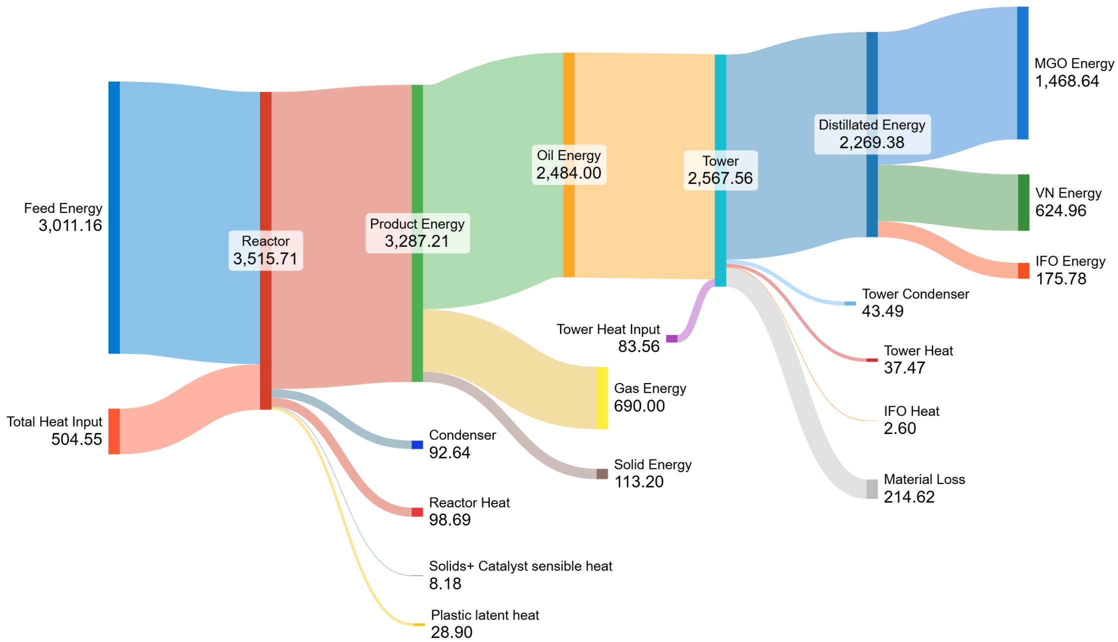

Figure 4.8: Heat flow diagram of 100 kg capacity for Beach case study

Energy	**Beach(MJ)**	**Floating(MJ)**	**Seabed-1(MJ)**	**Seabed-2(MJ)**
Feed Energy	3011.16	3386.58	2745.38	2923.19
Product Energy	3287.21	3618.92	2958.75	3021.29
Total Heat Input	504.55	474.66	431.89	322.42
Reactor Heat	98.69	98.69	98.69	98.69
Condenser	92.64	94.52	81.48	84.78
Solids + Catalyst	8.18	4.81	9.07	7.91
Plastic Latent Heat	28.9	44.3	29.27	32.91
Oil Energy	2484	2548.5	1725.16	1896.59
Gas Energy	690	948.75	1097.1	966
Solid Energy	113.2	121.67	136.48	158.7
Tower Heat Input	83.56	74.09	79.5	83.8
Tower Condenser	43.49	33.97	40.21	44.33
Tower Heat	37.47	37.47	37.47	37.47
IFO Heat	2.6	2.65	1.82	2
Material Loss	214.62	234.43	138.01	151.73
MGO Energy	1468.64	1497.43	1027.12	1129.18
VN Energy	624.96	637.31	437.05	480.48
IFO	175.78	179.04	122.98	135.2

Table 4.17: 100 kg per cycle (180 ton/year) scale, energy balance results

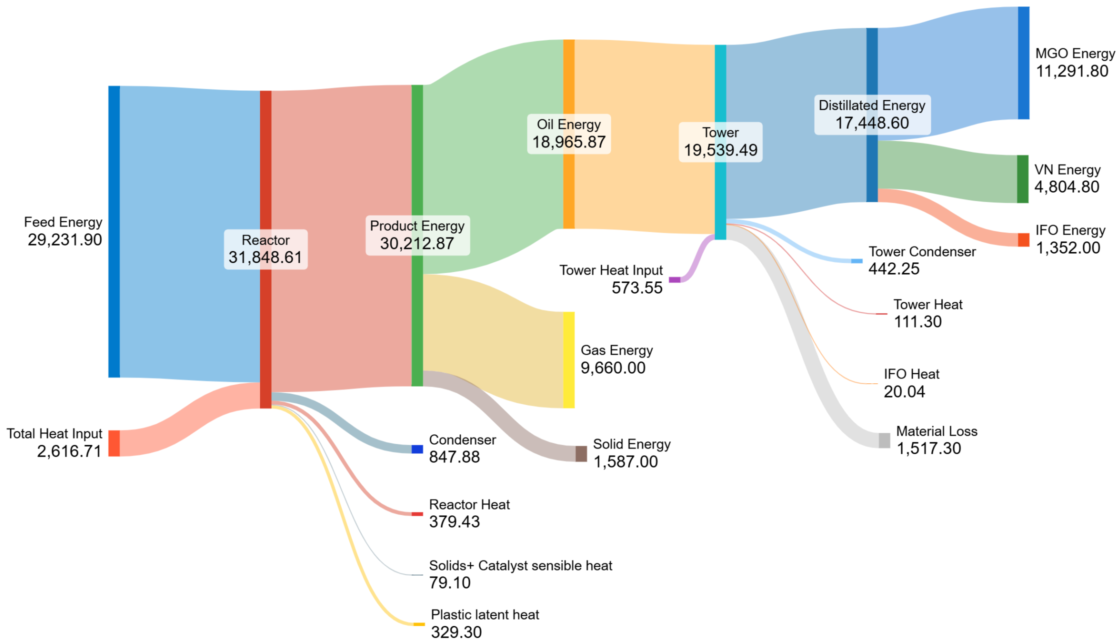

Figure 4.9: Heat flow diagram of 1000 kg capacity for Seabed-2 case study

Energy	Beach(MJ)	Floating(MJ)	Seabed-1(MJ)	Seabed-2(MJ)
Feed Energy	30111.66	33865.8	27453.8	29231.9
Product Energy	32872.12	36189.17	29587.47	30212.87
Total Heat Input	4438.01	4139.24	3711.47	2616.71
Reactor Heat	379.43	379.43	379.43	379.43
Condenser	926.36	945.2	814.8	847.88
Solids + Catalyst	81.8	48.14	90.71	79.1
Plastic Latent Heat	289.96	443.1	292.3	329.3
Oil Energy	24840.05	25484.97	17251.65	18965.87
Gas Energy	6900	9487.5	10971	9660
Solid Energy	1132.06	1216.7	1364.82	1587
Tower Heat Input	573.79	477.56	531.67	573.55
Tower Condenser	436.44	339.76	402.14	442.25
Tower Heat	111.3	111.3	111.3	111.3
IFO Heat	26.2	26.5	18.23	20.04
Material Loss	2146.2	2347.17	1380.1	1517.3
MGO Energy	14686.46	14974.32	10271.19	11291.8
VN Energy	6249.61	6373.08	4370.52	4804.8
IFO Energy	1757.81	1790.4	1229.8	1352

Table 4.18: 1000 kg per cycle (1800 ton/year) Scale, energy balance results

In the above tables, **Feed Energy** and **Product Energy** represent the total energy content of the feedstock and product streams entering and leaving the pyrolysis reactor. The difference between these values indicates the Heat of Reaction. The **Total Heat Input** parameter is the sum of all sensible and latent heats within the pyrolysis reactor, along with the **Reactor Heat**, which accounts for the energy needed to heat the reactor itself. This Reactor Heat value was derived by analyzing the reactor's geometry and weight, following guidelines from chemical engineering handbooks. The **Condenser** parameter shows the heat dissipated by the condenser as volatile matter exits the pyrolysis reactor. The **Plastic Latent Heat** parameter reflects the heat required to melt and vaporize the plastic feedstock, which is a critical component, as most of the plastic has now been converted into oil and gas [90].

Oil Energy, **Gas Energy**, and **Solid Energy** represent the total energy content of the output products based on their respective streams. After pyrolysis, the oil stream is directed to the distillation tower. The **Tower Heat Input** parameter includes the heat required to vaporize the MGO and VN cuts and to heat the IFO cut to 320°C. Additionally, the energy needed to heat the distillation tower and its packing is represented by the **Tower Heat** parameter, which is also included in the **Tower Heat Input**. The **Tower Condenser** parameter reflects the total energy dissipated by the condensers for both the MGO and VN streams. During the experiment, some oil was lost due to secondary reactions. Although the detailed effects of these reactions were not analyzed to simplify calculations, their impact was estimated and represented by the **Material Loss** parameter. This loss is calculated as the mass of the lost oil multiplied by its heating value [90].

A crucial parameter in the energy balance is the energy yield of the product streams, which indicates how much of the original feedstock's energy can be recovered as usable fuel. By analyzing energy yields, process parameters can be optimized to maximize output, minimize energy losses, and reduce reliance on external energy sources. This contributes to a more efficient conversion of waste materials into valuable resources, enhancing both the sustainability and economic feasibility of the process. The following tables and chart indicate the energy yields of products at different stages.

Product	**Beach**	**Floating**	**Seabed-1**	**Seabed-2**
Oil	70.65	66.00	54.30	58.44
Gas	19.63	24.57	34.53	29.76
Solid	3.22	3.15	4.30	4.89
Total	93.50	93.72	93.12	93.09

Table 4.19: Energy yields for different case studies for 100 kg per cycle capacity

Product	**Beach**	**Floating**	**Seabed-1**	**Seabed-2**
Oil	71.90	67.06	55.36	59.55
Gas	19.97	24.96	35.20	30.33
Solid	3.28	3.20	4.38	4.98
Total	95.14	95.22	94.94	94.86

Table 4.20: Energy yields for different case studies for 1000 kg per cycle capacity

The energy yields of the product streams from the pyrolysis reactor indicate that approximately 55% to 70% of the plastic feedstock's energy can be recovered in the form of oil, while an additional 20% to 35% is recoverable as gas. This gas can be repurposed as an energy source to sustain the pyrolysis process, making it a self-sufficient system to some extent. The high energy yields for both oil and gas demonstrate the potential of pyrolysis as an effective method for converting plastic waste into valuable fuel sources, making it a promising candidate for energy recovery and waste reduction applications.

Although the scaling up was done linearly, there were slight variations in energy yields between the 100 kg and 1000 kg per cycle capacities. These minor differences were primarily due to the Reactor Heat parameter, as the energy required to heat up the reactor did not scale linearly with the increase in reactor size. Thus, the results for both capacities were reported.

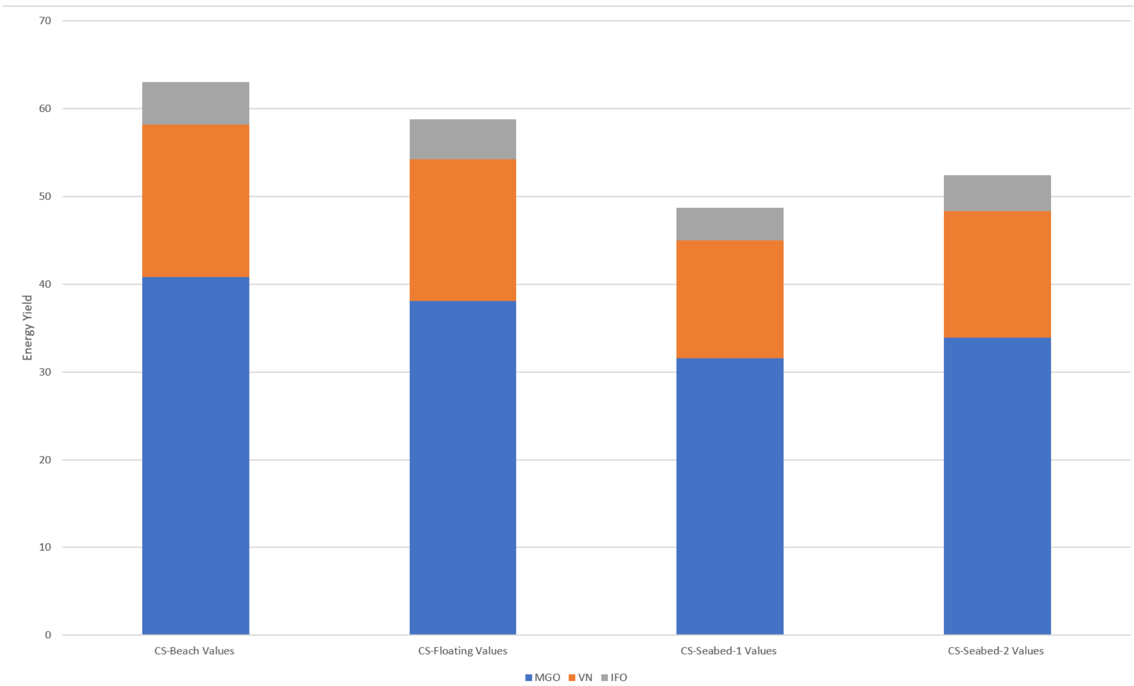

Figure 4.10: Energy yield of final products

The chart above illustrates the energy yields of the final products from the distillation tower. The energy yield for MGO ranges from 30% to 40% of the total energy input, while VN, considered the secondary product, accounts for 13% to 17%. Although there were slight differences in yields between the 100 kg and 1000 kg per cycle capacities, these variations were minimal. Therefore, only the results for the 100 kg per cycle capacity are presented here, as they can be considered representative across scales.

4.6 Final Remarks

This chapter presented the energy and mass balance results for the pyrolysis of marine litter plastic waste at two different processing capacities. The mass balance findings demonstrated high oil yields, consistent with other mixed plastic pyrolysis studies. Notably, a significant portion of the produced oil was recovered as MGO through distillation, making it a viable alternative fuel for the shipping industry.

The energy balance results indicate that the process is efficient, with most of the feedstock's energy recoverable from the oil output. Additionally, the energy analysis showed that the gas produced during pyrolysis is sufficient to fully sustain the energy needs of the process across all case studies, highlighting the potential for energy self-sufficiency.

These findings illustrates the feasibility and sustainability of converting marine litter into valuable resources, contributing to both waste management and energy production.

Chapter 5

Real-Plant Energy and Mass Balances: Practical Design, Economic Feasibility, and Environmental Impact Analysis

The energy and mass balance calculations for a plastic pyrolysis plant using marine litter plastics have shown promising results, demonstrating high product yields, high energy recovery, and the possibility of a self-sustaining process. However, it is essential to recognize that these findings are based on bench-scale experiments, which do not fully account for the technical challenges and difficulties encountered in industrial-scale applications. For marine plastic pyrolysis to be a viable waste management and fuel producing solution, a full-scale operational plant must be designed, accompanied by a detailed analysis of its economic feasibility and environmental impact. This chapter addresses these critical aspects by presenting the practical design of a pyrolysis plant, refining the energy and mass balances to account for industrial factors such as thermal losses and unit efficiencies, and finally assessing both the economic viability and environmental implications of the proposed system.

5.1 Pyrolysis Process Description

The marine plastic waste from the PRF first enters an industrial dryer, as this waste is assumed to retain residual seawater. Since plastics do not inherently contain water within their internal structure, it is expected that a standard industrial dryer can reduce the moisture content to an acceptable level. The dryer utilizes flue gases from the reactor as its heat source, thereby enhancing the overall thermal efficiency of the process.

After drying, the waste plastics proceed to an industrial shredder. Particle size significantly influences product distribution in pyrolysis and enhances heat transfer within the reactor. Literature suggests that particle sizes between 5 mm and 50 mm are suitable for slow pyrolysis. Smaller particle sizes can increase the production of H_2 and CO gases, as well as the ash and carbon content in the resulting char, which is not optimal for this process which is focused on oil production. Additionally, since the feedstock remains contaminated with metals and glass, it is essential to use a shredder designed to withstand potential wear from these materials [72].

After pretreatment, the waste plastics are introduced into the pyrolysis reactor along with Dolime. A rotary kiln reactor is chosen due to its straightforward design, suitability for extended batch operations, and its prevalence in the emerging plastic pyrolysis industry. In this setup, the plastic waste undergoes pyrolysis over a four hour period, consistent with the experimental conditions. The kiln is externally heated by a burner that uses gas generated from the pyrolysis process itself. Initially, however, since pyrolysis gas is not yet available, a certain amount of natural gas is used to start the reactor and initiate the process [42].

The volatile compounds exiting the reactor are directed into a water cooled condenser, where they are cooled to ambient temperature. Upon cooling, the gas and liquid phases are separated in a liquid-gas separator. The liquid pyrolysis oil is then collected in a storage tank, while the gas stream flows through a caustic scrubber to remove hazardous components before entering the burner. Due to the nitrogen and acidic compounds present in marine litter, gases such as hydrogen sulfide, hydrochloric acid, sulfur dioxide, ammonia, and hydrogen cyanide may form within the reactor. While Dolime is added to the feedstock to reduce some acidic gas formation, the caustic scrubber ensures that any remaining harmful gases are neutralized, thereby protecting sensitive equipment and preventing emissions into the environment [43].

The pyrolysis oils are pumped into the distillation tower, which, like the experimental setup, is packed to enhance separation efficiency. The oil is heated by the tower's reboiler burner to 320°C, causing the lighter fractions to evaporate. Two condensers are used to separate these vaporized fractions into MGO and VN cuts. The remaining oil at the tower's bottom exits as a third product. In an alternative design, this residual oil can be recycled back into the reactor for further thermal decomposition, maximizing product yield.

At the burner's exit point, a heat exchanger is installed to recover heat from the flue gas. In addition to the hot flue gas, a portion of gas from the plastic pyrolysis process remains unused, depending on the case study. Although the volume is insufficient for a combined heat and power (CHP) unit, it is still combusted to recover energy for district heating. Similarly, the heat removed by the condensers is sufficient to heat water to 70°C, allowing it to also contribute to district heating.

The PFD of the process is presented in the image below:

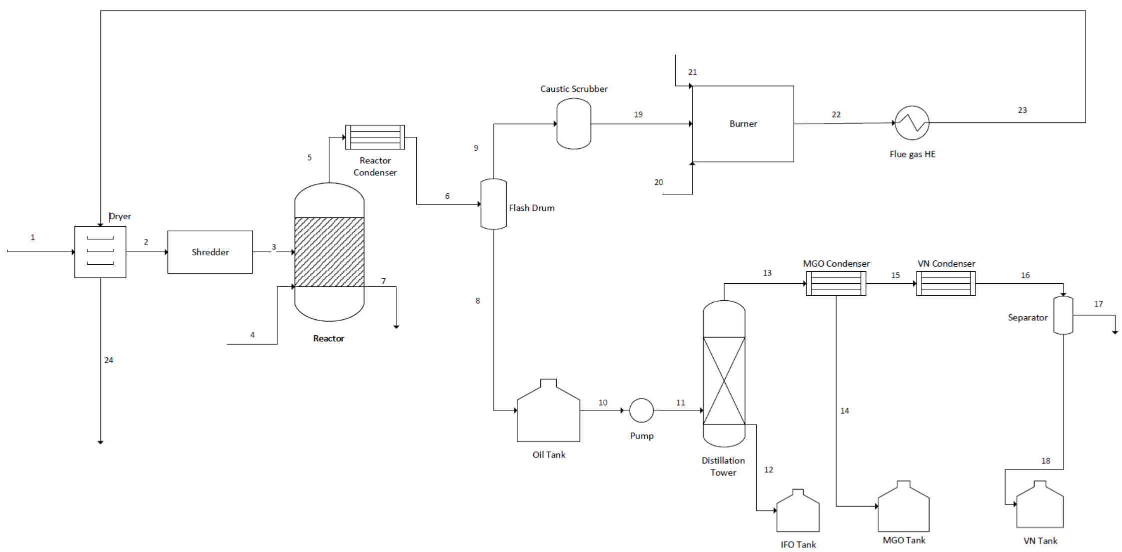

Figure 5.1: PFD of pyrolysis process

5.2 Energy Balance for Pyrolysis Plant

The energy balance for the pyrolysis plant builds upon the calculations and results from the modeled process in Chapter 4, incorporating additional energy streams and modifications to more accurately reflect real-world conditions. This section provides a detailed examination of these adjustments, highlighting the factors and design changes essential for achieving a comprehensive and practical energy balance for the process.

5.2.1 Energy for New Equipment

Two new equipment have been added to the process that require an energy input, which are dryer and shredder. The sizing and duty of these equipments are analyzed during the equipment sizing and cost estimation. A summary of these units duty, duration of operation, and finally calculated energy consumption is provided in the table below.

Equipment	Duty (KW)	Duration of Operation (h)	Energy (MJ)
Dryer (100 kg/cycle)	5.5	1	19.8
Shredder (100 kg/cycle)	15	1	54
Dryer (1000 kg/cycle)	15	1	54
Shredder (1000 kg/cycle)	55	1	198

Table 5.1: Energy consumption of pretreatment equipment

A pump is also exist within the process however its energy consumption was deemed negligible compare to the whole process.

5.2.2 Efficiency of Reactor and Burner

Both the reactor and the burner have losses and inefficiencies during the operation, which must be accounted for. Energy efficiency of a rotary kiln pyrolyzing plastics with addition of heat carriers within an experimental setup was found in literature. The reported value was 61%. Current modern burners have high efficiencies. The value of 95% was selected for the burner efficiency [86, 111].

5.2.3 Natural Gas to Initiate the Process

At the start of the pyrolysis process, the gas which is the result of plastic pyrolysis process have not been formed yet. Thus it is required that an external heating source provide the necessary energy for the pyrolysis process. This is done by burning natural gas. To estimate the amount of natural gas it is assumed that natural gas covers the heat required to heat up the reactor, and the heat necessary to convert plastic waste to volatiles.

Capacity	Beach (MJ)	Floating (MJ)	Seabed-1 (MJ)	Seabed-2 (MJ)
100 kg/cycle	220.32	237.49	209.39	216.39
1000 kg/cycle	1595.76	1767.74	1487.09	1556.64

Table 5.2: The amount of energy covered by NG in each setting

5.2.4 Heat Recovery

Considerable amount of energy is present within the flue gas. This energy is recovered by a heat exchanger after heating the necessary component. The recovered heat value was obtained through simulation of the burner component and subsequent heat exchanger in Aspen Hysys. The heat removed by reactor and distillation tower is simply shown by a cooler.

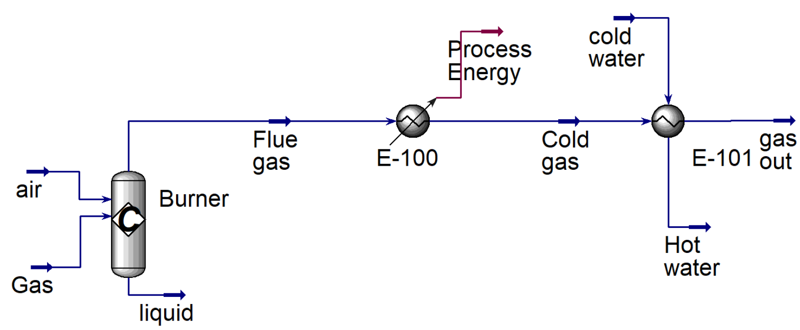

Figure 5.2: Simulation schematic in Aspen Hysys

The temperature of Hot water stream used for district heating is maintained at 70°C, while the outlet temperature of the flue gas, after heat recovery, is set at 80°C.

5.2.5 Energy Balance Results for Pyrolysis Process

The tables below presents the results of energy balance after employing the necessary adjustments.

Energy	Beach (MJ)	Floating (MJ)	Seabed-1 (MJ)	Seabed-2 (MJ)
Pretreatment Energy	73.8	73.8	73.8	73.8
Real Input by NG	361.18	389.32	343.26	354.73
Real Input by Pyro gas	465.95	388.8	364.75	173.82
Real Total Input of Reactor	827.13	778.12	708.01	528.55
Reactor Condenser	92.64	94.52	81.48	84.78
Tower Heat Input	83.56	74.09	79.5	83.8
MGO Condenser	23.58	23.98	18.83	20.8
VN Condenser	20.1	9.98	21.76	24.11
Real Total Output of Burner	958.62	897.07	828.96	644.58
Recovered from Flue gas	19.5	342.96	501.2	579.2
Remain in Flue gas	92.07	118.53	128.27	115.62
Oil Energy	2484	2548.5	1725.16	1896.59
Gas Energy	690	948.75	1097.1	966
Solid Energy	113.2	121.67	136.48	158.7

Table 5.3: Energy Balance for 100 kg per cycle (180 ton/year) scale.

Energy	Beach (MJ)	Floating (MJ)	Seabed-1 (MJ)	Seabed-2 (MJ)
Pretreatment Energy	252	252	252	252
Real Input by NG	2616	2897.93	2437.85	2551.86
Real Input by Pyro gas	4659.42	3887.7	3646.52	1737.82
Real Total Input of Reactor	7275.42	6785.63	6084.37	4289.68
Reactor Condenser	926.36	945.2	814.8	847.88
Tower Heat Input	573.79	477.56	531.67	573.55
MGO Condenser	235.8	239.8	188.3	208
VN Condenser	200.2	99.8	217.6	241.1
Real Total Output of Burner	8262.33	7645.47	6964.26	5119.2
Recovered from Flue gas	544.8	3768.8	5324	6108
Remain in Flue gas	846.55	1123.68	1248.9	1118.97
Oil Energy	24840.05	25484.97	17251.65	18965.87
Gas Energy	6900	9487.5	10971	9660
Solid Energy	1132.06	1216.7	1364.82	1587

Table 5.4: Energy Balance for 1000 kg per cycle (1800 ton/year) scale.

In the tables above, the **Pretreatment Energy** parameter represents the energy used to prepare the feedstock for processing. The parameters **Real Input by NG** and **Real Input by Pyro Gas** indicate the energy supplied by natural gas and pyrolysis gas, respectively, with reactor efficiency factored in. The combined value of these two parameters is noted as **Real Total Input of Reactor**, representing the total energy requirement of the reactor.

Tower Heat Input and **Reactor Condenser** parameters remain consistent with those in previous tables, while the **Tower Condenser** parameter is divided into its individual components, the MGO and VN condensers. **Real Total Output of Burner** reflects the total energy demand for a complete cycle of the process, accounting for both reactor and burner efficiencies. The **Recovered from Flue Gas** parameter denotes the energy expected to be reclaimed from the flue gas, with values derived from Aspen HYSYS simulations. Finally, **Remain in Flue gas** is the energy that leaves the heat exchanger with flue gas. Its amount is the difference between total input and total output of the system. Part of this energy is used in dryer to evaporate water. The precise energy balance of the dryer was not calculated due to lack of any useful information. However, a basic calculation has shown that the amount of energy in flue gas is more than enough to cover water content well over 50% in all cases except Beach case study which is only suitable for 36% water content. Still such water contents are highly unlikely for a plastic waste.

5.2.6 System Efficiency

To calculate what percentage of the energy input to the system is recoverable, the whole system was simplified to its main inlet and outlet streams.

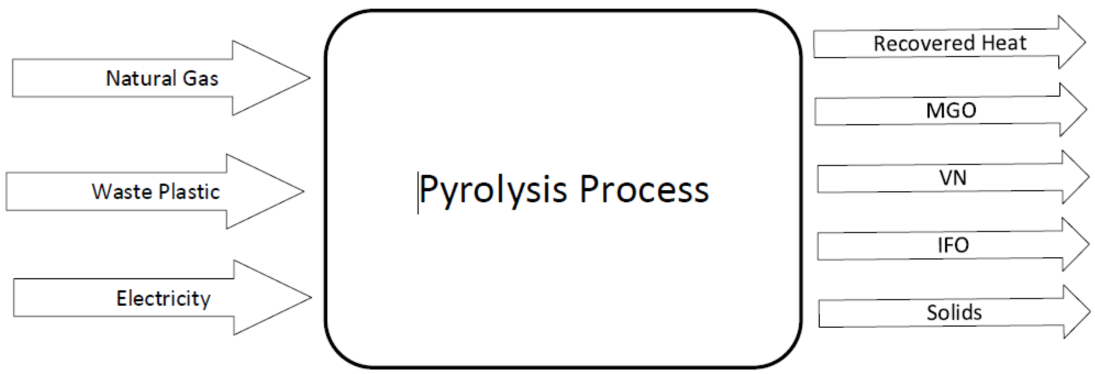

Figure 5.3: Main energy input and output streams of pyrolysis system

With determining the main energy inlets and outlets, and having the value from the each of the streams from energy balance calculations, the energy recovery percentage for each of the outlet streams can be obtained. Their values have been reported in the tables below.

Products	**Beach**	**Floating**	**Seabed-1**	**Seabed-2**
Recovered Heat	4.52	12.25	19.71	21.15
MGO	42.62	38.90	32.48	33.69
VN	18.14	16.55	13.82	14.34
IFO	5.10	4.65	3.89	4.03
Solid	3.28	3.16	4.32	4.73
Total Recovered	73.66	75.51	74.21	77.94

Table 5.5: Recovered Products for 180 ton/year capacity

Products	**Beach**	**Floating**	**Seabed-1**	**Seabed-2**
Recovered Heat	5.78	13.65	21.71	23.11
MGO	44.53	40.45	34.07	35.25
VN	18.95	17.22	14.50	15.00
IFO	5.33	4.84	4.08	4.22
Solid	3.43	3.29	4.53	4.95
Total Recovered	78.03	79.45	78.89	82.53

Table 5.6: Recovered Products for 1800 ton/year capacity

The energy recovery values in general have increased for all of the products. This is attributed to the fact that in this setting pyrolysis gas is covering part of the energy input necessary for the process. Another factor is the extensive heat recovery from almost all of the main streams, which avoids thermal energy loss to the environment and thus increasing the overall energy recovery. Another interesting point is the slight increase in energy recovery at the 1800 ton/year capacity compared to the 180 ton/year capacity, despite the linear scaling. This is primarily due to the energy required to heat the reactor, which depends on the reactor's mass, a factor that does not scale linearly with processing capacity. As capacity increases, the relative proportion of energy needed for heating becomes smaller, allowing for a higher percentage of energy recovery.

5.3 Mass Balance for Pyrolysis Plant

The mass balance for the pyrolysis plant is same as the Modeled process, since the main process conditions did not change. The main change to the process is the inclusion of the burner and addition of the of the natural gas to the system. Thus in this section, the focus will be only on the burner.

The burner has three inlet streams and one outlet streams. The mass of Pyro Gas stream is same as the Gas stream in Modeled process. The mass of air was calculated in Aspen Hysys in a way that all the fuel components of the gas completely burn. The mass of Natural Gas was calculated based on its heating value. The heating value was determined by the composition of the Natural Gas. It is assumed that natural gas composition is the same as Passo Gries (Northern Europe) natural gas found in Snam Co. website. From the Flue gas, the mass of CO_2 generated from the combustion was deemed relevant and thus was reported. The values for each case study was reported in the tables below [93].

Case Studies	**Natural Gas (kg)**	**CO_2 (kg)**
Beach	7.65	70.84
Floating	8.24	90.56
Seabed-1	7.27	97.92
Seabed-2	7.51	89.44

Table 5.7: Natural Gas and CO_2 mass for a single cycle (180 ton/year)

Case Studies	**Natural Gas (kg)**	**CO_2 (kg)**
Beach	55.41	645.36
Floating	61.37	843.8
Seabed-1	51.6	919.04
Seabed-2	54.05	834.48

Table 5.8: Natural Gas and CO_2 mass for a single cycle (1800 ton/year)

The complete mass balance table is presented below, with all streams reported in units of kg/h. Although the system operates in batch mode, a time basis has been attributed for consistency in reporting. A time duration of 4 hours, corresponding to the pyrolysis process, was assumed for these calculations.

Streams	Type	Beach (kg)	Floating (kg)	Seabed-1 (kg)	Seabed-2 (kg)
1	wet plastic	27.5	27.5	27.5	27.5
2	dry plastic	25	25	25	25
3	dry plastic	25	25	25	25
4	dolime	2.5	2.5	2.5	2.5
5	volatile	20.65	21.87	19.77	40
6	volatile	20.65	21.87	19.77	40
7	solids	6.85	5.62	7.72	7.5
8	pyro oil	15.65	15	11.82	13
9	pyro gas	5	6.87	7.95	7
10	pyro oil	15.65	15	11.82	13
11	pyro oil	15.65	15	11.82	13
12	IFO	1.09	1.12	0.77	0.84
13	distilled	13.19	12.5	10.11	11.11
14	MGO	8.54	8.71	5.97	6.56
15	light cut	4.66	3.79	4.14	4.55
16	light cut	4.66	3.79	4.14	4.55
17	water	0.94	0	1.54	1.69
18	virgin naphtha	3.72	3.79	2.6	2.86
19	clean gas	5	6.87	7.95	7
20	air	124	143	137	129
21	natural gas	1.91	2.06	1.82	1.87
22	flue gas	130.9	151.9	146.8	137.9
23	cool flue gas	130.9	151.9	146.8	137.9
24	wet flue gas	133.4	154.4	149.3	140.4

Table 5.9: Mass balance table for 100 kg per cycle (180 ton/year) scale.

Streams	Type	Beach (kg)	Floating (kg)	Seabed-1 (kg)	Seabed-2 (kg)
1	wet plastic	262.5	262.5	262.5	262.5
2	dry plastic	250	250	250	250
3	dry plastic	250	250	250	250
4	dolime	25	25	25	25
5	volatile	206.5	218.75	197.75	200
6	volatile	206.5	218.75	197.75	200
7	solids	68.5	56.25	77.25	75
8	pyro oil	156.5	150	118.25	130
9	pyro gas	50	68.75	79.5	70
10	pyro oil	156.5	150	118.25	130
11	pyro oil	156.5	150	118.25	130
12	IFO	10.98	11.19	7.69	8.45
13	distilled	131.98	125	101.11	111.15
14	MGO	85.38	87.06	59.71	65.65
15	light cut	46.59	37.93	41.4	45.5
16	light cut	46.59	37.93	41.4	45.5
17	water	9.39	0	15.37	16.9
18	virgin naphtha	37.2	37.94	26.03	28.6
19	clean gas	50	68.75	79.5	70
20	air	998	1238	1265	1189
21	natural gas	13.85	15.34	12.9	13.51
22	flue gas	1062	1322	1357	1273
23	cool flue gas	1062	1322	1357	1273
24	wet flue gas	1074.5	1334.5	1369.5	1285.5

Table 5.10: Mass balance table for 1000 kg per cycle (1800 ton/year) scale.

5.4 Economic Analysis

Evaluating the economic feasibility of a new process is essential, especially in the early stages of development. While the proposed processes and their capacities may not yet be at full industrial scale, conducting an economic analysis will help determine their potential for scalability and commercial viability. This analysis will also identify key cost drivers, highlight areas for cost optimization, and provide a preliminary estimate of the financial investment required to bring the process closer to industrial application. In the table below general assumptions of the pyrolysis plant has been defined. These values are based on relevant studies [87, 95].

Parameters	Values
Reference year	2024
Plant life	20
Financing	Bank loan
Interest Rate	8%
Operating time	300 day/year, 7200h/year
Operation	24h, 7 day, 3 shifts, 6 cycles

Table 5.11: General Parameters for Plant Operation and Financing for both capacities

Another important factor that should be determined before the analysis is the flow of the materials. This is particularly important for operational costs calculations. Since there are four case studies, each with different values, an average value of all of the case studies will be used for the evaluations. It is crucial to note that these average values may not accurately represent the precise heat and mass balance. These values are reported in the table below.

Streams	Capacity (180 ton/year)	Capacity (1800 ton/year)
MGO (kg)	29.77	297.8
VN (kg)	12.97	129.76
IFO (kg)	3.82	38.31
Solids (kg)	27.7	277
Water (kg)	4.16	41.66
Natural gas (kg)	6.97	50.53
CO_2 (kg)	85.1	786.95
Heat (MJ)	489.85	5227.61

Table 5.12: Average mass and energy of products and wastes for both case studies

Lastl, the methods used for economic analysis are based on *Turton's Analysis, Synthesis, and Design of Chemical Processes*, as it provides a comprehensive and practical framework for evaluating process costs and economic factors [102].

5.4.1 Component Sizing

To initiate the capital cost calculations, it is essential to determine the size of the components used in the process. For this process, the equipment can be broadly categorized into three groups: heat transfer equipment, volume-based equipment, and general equipment. Heat transfer equipment is used for heat exchange and requires calculating the heat transfer surface for proper sizing. Volume-based equipment is sized based on the volume that fluids occupy within the vessel. Lastly, general equipment requires distinct parameters for sizing. The table below reports the name, category, and designated size of the equipment for both capacities.

For the sizing and capital expenditure (Capex) calculations, none of the specific case studies were directly used; instead, a maximum value was selected from among the case studies. This approach ensures the plant can handle all potential variations in operating conditions.

Name	**Type**	**Size (100 kg/cycle)**	**Size (1000 kg/cycle)**
Dryer	General (m^3)	1	10
Shredder	General (KW)	15	55
Reactor	Volume (m^3)	0.51	5.1
Reactor Cond.	Heat Transfer (m^2)	1.4	13
Flash Drum	Volume (m^3)	0.1	0.15
Oil tank	Volume (m^3)	0.5	5
Distil. Tower	Volume (m^3)	0.3	1.2
Packaging	Volume (m^3)	0.06	0.24
Burner	General (KW)	150	1389
VN Cond.	Heat Transfer (m^2)	1.1	11
MGO Cond.	Heat Transfer (m^2)	1	2
Separator	Volume (m^3)	0.1	0.14
VN tank	Volume (m^3)	0.124	1.24
MGO tank	Volume (m^3)	0.26	2.62
IFO tank	Volume (m^3)	0.1	0.35
Conveyors	General (m^2/s)	7.5	80
Fan	General (m^3/s)	1	1
Flue gas HE	Heat Transfer (m^2)	4	52.5

Table 5.13: Equipment Sizes for Different Capacities

The component Dryer required multiple parameters for its sizing. These auxiliary parameters were obtained by checking TIC Technology Co. catalogs. Turton cost analysis did not include any specifications for Shredder. The component cost and its size were obtained my checking multiple vendors and websites. Several equipment including Flash Drum, Distillation Tower, Fan, and Separator are oversize for 100 kg/cycle capacity since the original values were smaller than Turton's introduced range.

5.4.2 Equipment Cost Calculations

Following Turton's instruction on calculating the cost of the single equipment (C_P) and using the material and pressure factors to calculate the sum of direct and indirect capital costs for each equipment C_{BM}, and finally updating the costs from 2001 to 2024 the direct and indirect cost for each equipment can be calculated. The results for both capacities are reported in below tables [102].

Equipment	**C_P($)**	**C_{BM} ($)**
Dryer	8165.42	10206.8
Shredder	5000	6250
Reactor	5768.74	37531.41
Reactor Cond.	4906.45	29070.72
Flash Drum	3772.8	11356.1
Oil tank	5731.88	17252.9
Distil. Tower	3976.66	31383.62
Packaging	37.5	266.4
Burner	70000	175000
VN Cond.	4602	15140.51
MGO Cond.	4484	26567.5
Separator	3772.8	11356.1
VN tank	3943	11868.2
MGO tank	4718.6	14203.6
IFO tank	3772.8	11356.02
Conveyors	6929.55	8662.03
Fan	2231.8	6026
Flue gas HE	6307	37368.7
Scrubber	14202.4	42749.2

Table 5.14: Equipment Costs for 100 kg/cycle capacity

Equipment	**C$_P$($)**	**C$_{BM}$ ($)**
Dryer	7497.8	9372.2
Shredder	12000	15000
Reactor	15005.52	104468.43
Reactor Cond.	38501.2	228119.5
Flash Drum	4112.34	12378.19
Oil tank	14856.24	44717.3
Distil. Tower	6931.86	54706.2
Packaging	142.8	1013.93
Burner	983459.9	2458649.76
VN Cond.	39570.5	130187
MGO Cond.	5370.53	31820.5
Separator	4048.8	12186.9
VN tank	7940.15	23899.9
MGO tank	10903.07	32818.3
IFO tank	5133.53	15451.8
Conveyors	3318.9	4148.72
Fan	2231.8	6026
Flue gas HE	36038.7	213529.16
Scrubber	30433.7	91605.34

Table 5.15: Equipment Costs for 1000 kg/cycle capacity

It is important to note that no such equipment as scrubber exist in Turton's equipment cost analysis data. To estimate the cost of the scrubber *Peters Plant Design and Economics for Chemical Engineers* were used [18].

5.4.3 Capex

With the direct and indirect costs of equipment estimated, it is possible to proceed to finalization of calculations of Capex. Aside from direct and indirect costs, 3 other parameters should be calculated: Contingency Costs, Contractor Fee, Auxiliary and Facilities costs. Following Turton's instructions, Contingency costs are set to be 15% of the direct and indirect costs. Similarly Contractor Fee is set to be 3% of the direct and indirect costs. Since the plant is being built from scratch it is necessary to compute Auxiliary and Facilities costs as well, which is 50% of direct and indirect costs in a base case condition. The summary of Capex components and its total value is reported in the table below [102].

Parameters	Capacity (100 kg/cycle)	Capacity (1000 kg/cycle)
Direct and Indirect costs	503615.81	3490099.13
Contingency	75542.37	523514.87
Contractor fee	15108.47	104702.97
Aux. and Facilities	199443.49	876503.99
TOTAL CAPITAL ($)	**793710.15**	**4994820.97**
TOTAL CAPITAL (€)	**729459.31**	**4590490.21**

Table 5.16: Capital Costs for Different Capacities

5.4.4 Costs of Manufacturing

The Costs of Manufacture (COM) refer to expenses associated with the day-to-day operation of the pyrolysis plant. This is also known as Opex or operational costs. COM can be divided into three categories: Direct Manufacturing Costs (DMC), Fixed Manufacturing Costs (FMC), and General Expenses (GE) [102].

$$COM = DMC + FMC + GE \tag{5.1}$$

To determine each of these elements and evaluate COM, these costs should be estimated: Cost of utilities (CUT), Cost of waste treatment (CWT), Cost of raw materials (CRM), Cost of operating labor (COL), and Fixed capital investment (FCI). FCI is the same as Capex or total capital which was evaluated beforehand. The other costs and their evaluation will be described in detail in subsequent paragraphs. The values used for calculating COM and its parameters are the average values of case studies [102].

CRM, include the price of waste marine plastic, Dolime, and materials necessary to stabilize the solid faction of the process. While there are sources providing detail analysis on the costs of cleaning marine litter and the damages they cause to the industries, no actual price was found for marine litter itself, so a price was chosen based on the price of the waste vehicle plastics, since these two waste streams have certain similarities to one another. Dolime or mixture of CaO and MgO is used along the feedstock to prevent the formation of acidic compounds. The price of Dolime was estimated through checking various online marketing sources. The solid material of the process are not suitable for non-hazardous disposal, thus following the instructions of the main reference study they are stabilized with cement, silica sand, and water to create concrete. The prices of cement and silica sand were found online for Europe region and they are used in the calculations. The tables below summarize the quantity and the price of raw materials [43, 95].

Name	Consume (/year)	Cost	Total (€/year)
Waste Plastic	180 ton	15 €/ton [95]	2700
Dolime	18 ton	184.8 €/ton [53, 98]	3326.4
Silica sand	41.52 ton	46.91 €/ton [16]	1947.70
Cement	19.44 ton	128.8 €/ton [15]	2503.872
Total			**10477.98**

Table 5.17: Annual Consumption and Cost of raw materials for 100 kg/cycle

Name	Consume (/year)	Cost	Total (€/year)
Waste Plastic	1800 ton	15 €/ton [95]	27000
Dolime	180 ton	184.8 €/ton [53, 98]	39916.8
Silica sand	414 ton	46.91 €/ton [16]	19420.74
Cement	196.2 ton	128.8 €/ton [15]	25270.56
Total			**111608.10**

Table 5.18: Annual Consumption and Cost of raw materials for 1000 kg/cycle

Utilities of pyrolysis process include Natural Gas for the burner, electricity for shredder and dryer, and finally soda to regenerate caustic scrubber. The amount of soda required for gas cleaning was estimated using a simplified Aspen Hysys simulation. The calculated values were 1.4 kg per cycle for a capacity of 180 ton/year and 13.94 kg per cycle for a capacity of 1800 ton/year. These values are likely overestimated, as the simulation assumed higher concentrations of acidic compounds compared to typical operating conditions. The prices for Natural Gas and electricity were found from Eurostat, while the price of soda was selected from online sources. The tables below summarize the quantity and the price of utilities.

Name	Consume (/year)	Cost	Total (€/year)
Electricity	55440 kwh	0.1515 €/kwh [39]	8399.16
Natural Gas	173204.5 kwh	0.0523 €/kwh [40]	9058.59
NaOH scrubber	2.52 ton	331.6 €/ton [14]	835.63
Total			**18293.38**

Table 5.19: Annual Consumption and Cost of Utilities for 100 kg/cycle

Name	Consume (/year)	Cost	Total (€/year)
Electricity	156330 kwh	0.1515 €/kwh [39]	23683.995
Natural Gas	1255670.5 kwh	0.0523 €/kwh [40]	65671.56
NaOH scrubber	25.09 ton	331.6 €/ton [14]	100314.48
Total			**189670.03**

Table 5.20: Annual Consumption and Cost of Utilities for 1000 kg/cycle

The pyrolysis plant generates two waste stream. The first waste is the water recovered from VN cut, which forms due to pyrolysis of Nylon 6,6. Also the caustic scrubber generates waste water due to changing of water and neutralization of soda. The second waste stream is CO_2 released due to burning of gas. Plastic is still a fossil fuel product, so a price is selected for its carbon emission. Part of CO_2 is absorbed in caustic scrubber as well. A scrubber if operated in optimum conditions can remove large quantities of CO_2. This is not the case for this process. It is estimated that around 23% of CO_2 is being removed by the scrubber. Since this value is being removed from the original pyrolysis gas, estimating a precise removal of CO_2 and its final effect on the flue gas was deemed too complex. Moreover the majority of that stream is hydrocarbons, thus this trivial removal was not considered in calculations.

Name	Produce (/year)	Cost	Total (€/year)
Waste Water	32.68 ton	150 €/ton [95]	4902
CO_2 produced	153.18 ton	64.5 €/ton [99]	9880.11
Total			**14782.11**

Table 5.21: Annual Production and Cost of Waste Products for 100 kg/cycle

Name	Produce (/year)	Cost	Total (€/year)
Waste Water	325.7 ton	150 €/ton [95]	48855
CO_2 produced	1416.51 ton	64.5 €/ton [99]	91364.9
Total			**140219.9**

Table 5.22: Annual Production and Cost of Waste Products for 1000 kg/cycle

The final operational cost is related to labor costs. From the supplementary data of Stalkamp study, the number and costs of labor is obtained and the values are summarized in the table below [95].

Type	Number	Wage	Total (€/year)
Plant Operators	1	55000 €/year	165000
Yard team maint.	1	59000 €/year	177000
Manage and engi.	1	70000 €/year	70000
Total			**412000.00**

Table 5.23: Annual Labor Costs for 100 kg/cycle

Type	Number	Wage	Total (€/year)
Plant Operators	2	55000 €/year	330000
Yard team maint.	1	59000 €/year	177000
Manage and engi.	1	70000 €/year	70000
Total			**577000.00**

Table 5.24: Annual Labor Costs for 1000 kg/cycle

Similar to Capex, in order to calculate COM, several parameters which are related to the above costs of operation must be calculated. However it is possible to simply fallow an equation which directly calculates the COM. This equation is presented below.

$$COM_d = 0.180FCI + 2.73COL + 1.23(CUT + CWT + CRM) \tag{5.2}$$

Here COM_d is the Cost Of Manufacturing without depreciation, FCI is the Fixed Capital Investment, COL is the cost of labor, CUT is the utility costs, CWT is the waste treatment costs and CRM is the costs of raw materials [102].

Using this equation, COM_d for capacity of 180 ton/ year is 1303313.3 €/year, and for 1800 ton/ year is 2944541 €/year.

5.4.5 Determining the Price of Product

The main product of pyrolysis process is MGO for marine transportation. With the capital and operational costs now available it is possible to calculate the minimum price of MGO for each capacity. However before that it is important to calculate secondary revenues and annuity factor.

Aside from MGO, the pyrolysis plant also produces VN, IFO, and heat for district heating. In the tables below the summary of these revenues is presented.

Type	Annual pro.	Price	Total €/year
District Heating	881730 MJ	0.02 €/MJ [95]	17634.6
Virgin Naphtha	23.34 ton	597.7 €/ton [101]	13950.318
IFO	6.87 ton	2.06 €/gallon [100]	4446.098
Total			**36031.02**

Table 5.25: Summary of secondary revenues of process for 100 kg/cycle

Type	Annual pro.	Price	Total €/year
District Heating	9409698 MJ	0.02 €/MJ [95]	188193.96
Virgin Naphtha	233.57 ton	597.7 €/ton [101]	139604.789
IFO	68.96 ton	2.06 €/gallon [100]	44613.0492
Total			**372411.8**

Table 5.26: Summary of secondary revenues of process for 1800 kg/cycle

The Annuity Factor (AF) is a coefficient used to spread a lump-sum capital cost into equal annual payments over the life of a project, considering the time value of money. Annualized Capital Cost applies this factor to represent the total capital investment as an equivalent yearly cost, simplifying project comparisons and annual cash flow calculations. To calculate AF interest rate and plant life is used.

Parameters	Capacity (100 kg/cycle)	Capacity (1000 kg/cycle)
Capex (€)	729459.31	4590490.21
Annualized capital (€)	74297.04	467551.57
MGO Production (ton/year)	53.59	536.06
Gross COM (€)	1303313.3	2944541
Gross COM per ton feedstock (€)	7240.63	1635.8
Net COM (€)	1267282.3	2572129.2
Net COM per ton feedstock (€)	7040.45	1429
MGO Price (€/ton)	25034.13	5670

Table 5.27: Economic Parameters for Different Capacities

The table above summarizes the economic parameters for both capacities. The Gross COM parameter represents the total operational costs excluding the revenue from secondary products, while Net COM accounts for this revenue. The COM per ton feedstock parameter indicates the operational expenditure required to process one ton of marine plastic waste, providing a useful metric for comparing this process to alternative waste treatment methods. The minimum price of MGO (Marine

Gas Oil) is calculated at 25034.13 €/ton and 5670 €/ton for the 180-ton/year and 1800-ton/year capacities, respectively. Given that the current market price of MGO is below 1000 €/ton, it is clear that the process, at these scales, is not profitable. However, this does not imply that marine plastic pyrolysis is inherently unviable. Numerous economic analyses of plastic pyrolysis suggest that a minimum plant capacity of 70 kton/year is typically required for profitability, often assuming a relatively high feedstock price, which is common for sorted plastics. In studies with lower feedstock costs, such as Stalkamp's study on pyrolysis oil from vehicle waste plastics at various capacities, a steep downward trend in production costs was observed. A similar trend appears in this study, where the MGO price for the 1800-ton/year capacity is over a quarter of that for the 180-ton/year capacity. Based on trends from other studies, it is speculated that a capacity between 35 kton/year and 55 kton/year could bring the price of the main product oil within a competitive market range [61, 95].

5.5 Environmental Analysis

While plastic pyrolysis offers an effective solution for reducing plastic waste and recovering valuable materials, it still relies heavily on fossil fuels, as most plastics are derived from them. Therefore, it is critical to assess the environmental impact of the process to ensure it does not inadvertently result in greater pollution than the baseline conditions it aims to improve.

The LCA was conducted for 1 ton of marine plastic waste, starting from its collection to the processing and evaluation of environmental impacts. The plastic waste is collected from the seas and delivered to a nearby port, with the Port of Venice selected as the reference port. This choice was made because the original reference study on marine plastic pyrolysis was conducted at this location. Additionally, the Port of Venice has access to the Adriatic Sea, one of the most heavily polluted areas in the Mediterranean with respect to plastic waste.

After collection, the marine plastic waste is transported to the pyrolysis plant, assumed to be located either within or very close to the port. This proximity minimizes transportation requirements for the feedstock, streamlining the delivery process. At the pyrolysis plant, the waste undergoes processing via pyrolysis, following the methodology described in previous sections. The environmental impacts of each output stream are then calculated using specialized software, ensuring a comprehensive analysis of the system's sustainability.

The figure below, shows the simple schematic of the process. The steps followed in OpenLca software is similar to these schematics.

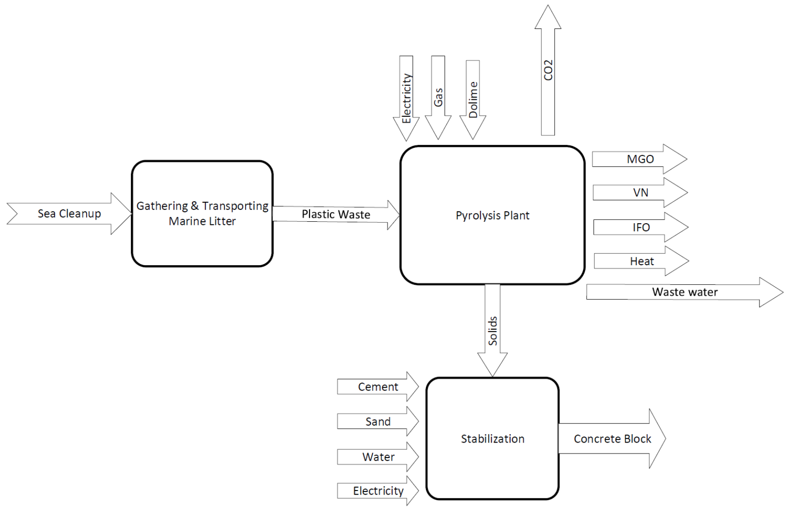

Figure 5.4: Pyrolysis process steps

Almost all streams required for modeling the process in OpenLCA were derived from mass and energy balance calculations. However, the fuel consumption for the ship used to clean up the sea was not available. No specific data, datasets, or research were found to provide this value. To estimate it, research papers analyzing fuel use in fishing activities were reviewed. A metric called "fuel use average," measured in kilograms of fuel per ton of landed fish, was identified. While the study did not specify the exact activities included, the average value for trawling fishing activities was used as an approximation. This choice was made because trawling somewhat resembles the sea cleanup operation, making it a reasonable proxy for the estimation [7].

After inserting all of the necessary streams, the processes were formed. Due to unavailability of Dolime ($CaO+$ MgO), this stream was created by adding lime and Magnesium Oxide together. Furthermore, it was decided to also include water and soda to the pyrolysis process as well, to improve the accuracy of LCA. The providers for each of the streams were set from Italy, and if Italy was unavailable Europe option were used.

The pyrolysis process has one main product and 4 co-products. Allocation were done based on energy. This was done in order to include the recovered heat in the calculations as well. In table below the values for allocations are reported.

Output	Value
MGO	0.45
VN	0.2
IFO	0.055
Solids	0.105
Pyro heat	0.19

Table 5.28: Product and co-products allocations

Finally, the processes were connected and added to a product system. The sankey diagram below shows the results of the system for Global Warming Potential (GWP), for the case of fossil.

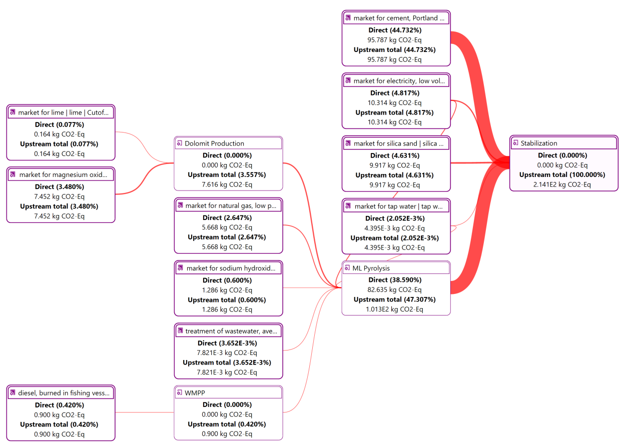

Figure 5.5: LCA sankey diagram

The results indicates that both pyrolysis process and cement used for stabilization are the main contributors. The amount of 214 kg CO_2-Eq were obtained for the whole process. Considering the plastic feed is 1 ton, the value of 0.214 kg CO_2-Eq per 1 kg of waste marine plastic is obtained. This value clearly shows a potential compare to operations such as municipal incineration and open burning which have a value in range of 2.3 to 2.5 kg CO_2-Eq per 1 kg of mixed waste plastics.

5.5.1 Challenges and Further Improvement

The overall LCA, while highlighting certain aspects of the process's environmental impact, does not provide a comprehensive assessment of its environmental viability. Specifically, no results are available for the impact assessment of MGO, the primary product of the process. Such an assessment could serve as a valuable comparison between MGO produced through the pyrolysis of marine litter and that derived from conventional fossil sources. Additionally, the environmental impact of removing marine litter from the seas remains unaddressed. Several reasons prevented the completion of an in-depth environmental analysis, which are summarized below:

Diverse Product Outputs: Since pyrolysis generates three products, each requiring a separate environmental analysis, assessing all outputs comprehensively would demand extensive resources and is outside the scope of this work, especially if it is considered that all three of these products can serve as fuel.

Carbon Storage Potential: The role of concrete in storing carbon after stabilization adds complexity, as its environmental benefits could offset some of the process impacts, but this has not been sufficiently studied.

Uncertainties in Key Parameters: The lack of detailed information on cleanup operations (e.g., vessel type, operational distance) and the variability in marine litter composition introduces significant uncertainty into the analysis.

Lack of Established LCA: The absence of dedicated LCA studies for marine litter makes it difficult to benchmark this process against others or validate the results.

These challenges can be addressed in future works, serving as a follow-up to this study. Such studies would build upon the foundation laid by this work and provide a more holistic view of the process's environmental viability.

Chapter 6

Conclusion

This study explored the potential of using marine litter as a source of alternative maritime fuels through pyrolysis. The policy framework analysis highlighted a strong push towards ocean cleanup initiatives, with programs like Fishing For Litter (FFL) becoming more widespread and mandatory for fishers in European waters. Additionally, policies aimed at decarbonizing the maritime sector target an 80% reduction in carbon emissions relative to 2020 levels by 2050. Multiple alternative fuels have been proposed to help the maritime sector achieve these goals.

The literature review on plastic pyrolysis revealed that this process is well-suited to handling challenging mixed plastic wastes similar to marine litter. The oil derived from pyrolysis shows characteristics that closely match marine fuel standards, though certain factors, such as flash point, prevent it from being a true drop-in fuel. Comparing previous studies with a potential marine litter composition, this study identified both opportunities and challenges related to marine litter as a feedstock. Marine litter contains high levels of polyethylene (PE) and polypropylene (PP), which are highly suitable for pyrolysis. However, it has relatively low levels of polystyrene (PS), which, although it yields high oil output, also contributes to aromatic compounds that are less desirable in marine fuels. A challenge arises in the presence of PVC, PET, and PA, particularly when litter is collected from the seabed, as these denser plastics often settle there. Therefore, surface or beach cleanups, where seawater naturally separates some plastics, are more desirable.

Analyzing the quantity and composition of marine litter revealed that, while substantial amounts of marine litter are present in the environment, cleanup efforts are often on a much smaller scale. Based on available data, removal capacities of approximately 300 tons/year and 3000 tons/year are feasible with current cleanup efforts. Accounting for non-plastic items, this translates to pyrolysis capacities of around 180 tons/year and 1800 tons/year of plastic waste.

Heat and mass balance calculations were conducted for these two capacities, drawing on current studies of feedstock compositions similar to marine litter. Four case studies were developed to represent different compositions of marine litter. The theoretical heat and mass balance calculations indicated that over 60% of the feedstock mass is recoverable as valuable products. The yield of marine gas oil (MGO), the primary product for maritime fuel, ranged from 20% to 35%, with a significant amount of high-heating-value gas also produced, which can self-sustain the process. The energy balance showed that the energy from the gas could fully cover the process requirements. Over 80% of the energy value in the process was recoverable as valuable products, with oil-based energy dominating across all cases and capacities, ranging from 71.9% to 55.36%. After distillation, the energy yield of MGO ranged from 30% to 40%, while virgin naphtha, the second most valuable product, ranged from 13% to 17%.

To address the limitations of the experimental heat and mass balance settings, an industrial-scale pyrolysis process was designed. This design recognized the operational impracticality of fully relying on the gas for process energy, necessitating a certain amount of natural gas to initiate the process. Additionally, excess heat from the process was utilized for district heating to improve energy recovery. The energy and mass balance analysis showed that despite considering losses and inefficiencies, the energy recovery can still remain high thanks to using amounts of pyrolysis gas within the process itself and by recovering heat, still high value of energy is recoverable.

An economic analysis of the designed pyrolysis process for both capacities indicated that, at 180 tons/year and 1800 tons/year, producing MGO is not profitable. However, the analysis also showed a significant decrease in production costs as capacity increases, suggesting that higher capacities could potentially yield market-competitive products.

Finally, LCA results of the whole process reported value of 0.214 kg CO_2-Eq per 1 kg of waste marine plastic in such process, which compare to processes like incineration is much more lower.

Future research should build upon this project by conducting an economic analysis of marine plastic pyrolysis processes at higher capacities, which could provide insights into their scalability and profitability. Additionally, a detailed environmental assessment of the primary pyrolysis products would help compare their environmental impact to that of other potential fuels. Finally, innovative approaches, such as integrating the pyrolysis process into ships, should be explored. Cleanup vessels could convert marine litter into fuel onboard, or cruise ships could adopt this technology to reduce their environmental footprint while at sea.

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