

# Article Municipal Plastic Waste Recycling through Pyrogasification

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**Abstract:** Conventional mechanical recycling technologies cannot recycle all types and amounts of generated plastic waste. Pyrolysis can convert these municipal mixed plastic streams into products with significant calorific value, which are likely to be used as energy sources. The present work describes a technology used to expand the portfolio of technical approaches to drive plastics circularity, i.e., thermochemical recycling. A base case scenario considered a capacity of 1.000 kg/h of municipal plastic waste, consisting of a mixture of polypropylene (PP), polystyrene (PS), polyethylene (PE), and plastic associated with paper, which were converted into non-condensable gases, oil, and char through a pyrogasification system. Based on mass and energy balances and experimental data from the literature, a total of 199.4 kg (48 MJ/kg) of liquid fuel and 832.85 kg (16 MJ/kg) of gas could be obtained with no need for external heating sources. The thermal requirement for the pyrolysis of 1.000 kg of municipal plastic waste (1.316 MJ) was supplied by the gasification of a fraction of the produced pyrolysis oil and gases. This feasibility analysis confirmed the technical adequacy of the proposed technology, which that will be further complemented by a technoeconomic study of the proposed solution.

Keywords: municipal plastic waste (MPW); pyrogasification; chemical recycling; green fuel

# 1. Introduction

Social and industrial advancement, together with the increase in population, are key driving factors in the current challenges related to waste management. A total of 29.7 million tons of municipal solid waste (MSW) was produced in Italy in 2021. Landfills received about 22% of MSW, which contained 25% of food waste, 12.5% of paper and cardboard, 8% of glass, and an approximate quantity of 1.7 million tons of plastic waste [1]. Plastics have represented a widely spread commodity during the last 50 years due to their specific properties, such as their low conductivity, density, weight, and cost, transparency, and high durability [2]. Thanks to these properties, they are heavily used (pure or with additives as plasticizers and stabilizers) in various sectors, such as household [3], industrial [4], agricultural [5], or medical, where the outbreak of the coronavirus has led to a dramatic increase in single-use plastics such as protective hospital suits, gloves, face masks, or product containers [6].

Plastic waste, very stable against degradation, has become a major environmental problem threatening landfills and aquatic life and increasing air and marine pollution. By 2050, it is estimated that plastic will be more abundant than fish in the oceans [7]. Moreover, it has been proven that microfragments of plastics (microplastics), blown into the oceans and degraded because of sunlight or waves, are now capable of effecting our nutrition intake through marine life as well as through the soil and crops [8,9]. Indeed, roughly 51 trillion microplastics, mainly from synthetic textiles or packaging products, are floating in the sea and can be consumed as sea food by marine animals [10]. A sustainable plastic waste-management strategy should adopt as its primary option the



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). application of the reduce, reuse, and recycle mindset, as per the European Waste Hierarchy [11], followed by energy recovery strategies, and lastly, landfilling [12]. In 2021, 36% of the total plastic waste generated in Italy was recycled, 21% was addressed for energy recovery, and 43% released to the environment or stored in landfills [1]. A lack of a complete post-consumer infrastructure, incorrect dumping techniques, or inadequate legislation are factors influencing the high values of unmanaged waste [13]. In this context, the European Union (EU) has adopted the target of reducing the landfilling of waste to 10% by 2035 [14]. The necessity of developing new and improved complementary plastic waste-management strategies, introducing modern and advanced technologies, arises as a crucial element in the accomplishment of this objective. Also, the growing use of bioplastics (i.e., plastics which are either biomass-based, biodegradable, or feature both properties as defined by the European Bioplastics Organization), despite their management currently posing uncertainties that need to be further studied, could help in minimizing fossil fuel plastic amounts.

Chemical recycling arises as an optimal option for this second material waste, as highlighted in the newly developed waste-to-x (WtX) strategy [15]. Pyrolysis is attracting a great deal of scientific attention as a process able to convert plastics into fuels or new valueadded products. One of the most recent and in-depth published works on the pyrolysis of plastic waste has highlighted the lack of commercial-scale units and identified the main challenges that this technology is facing [16]. First, plastic waste is an extremely complex feedstock, with an inconsistent feed quality—highly dependent on the efficiency of the separation steps from other solid wastes-and quantity, and a limited availability of quality plastic [12]. Chemical properties are heterogeneous and lead to complex kinetics reactions, making their up-scaling difficult. Also, their elemental composition (i.e., the presence of oxygen, chlorine, nitrogen, etc.) can result in toxic pollutants if the reactions are not well controlled [17]. In addition, a large amount of energy is required to achieve the full conversion of plastics, which impacts the cost balance of the process. Catalysts can be used to accelerate these mechanisms, although they can face difficulties due to the formation of coke and the consequent catalyst deactivation [18]. Alongside technical challenges, financial barriers, ambiguous legislation, and uncompetitive marketing strategies hinder the full implementation of the pyrolysis of plastics [19].

In this framework, the main aims of this work are to shed light on opportunities for the valorization of plastic waste to produce fuels and, based on the current scientific limits, to propose a strategy for a waste-to-fuel scenario, applied to the specific case of the Italian regions of Genoa, Savona, and southern Piedmont, accounting for one million inhabitants.

#### 2. Fundamentals on Pyrolysis

The pyrolysis of plastics is a complex chemical route that consists of breaking the polymer carbon chain at high temperatures (400–900 °C) in the absence of oxygen, preventing the formation of dioxins and reducing the formation of carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) [20]. The long polymeric chains break down into shorter hydrocarbons of lower molecular weight to produce a gaseous stream, including condensable and non-condensable gases and char, with a distribution of products dependent on the applied conditions [21]. The transformation route is a multi-step reaction scheme, highly dependent on the initial feedstock, starting with an initial random chain scission forming unstable secondary compounds, followed by a propagation step to form smaller chains, and ending with a termination step in which free radicals recombine or the hydrocarbon chain breaks [22].

The gaseous product mainly contains  $H_2$ ,  $CO_2$ , CO, and  $CH_4$ , along with trace amounts of other lighter hydrocarbons, including ethane ( $C_2H_6$ ), ethylene ( $C_2H_4$ ), propane ( $C_3H_8$ ), propene ( $C_3H_6$ ), butane ( $C_4H_{10}$ ), and butene ( $C_4H_8$ ). The solid product, char, has various applications as solid fuel in energy applications, soil amendment, catalyst support, or absorbent of heavy metals or emergent contaminants in water treatment for cosmetic and pharmaceutic industries [23]. Finally, condensable gases can condense and form a wax/oil, which generally contains hydrocarbons in the range of light and heavy crude oil, middistillates, and naphtha. The light oil, with a boiling point of 250–350 °C, is made up of olefins and paraffin. In contrast, heavy oil, containing olefins, paraffin, aromatics, and high-molecular-weight components, has a boiling point of more than 350 °C [24]. This fraction of oil can be used as a liquid fuel, as a precursor for jet fuels, or as a raw material for chemicals [25].

As stated in the Introduction, the distribution of pyrolysis products is highly dependent on the applied reaction conditions and can vary with the properties of raw material (see Section 2.1), type of reactor (see Section 2.2), and applied operational conditions such as temperature, residence time, heating rate, or the presence of catalysts (see Section 2.3). On the other hand, if well-controlled, pyrolysis can be a flexible technology whose operating conditions can be optimized to maximize the production of a targeted product.

#### 2.1. Properties of Feedstock: HDPE, LDPE, PP, PS, PET, PVC

Plastic waste streams are mainly composed of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and combinations of other plastics [26]. It is necessary to achieve a good degree of knowledge of their chemical, physical, and thermal characteristics to design an efficient process. Properties such as the proximate analysis, ultimate analysis, higher heating value (HHV), cracking temperature, and degradation profiles will define the outputs of reaction. Table 1 contains a summary of averaged values for the proximate and ultimate analysis and HHV for single plastic wastes, together with a mixture of domestic plastic [27].

The proximate analysis defines the composition of plastic waste as its percentage of moisture (M), volatile matter (VM), fixed carbon (FC), and ash (A). In general terms, this waste presents high volatile and very low ash contents. This suggests a high suitability of plastics for pyrolysis [28], with high liquid and gas yields, a low quantity of char (due to the low fixed carbon content), and no need of drying before treatment (due to the low humidity content). When the composition of single plastics is compared with real domestic waste, it can be observed that the residual carbon and ashes of the latter increase with respect to most of the single materials, which indicates that domestic waste is a more complex feedstock which can contain additional compounds in its chemical structure.

| Plastic Waste | Proximate Analysis<br>(wt% <sup>1</sup> ) |      |     |     | Ultimate Analysis<br>(wt% <sup>2</sup> ) |      |                |     |     | HHV<br>(MJ/kg) |         |      |            |
|---------------|---|------|-----|-----|--|------|----------------|-----|-----|----------------|---------|------|------------|
|               | Μ   | VM   | FC  | Α   | С  | Н    | O <sup>3</sup> | Ν   | S   | Cl             | Ref     |      | Ref.       |
| HDPE          | 0.2                                       | 99.1 | 0   | 0.6 | 86.0                                     | 13.8 | 0.1            | 0   | 0.1 | 0              | [29,30] | 44.6 | [29,31–33] |
| LDPE          | 0   | 99.5 | 0   | 0.5 | 86.1                                     | 13.9 | 0              | 0   | 0   | 0              | [34,35] | 45.5 |            |
| PP            | 0.1                                       | 95.3 | 0.8 | 2.7 | 83.8                                     | 14.4 | 0.1            | 0.3 | 0.9 | 0.5            | [29,36] | 45.6 |            |
| PS            | 0   | 99.7 | 0.3 | 0   | 91.1                                     | 8.2  | 0.4            | 0.1 | 0.2 | 0              | [37,38] | 41.5 |            |
| PET           | 0   | 89.5 | 8.5 | 0   | 63.6                                     | 4.1  | 32.3           | 0   | 0   | 0              | [29,39] | 22.8 |            |
| PVC           | 0   | 95.5 | 4.6 | 0   | 38.5                                     | 4.6  | 0              | 0.1 | 0.3 | 56.5           | [40,41] | 20.1 |            |
| Domestic      | -   | 93.4 | 5.3 | 1.2 | 84.4                                     | 12.4 | 0.1            | 2.7 | 0.4 | 0              | [27]    | 40.4 | [27]       |

Table 1. Composition of plastic and domestic waste.

<sup>1</sup> dry basis; <sup>2</sup> dry ash-free basis; <sup>3</sup> by difference.

The plastics' elemental composition is described through the elemental analysis. They are mainly composed of carbon and hydrogen, with low levels of oxygen, nitrogen, or chlorine. The latter are undesired elements as they can generate NOx, SOx, or HCl [42]; thus, a specific solid pre-treatment and gas treatment section will be needed to ensure safe and clean reactions. Although the high C and H content make plastics an excellent candidate for pyrolysis, their relative ratio (H/C) impacts on the energy efficiency and, consequently, on the exhaust emissions of CO and CO<sub>2</sub> [43]. The elemental composition also defines plastics' HHV as low oxygen contents result in high heating values [44]. This

would suggest that plastics with high HHV, like LDPE or HDPE, will produce oils with higher HHVs. According to their elemental composition, the most suitable plastics for pyrolysis can be identified as HDPE, LDPE, PS, and PP thanks to their high C and H content and low N, S, and Cl. PET is less suitable due to its high O content and PVC is the least suitable material as per its low C and H and high Cl contents.

It is also important to consider pyrolysis products, such as PET which can release benzoic acid, or the condensed terephthalic acid that can result in pipe clogging and problems of corrosion [45], and the already-cited undesired emissions due to the decomposition of PVC in the form of chlorinated gas [42].

Finally, the thermal degradation of plastics depends on their chemical composition and structure. Polymers with linear chains or with little or no crosslinking, like polyesters, present higher cracking temperatures ( $T_c$ ) compared to polymers that are more easily degraded due to defects in their structure. That is the case for PVC ( $T_c$  from 250 °C) [46], wherein its chlorine atoms create thermally liable defect molecules [47]. Cracking temperatures range from 300 °C (PP [48]) to 380 °C (PET [39]), whose similar degradation conditions benefit pyrolysis reactor design.

In summary, HDPE, LDPE, PS, and PP can be identified as the most suitable plastics for pyrolysis due to their physicochemical, chemical, and thermal properties. For the discussed case study (Section 3), the mixture of plastic waste will mainly contain these plastics, together with low amounts of PVC and PET (6%wt), as they are present in the municipal waste plastic recycled stream. Special attention will be given to the described potential difficulties during the design of the whole system.

#### 2.2. Reactors

An adequate selection of technology is key to achieving optimal oil yields. Significant research has resulted in the development of different pyrolysis systems such as fixed beds [49,50], moving beds [51], fluidized beds (such as bubbling [52], circulating [53,54], and spouted reactors [55]), auger [56], and rotary kilns [57,58], which can be operated in batch and semi-batch [59] or continuous mode [56]. Diverse scales can be found in the literature, although the great majority of systems are still at lab scale and some at pilot scale [16], with scarce applications at the industrial level [17,60].

As described in high detail in [61], the research on reactors for slow and fast pyrolysis has been growing steadily over the last 30 years. The decision regarding the applied reactor will lay mostly on economic trade-offs and the specific target products. Table 2 gathers the distribution of products resulting from the pyrolysis of waste plastics using different pyrolysis reactors.

**Table 2.** Distribution of products from the pyrolysis of plastic waste (G = gas; L = liquid; W = wax) using different reactors [62,63].

| Feedstock         | Fixed Bed—Batch  | Fluidized Bed                  | Spouted Bed                      | Moving Bed      |
|-------------------|--|--------------------------------|----------------------------------|-----------------|
| Plastics from MSW | G 25, L 34, W 6 G 28.5, L 36.5 G 19.6, L 37.6, W 7.8 G 26.6, L<br>Inerts 28, Char 5, Ash 2 |                                |                                  |                 |
| Plasmix           | G 32, L 43, W 12   | G 36, L 46, W 5<br>Inerts 6; C | G 30, L 49, W 8<br>Char 5; Ash 2 | G 34, L 45, W 8 |

Since the considered feedstock has a high content of inerts (approximately 30%wt), it is necessary to individualize the best reactor, which will avoid mixing or the creation of suspended particulates. Batch pyrolysis is discarded due to its low productivity. A moving bed reactor is chosen with the aim of easily sprinkling the material with substances that counteract the negative effects linked to the presence of chlorinated plastics during the deposition phase [64].

In addition, pyrolysis is an energy-intensive process and efficient heating methods are needed to achieve high mass and heat transfer phenomena within the reactor. Electric heating is the most-used heating method supplied to a furnace, burner, or heater around the reactor, but its high operating costs mean that it is not suitable for large scale applications. Recycling high-temperature gases promotes a self-sustained system and can keep the costs within a reasonable range. Several technologies have been developed based on a pyrolysis-gasification chemical scheme [65,66], where pyrolysis is the main chemical reaction defining the target products and the gasification of pyrolysis gases provides the energy to the system necessary to achieve a self-sustained reaction.

## 2.3. Operational Conditions

Beyond the type of reactor, process conditions like temperature, heating rate, residence time, presence of catalyst, and feedstock (single/mixed plastics or addition of other components as biomass) have a significant role in the final oil yields.

Temperature is without a doubt the most influential parameter as it governs the thermal degradation of plastic waste. As previously mentioned, the action of heat decomposes the long polymer chains into shorter ones with the release of free radicals. These facilitate plastics degradation through mechanisms such as depolymerization, chain scission, and side-group elimination [67]. The applied temperature will define the degradation of plastics and, consequently, the distribution of products (i.e., gas, liquid, solid). In general, higher temperatures will lead to high oil yields below the cracking temperature, while gas will be produced preferentially over this temperature. The optimal pyrolysis temperature will differ from one system to another as it is highly dependent on the quality and composition of the feedstock, as discussed in Section 2.1.

Heating rate, defined as the rate in which temperature increases inside the reactor, and residence time, defined as the time in which feedstock is inside the reactor until the target temperature is reached, impact on the mass and heat transfer phenomena within the reactor and, consequently, on the distribution of products [68]. Low-to-moderate heating rates (5–100  $^{\circ}$ C/min) or moderate residence times (15–200 min) promote the production of oil with relatively low yields of char and gas, while higher heating rates or shorter residence times result in increased char yields.

Catalysts can play a vital role in pyrolytic reactions as they can lower the activation energy, which results in lower pyrolysis temperatures and energy requirements and can also influence the distribution of products by favoring the selectivity towards target products [69]. The use of numerous catalysts can be found in the literature as zeolites and zeolites-based compounds (i.e., ZSM-5, H-ZSM-5, spent fluid catalytic cracking catalyst [70,71], Zn-ZSM-5 [72], and natural zeolites [73]), metals (i.e., magnesium oxide [74], copper carbonate [75], nickel-based [76], zinc [77], and sulphated zirconia [78]), or minerals (i.e., kaolin [79], iron-pillared clay [80], and dolomite [81]).

#### 3. Case Scenario

#### 3.1. Input Data

The presented case study considered the Italian provinces of Genoa, Savona, and southern Piedmont (accounting for a population of one million people), where 500,000 tons of waste were produced in 2019 (https://www.isprambiente.gov.it/en, accessed on 10 January 2024). Among them, 220,000 tons of waste were not efficiently managed, representing a significant and valuable source for waste-to-fuel strategies. A quantitative study was conducted to evaluate the feasibility of the use of 1000 kg of this waste in a technology based on an auto-thermal pyrogasifier. The designed system is proposed as a suitable technology able to surpass all the current technological challenges, broadly described in Section 2. The presented analysis aims to demonstrate the benefits of a well-designed plastic waste-management strategy in producing gas and liquid fuels with high calorific values, obtained using a thermally auto-sustained system.

Table 3 gathers the initial feedstock composition. PET and PVC, even though not highly performant due to their properties (Section 2), were included in the study to approximate the considered input to the real treated stream. A pre-treatment section is

first considered to submit plastics to an initial conditioning to obtain adequate solids dimensions (20–40 mm). A treatment with adsorbents such as  $Na_2CO_3$  or  $CaCO_3$  is needed to capture HCl and remove chlorinated compounds before any action [82], and slagging phenomena due to the softening of plastics at high temperature are expected to be avoided. Also, the presence of waste recycled paper (containing kaolin) is expected to act as a catalyst for the pyrolysis reaction, (see Section 2.3). The obtained briquettes then pass through an alignment section, are introduced into a loading chamber, subjected to a weak vacuum, and rendered inert with nitrogen.

| Component  | Weight (kg) | HHV (MJ/kg) | Energy (MJ) |
|--|-------------|-------------|-------------|
| Mixed plastic waste:   |             |             |             |
| <ul> <li>LDPE and HDPE = 35 wt%</li> <li>PP = 40 wt%</li> <li>PS = 19 wt%</li> <li>PET = 5 wt%</li> <li>PVC = 1 wt%</li> </ul> | 600         | 42          | 25.200      |
| Plastic associated with paper  | 167         | 35          | 5.845       |
| Glass and inerts   | 180         | -           | -           |
| Metals (Al,)   | 53          | -           | -           |
| Total  | 1000        | 31.045      | 31.045      |

Table 3. Composition of input plastic waste stream [63].

#### 3.2. Description of the Technology

The proposed technology, currently in an advanced design stage, requires temperatures in the pyrolizer between 430 °C and 480 °C in the absence of air and in a controlled atmosphere. The thermal input for these pyrolytic reactions is provided by the partial recovery of the thermal energy contained in the mixture of gases and vapors exiting from the subsequent gasification section.

The system (represented in Figure 1) can be modulated into sections, all identical, equipped with a pyrolizer with a loading and unloading system; a gasifier; gas cleaning and reduction of temperature (with heat recovery) sections; and a gas separator from condensates. The possibility of operating in a modular configuration allows us to equip the system for flexible waste flow rates and it also permits us to continue working in the plant in the event of faults or ordinary and extraordinary maintenance works and to do so without influencing the production rate. The process is controlled via an in-line analysis to detect the produced gases and vapors to allow us to constantly control of the gasification agent (air, oxygen, or water vapor), to quantify the possible presence of dust, tar, and acid compounds, and, if needed, to adapt the successive gas cleaning section.

Plastic waste (1) is introduced into a hopper and sent for pyrolysis. The pyrolizer is placed horizontally and has a moving belt where solids are transported at a controlled speed which defines the residence time. The reactor can be easily adjusted depending on the plastic components and decomposition profiles by modifying the speed of the moving belt. It is also expected that the production of dust is minimized using this type of reactor. The indirect heating of the pyrolizer can be easily achieved via radiation through a series of tubes, located on the external perimeter of the reactor, through which high-temperature gases can flow (Figure 2).

The pyrolizer is heated by the syngas and vapors coming from the gasifier, after passing through a cyclone for an initial dedusting. The solid post-pyrolysis residue, char, is discharged into a special tank, while the pyrolysis gases are introduced into the gasifier for the subsequent thermal treatment. The syngas coming out of the cyclone is partly used to heat the pyrolizer and partly sent directly to the cooling section, composed of a gas–water exchanger from 600 °C to the temperature of condensation of oils, keeping the waxes liquid, with an energy recovery step. The cleaning section is composed of a scrubber, whose wastewater is collected in a filtering tank and reintroduced into the scrubber, and bag

filters, and the gas finally is stored in a ballon to be introduced into the methane pipeline. The liquids are collected in a settling tank, cleaned by filtration, and possibly subjected to separation via centrifugation depending on the final use. The ash from the gasifier and the dust collected by the cyclone are periodically removed and kept for other applications as sintered granules. The process flow diagram is shown in Figure 3.



Figure 1. Scheme of the pyrogasifier system.



Figure 2. Irradiating tubes for indirect heating.

The thermal energy required for the pyrolysis, 1.316 MJ for 1 kg of plastic waste [83], is supplied by the gas obtained in the gasification of pyrolysis products in an entrained flow gasifier. The produced gases flow through 13 tubes, 7 m in length, located at the external wall of the pyrolizer, to heat the system at the reaction temperature. Pyrolysis reactions occur at a fixed temperature, in the range 450–480 °C, in the absence of air and in a controlled atmosphere. This temperature is set to maximize oil/was yields, according to

the current literature [63]. The gasifier is pre-heated by part of the condensed, filtered, and clean pyrolysis oils, at a maximum temperature of 900 °C. The system is completed with a gas treatment section (scrubber and filters), storage tanks for pyrolysis products (solids and oils), and a gas holder. The modular characteristic of the system permits us to adapt the system to the available quantity of plastic waste and/or to periodic or extraordinary maintenance. The process design incorporates flow indicators to measure the gas flows and temperature control indicators to regulate the heating rate and to ensure that the determined cracking temperature is reached.



Figure 3. Process flow diagram for the pyrogasification process.

#### 3.3. Definition and Quantification of Products

Initial design calculations, based on mass and energy balances, together with the available literature data [62,63] and the results from experimental activities using processing waste on the pilot plant ERPICE (assuming that they are transferable, to a great extent, to heterogeneous waste or single-use plastics that are easy to clean) (https://www.sintesimastermind.it/portfolio-items/progetto-erpice/?portfolioCats=45, accessed on 10 January 2024), were used initially to quantify the potential products of the described plastic waste using the designed pyrogasifier. Table 4 shows the calculated composition of the gas produced in the final gasification stage from an input feedstock of 1000 kg.

Table 4. Composition of the produced gasification gas from an input of 1000 kg.

| Component         | Volume (Nm <sup>3</sup> ) | % vol | Weight (kg) | HHV (MJ/kg) | Total Energy (MJ) |
|-------------------|---------------------------|-------|-------------|-------------|-------------------|
| H <sub>2</sub>    | 152                       | 19    | 13.6        | 120         | 1.632             |
| CO                | 138                       | 18    | 172         | 10.05       | 1.729             |
| CO <sub>2</sub>   | 44                        | 6     | 86.4        | 0           | 0                 |
| $CH_4$            | 19                        | 2     | 13.6        | 50          | 680               |
| $C_2 - C_6$       | 99                        | 13    | 188.5       | 50          | 9.425             |
| $C_5-C_9$         | 41.5                      | 5     | 160         | 47.8        | 7.648             |
| $C_{10} - C_{13}$ | 5.5                       | 1     | 39.4        | 49          | 1.931             |
| N <sub>2</sub>    | 287                       | 37    | 359         | 0           | 0                 |
| Total             | 786                       | 100   | 1032.25     |             | 23.045            |

This gaseous fraction is then cooled to obtain a condensed product (fractions  $C_5$ – $C_9$  and  $C_{10}$ – $C_{13}$ ) together with the non-condensable gas fraction (Table 5). The energy efficiency, calculated as the input energy contained in the waste plastic stream related to the output energy obtained from condensable and non-condensable products, is equal to 74%.

Table 5. Quantification of non-condensable and condensable products of the pyrogasifier.

|                     | Weight (kg) | Energy (MJ) |
|---------------------|-------------|-------------|
| Non-condensable gas | 832.85      | 13.466      |
| Condensed product   | 199.4       | 9.579       |

Energy balances were applied to calculate the energy requirements of the pyrolysis reaction and the sources of energy present in the system to satisfy them. The thermal energy needed to pyrolyze 1000 kg of plastics, that is, 1.316 MJ [83], together with the energy required by the system utilities (compressors, blowers, etc.) is supplied by the energy provided by the gasification of two sources: a fraction of the produced pyrolysis oil (HHV = 48 MJ/kg) and the pyrolysis gases (Cp = 2.56 KJ/kg·K, based on product gas distribution).

In summary, Figure 4 contains the overall scheme of the process. A total of 199.4 kg (48 MJ/kg) of liquid fuel and 832.85 kg (16 MJ/kg) of gas can be obtained from the pyrogasification of 1000 kg of mixed plastic waste (and 32 kg/h of air for the gasification stage). In energy terms, the system is auto-sustained thanks to the thermal energy supplied by the gasifier, which covers the thermal energy required for pyrolysis reactions (366 kW), with, consequently, no need for external heating sources. If these figures are applied to the initial case scenario (220,000 tons of plastic waste for a population of 1 million people), the following conclusions can be drawn:

- A total of 183.227 tons of green gas (calorific value of 16 MJ/kg (corresponding to 0.0044 MWh/kg)), which can generate 0.81 million MWh, providing 44% of the initial thermal energy contained in the feedstock. Methane's heating value is 40 MJ/m<sup>3</sup> [84], equivalent to 0.0111 MWh/m<sup>3</sup>, which correspond to 73 million m<sup>3</sup> of methane. Considering that a family composed of 2.3 people (https://www.istat. it/en, accessed on 10 January 2024) consumes 1400 m<sup>3</sup> of methane in one year (https://www.arera.it/en, accessed on 10 January 2024), the production of green gas would satisfy the annual methane need of 120,000 inhabitants.
- Approximately 43.9 thousand tons of liquid green fuel are generated, which can provide 0.57 million MWh, representing 30% of the initial thermal energy in the feedstock. If the produced liquid has a density equal to that of diesel, 0.85 kg/L [85], a total of 52.6 million liters can be produced, corresponding to the consumption of over 47,000 cars (for approximately 70,000 inhabitants) traveling 20,000 km per year at 18 km/L (estimated from https://www.quattroruote.it/magazine/, accessed on 10 January 2024)

The use of the proposed pyrogasifier could be also combined with bi-fuel endoscopic engines that could allow for an overall electrical efficiency of 40% (https://www.man-es.com/, accessed on 10 January 2024), higher than the current waste-to-energy plants that produce steam, which have a maximum overall electrical efficiency of 27% [86]. In addition, metallic products and char could be recovered from the waste stream to be used in the production of advanced materials or as fillers for ceramic composite materials, or the unsaturated hydrocarbons could be re-polymerized to produce new recycled plastics, thus closing the loop in a true cyclical economy.



Figure 4. Mass balance of the pyrogasification of plastic waste.

#### 4. Conclusions

Conventional mechanical recycling technologies cannot recycle all the types and amounts of generated plastic waste. Pyrolysis can convert these municipal mixed plastic streams into products with a significant calorific value, which are likely to be used as energy sources. The quality of these fuels is greatly affected by the composition of the feed, the reactor, and the applied operational conditions, and the correct design of the thermo-chemical technology is crucial to achieving optimized yields.

The present work described a technology to expand the portfolio of technical approaches to drive plastics circularity, e.g., chemical recycling. The feasibility of a novel municipal plastic waste pyrogasification system for the sustainable production of fuel oil was verified. A base-case scenario considered a capacity of 1000 kg/h of municipal plastic waste, consisting of a mixture of PP, PE, PS, and plastic associated to paper, which were converted into non-condensable gases, oil, and char. A total of 199.4 kg (48 MJ/kg) of liquid fuel and 832.85 kg (16 MJ/kg) of gas could be obtained in an auto-sustained system, which did not need external heating sources as the thermal requirements (1.316 MJ for 1000 kg) were supplied by the gasification of a fraction of the produced pyrolysis oil and gases.

As numerical perspectives applied to the initial case scenario (220,000 tons of plastic waste for a population of 1 million people), the obtained green gas could satisfy the annual methane needs of 120,000 inhabitants, and the produced liquid fuel could correspond to that consumed by over 47,000 cars.

This initial feasibility analysis confirmed the technical adequacy of the proposed technology, which will be complemented by a technoeconomic study of the solution.

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