Exergoeconomic Analysis and Optimization of Solid Waste Treatment Plants with Uncertainty inclusion

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Exergoeconomic Analysis and Optimization of Solid Waste Treatment Plants with Uncertainty inclusion

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Summary

Solid Waste Management (SWM) is still a crucial issue for European countries, being strongly influenced by heterogeneous factors (i.e. social, political, technological, economic). The general objective of the present work is to use exergy criteria to assess the resource utilization into the Solid Waste (SW) treatment systems, including multiple scenarios and conflicting objectives. To include the systemic uncertainties, stochastic tools are adopted for generating simulation scenarios. The instruments of Exergoeconomics are used since exergy is considered a rational basis to compare flows of different nature. In a system-based analysis, a typical kerbside collection system is modelled and the influence of design and external variables on SW collection cost is evaluated. Then, an Exergoeconomic analysis of a Mechanical Biological Treatment (MBT) of unsorted Municipal Solid Waste (MSW), for Solid Recovered Fuel (SRF) production is performed. The primary sources or irreversibility are linked to material losses in the pre-screening phase (70% of the global input exergy). A crude Monte Carlo method is then used for reproducing the randomness in unsorted waste composition. The equipment energy consumption is considered as the internal uncertain variable. The results show the capacity of the system to dampen the fluctuations and confirm the primary influence of the external uncertain variables over the internal ones (RStD values about 90% lower). The analysis is then extended by including paper and plastic recycling chains. The concept of Embodied Exergy (EE) is used to account for the avoided or additional exergy in different scenarios of SC. In general, the system shows a good degree of self-regulation, even if savings in EE diminish for high SC, because of the influence of SW transport and alternative fuel supply cost. Three exergy-based indicators, i.e. the Global Exergy Efficiency (GEE), the Additional Exergy Indicator (AEI) and the Exergy Scenario Comparison (ESC), are developed for comparing different recycling scenarios. Moreover, a Multi-Objective Functions (MOFs) Optimization between the GEE and the total monetary cost is performed for seeking the best trade-off solutions; the optimization variables are linked to the amount of recycled materials. In general, the values of exergy-based indicators confirm the advantage of having recycling options for a better use of resources with respect with the no-treatment case. The additional exergy investment for recovering the input waste

internal chemical exergy amounts to about 3.21% for transport and 6.22% for recycling, expressed as a percentage of the total invested exergy. The output solutions from MOFs optimization show a series of trade-off points, even if higher monetary costs are associated to total recycling options. In a specific material-based view, exergy is also used for comparing the resources invested in producing polymers from primary material with those from secondary materials through recycling. The production routes of nine polymers (i.e. PE, PP, PVC, ABS, PU, PA6.6, PET, SBR, EPDM) are established according to the 'grave-to-cradle' path (including polymerization, oil derivatives production and fossil fuel extraction). The mechanical and chemical recycling indexes are developed depending on the final product (e.g. the new crude polymeric material or the oil derivatives). The comparison confirms the convenience of some already used practices and the benefit of recycling in terms of global resource utilization. Finally, a specific application for a thermodynamic assessment of End-of-Life vehicle plastic components is presented. Calculating the total EE of the vehicle plastic components gives an idea of the order of magnitude of the resources that are definitively dispersed in case that the materials are not reused or recycled.

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Chapter 1

The Integrated Solid Waste Management

Waste generation is an unavoidable consequence of the contemporary communities lifestyle. In a consumerism-based society, the constant population growth and economic development lead to a non-stop increment of waste generation in residential, commercial and industrial sector. Inappropriate waste disposal may potentially cause a wide range of problems (e.g. water and soil contamination, disease propagation trough animals, flood increasing due to drain blockage, release of hazardous substances from fire and explosions, greenhouse gas emissions), with severe consequences on the environment and human health.

Therefore, it appears evident the necessity of planning and implementing operations for an efficient waste collection, transport and treatment or disposal, together with activities to reduce waste generation and increase waste recycling. An Integrated Solid Waste Management (ISWM) system is defined as "the comprehensive waste prevention, recycling, composting and disposal program" [1]. The goal of an efficient ISWM is to optimize the operation and connection between its subsystems according to environmental and human health safety principles, including the economic constraints and considering the specificity of the local context. The result is then a combination of different waste management activities that best meet the needs of each community.

In this Chapter, an overview on some fundamental fields of Solid Waste Management (SWM) is offered. First of all, in Section 1.1 the main European Directives in matter of wastes are listed. The knowledge of the legislative framework allows to be aware of the goals and targets to which the European countries have to align in the next years. Section 1.2 is focused on Municipal Solid Waste (MSW), providing data on generation and material composition (Section 1.2.1), collection schemes and volumes (Section 1.2.2) and an overview of the alternatives for treatment and disposal after collection (Section 1.2.3).

1.1 Framework legislation

Before analysing the SWM issues and alternatives, it is important to understand the legal framework the European countries have to refer to. According to [2],the European Union (EU) approach to waste management is based on the "waste hierarchy" (Figure 1.1), which sets the following priority order at the time of making policy and managing waste at the operational level: prevention, (preparing for) reuse, recycling, recovery and, as the least preferred option, disposal (which includes landfilling and incineration without energy recovery).

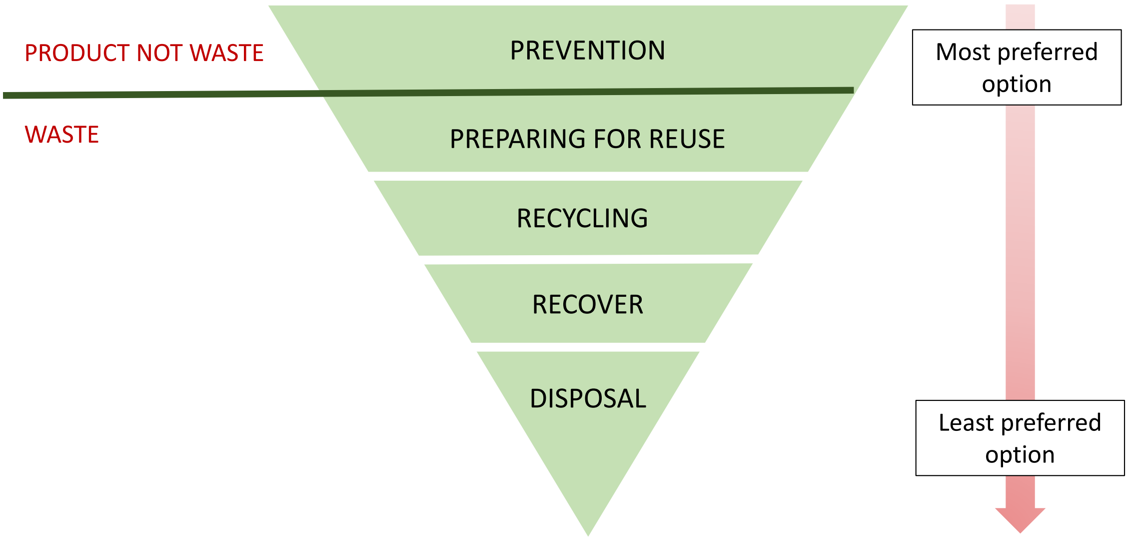


Figure 1.1: Waste hierarchy according to the EU Directive 2008/98

In line with this,the [3] reports a list of priority objectives for waste policy in the EU, which include:

- To reduce the amount of waste generated;
- To maximize recycling and re-use;
- To limit incineration to non-recyclable materials;
- To phase out landfilling to non-recyclable and non-recoverable waste;
- To ensure full implementation of the waste policy targets in all Member States.

In order to reach these goals, some concrete measures have been proposed [4], among the others:

- A common EU target for recycling 65% of municipal waste by 2030;
- A common EU target for recycling 75% of packaging waste by 2030;
- A common EU target for reducing landfill to maximum of 10% of municipal waste by 2030;

- A ban on landfilling of separately collected waste and a promotion of economic instruments to discourage landfilling ;
- Simplified and improved definitions and calculation methods for recycling rates;
- Concrete measures to promote industrial symbiosis for by-products re-use or for implementing recycling schemes.

A general framework of waste management definitions and requirements is provided by the Waste Framework Directive (WFD) 2008/98/EC of the European Parliament. The regulation EC N°1013/2006 regulates waste shipment between countries, while the Decision 2000/532/EC establishes the classification system for wastes. According to this, some macro-categories can be identified [5].

- Wastes from industrial activities;
- Wastes from chemical processes;
- Wastes from thermal processes;
- Wastes from mining and refining processes;
- Construction and demolition wastes;
- Sanitary wastes;
- Municipal wastes.

Between them,the characteristics of hazardous waste are specified in the Annex III of Directive 2008/98/EC. Moreover, EU legislation regulates waste management operations, such as incineration (Directive 2000/76/EC) or landfilling (Directive 1999/31/EC), or the disposal of specific waste streams, e.g. End of Life (EoL) vehicles (Directive 2000/53/EC) or packaging waste (Directive 94/62/EC).

In matter of material recovery, the Directive 2018/851/EC has redefined the Selective Collection (SC) as the collection where a waste stream is kept separately according to the type and nature in order to facilitate a specific treatment. From 2015, SC is mandatory for for paper, metal, plastic and glass, by 31 December 2023 for bio-waste and by 1 January 2025 for textile and hazardous household waste.

As a European country, Italy must receive and implement the European legislation in matter of wastes. Recently, the Legislative Decree 116/2020 has introduced the modifications of the Directives 2018/851/EC and 2018/852/EC in terms of circular economy and related to landfill disposal, EoL vehicles and Waste Electrical and Electronic Equipment (WEEE).

1.2 Municipal Solid Waste

1.2.1 Generation and composition

Among the waste categories, Municipal Solid Waste (MSW) is defined as the waste from household and similar commercial, business and institutional activities (e.g. schools, government buildings), including separately collected fractions and waste from municipal services [6]. According to [5], waste belonging to this category are tagged with the 6-digit codes 20 XX XX and 15 01 XX.

According to [7], 2.01 billion tons of MSW are generated worldwide annually; this number is expected to grow to 3.4 billion tons by 2050, doubling the population growth in the same period. Looking at the global picture, it is evident the positive correlation between economic wealth and waste generation. The daily per capita generation is now 1.58 kg/day for high-income countries and it is expected to grow of 19% in 2050. At the same time, the predicted increment for low-middle income countries is about 50%, (passing from 0.53 to 0.79 kg/day), corresponding to more than two times the actual generation.

In Europe, the global MSW generation has increased from 227 to 284 millions of tons in the period between 1990 and 2018 [6], even with some fluctuations during the years and significant differences between countries. Figure 1.2 reports a comparison between the 2005 and 2018 per capita MSW generation in the European countries. The countries are ranked in increasing order by MSW generation in 2018.

Figure 1.2: Municipal Waste generated in EU countries: comparison between 2005 and 2018 [6]

As can be seen, Italy is located halfway in the countries ranking. The detailed Italian scenario in terms of total and per capita MSW generation is reported in Figure 1.3, where the Total Unsorted Waste (TUW) generation and the total (SC_{tot}) and per-capita (SC_{pc}) wastes collected by Selective Collection are reported according to the data of [8]. It can be seen that the total generation is quite stable during the years: apart from a reduction due to the economic crisis (-8% in 4 years), there are no significant changes from 2012. At the same time, the degree of SC has constantly grown, from 24% in 2005 to 61% of 2019. These are average data referring to the entire country, since regional differences can be consistent. This growth is the effect of SC oriented policies due to the implementation of the EU directives and the gradual citizens education. This is confirmed by the increment of the per-capita amount of sorted wastes, considering that the total population was quite stable in the same period.

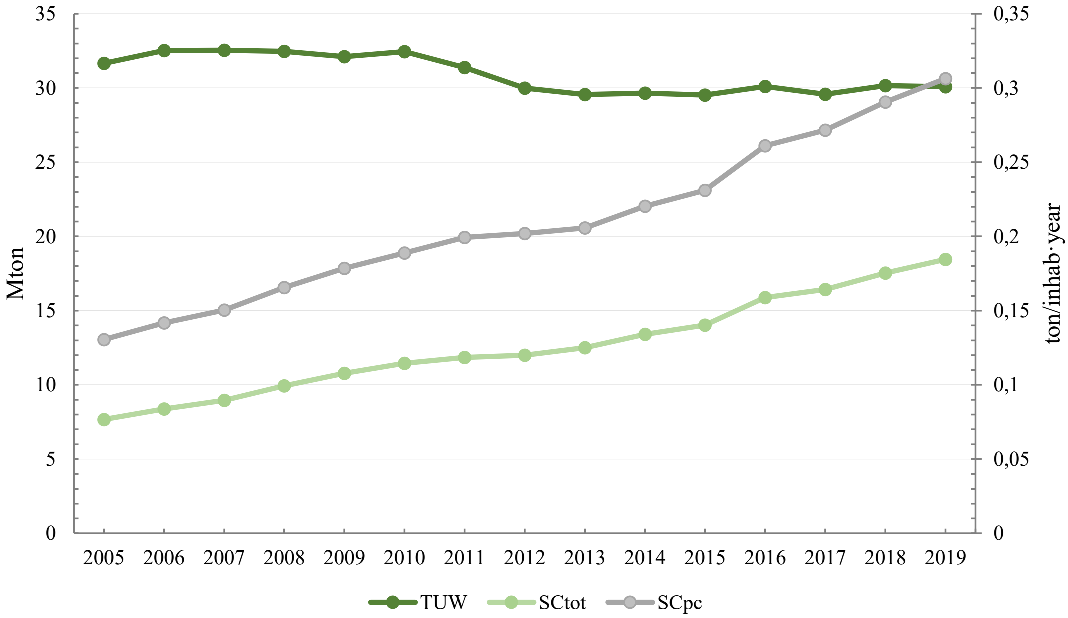


Figure 1.3: Total Unsorted Waste and Total and Per-Capita Selective Collection in Italy between 2005 and 2019, elaborated by the author based on [8] (TUW and SC_{tot} are in Mton, SC_{pc} is in ton/inhab·*year*)

Various techniques are employed to identify the material composition of the generated MSW. For large scale analysis, statistical projections and calculations can be used, based on historical data, population, surveys and hypothesis on degree of SC. As an example, in [7] an average MSW composition is reported for high-income areas (Figure 1.4), including European countries.

In local contexts, the material characterization of MSW can be commissioned by the municipalities; in fact, information on waste quality are necessary for properly designing a new collection, treatment and disposal system or verifying the effectiveness of the existing one. Various standardized methodologies exist [9], resulting from the combination of the following actions:

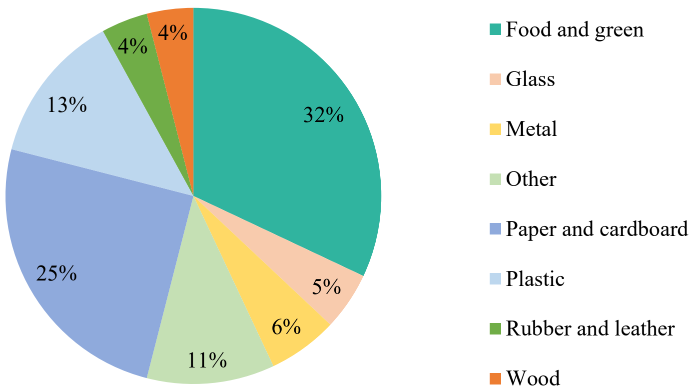


Figure 1.4: Average waste composition in high-income EU countries, elaborated by the author based on [7]

1. sample weighing;
2. disposition of waste in circular layers;
3. sample reduction;
4. screening;
5. weighing and identification of the remaining waste fractions;
6. calculation of Moisture Content (MC) and Lower Heating Value (LHV).

Some examples of material composition analysis results for different Italian cities are reported in Table 1.1. It is not easy to find publicly available updated data on the Unsorted Residual Waste (URW) composition (namely, the residual wastes after the SC). There is not a reproducible correlation between gravimetric composition and other factors, but the values depend on a combination of:

- the methodology adopted for doing the analysis;
- period of the year;
- degree of SC of the area;
- population of the area;
- location.

Some regions (e.g. mountain communities as Val Venosta or seaside touristic cities as Imperia) can be strongly influenced by seasonal variations in waste composition (e.g. increasing of packaging waste in summer or of forest cutting waste in winter). Big cities can be subject to variations due to the presence of street markets, stores or factories. The URW composition can significantly change during the years with the adoption of different recycling policies.

Table 1.1: Unsorted Residual Waste gravimetric composition in Italian cities [10–13]

	Gravimetric composition of URW %wg (w.b)			
	Torino (2015)	Val Venosta (2016)	Napoli (2012)	Imperia (2010)
Population (people)	2,283,080	34,307	961,106	222,648
SC (%)	51.8	64.7	20.62	22.45
Material Stream				
Paper	26.97	19.45	20.14	18.7
Plastics	17.16	26.1	19.71	8.3
Other Plastics	0.94	0.9	3.3	5.3
Organic Matter	33.8	33.45	33.05	30.9
Wood	6.13	2.8	4.4	2.5
Leather	0.26	0	0	8.8
Non-Ferrous Metal	1.08	0.9	3.6	0.4
Ferrous metal	1.49	1.3	2.8	1.7
Glass	6.29	1.3	4.8	6.9
Textile	3.05	5.6	4.6	0
Other Inerts	2.8	8.2	3.6	16.5

wg: weight; w.b.: wet basis

1.2.2 Collection

Waste separation first occurs at the household level, according to the existing SC principles of the municipality. An efficient source separation is the first fundamental step in order to reduce the treatment cost and maximize the material recovery. Therefore, it is important to raise citizens awareness and furnish them correct information on SC. Moreover, keeping citizens informed about recycling chains and outcomes is important to motivate them to appropriately manage waste [14]. In order to reach the goal, a correct communication should be accompanied by economic incentives.

In Italy, waste collection is generally carried out by private companies which conclude service-level agreements with the municipalities. At local level, the MSW collection and management activities are structured according to optimal macro-areas (e.g. provinces), which are then divided into smaller micro-areas with homogeneous socioeconomic and morphological characteristics. Inside these micro-areas, the government functions are handled by local Consortia, while the operational management of the services are entrusted to the management companies, according to the regional waste management plans [15]. The cost of the collection falls on the citizens, trough the Municipal Waste Tax (MWT). This is composed by a fixed quota that covers the service and the investments costs (e.g. vehicles, bins), plus a variable part depending from the estimated per-capita URW generated by the residents [16]. Recently, some municipalities have adopted a more precise charging system based on the Pay-As-You-Throw (PAYT) principle: the variable fee is calculated for each household according to the URW weight. This solution can produce a strong positive incentive to increase material separation at source. Besides, the decomposition of the municipal collection cost shows that about 46% is due to the management of the URW, 31% to that of the separated fractions and the remaining 23% to the other management costs [8].

Different waste collection schemes exist. Generally, each micro-area is subdivided into smaller districts of similar size, which can be defined as unitary collection areas. Then, the most common configurations are [17]:

- kerbside (or 'door-to-door') collection, when the waste is daily collected from every housing unit, according to the type of material;
- traditional (or 'bring point') collection, when the waste is dropped off by citizens in separated street bins;
- reception systems or pick up collection for specific waste streams.

In many European countries, the recent trend is to gradually change in favour of the kerbside collection, since it allows to reach higher degree of separation. According to [18],citizens practising kerbside separation have a higher recycling conscience and are more satisfied with the city waste management system. The collection frequency determines comfort and incentives for households; besides, during pick-up waste workers can execute a visual control on potential impurities. In general, the quality of the kerbside SC is better than the street containers one. However, the Directive 2018/851 allows the Member States to deviate from the general obligation to separately collect waste in case that the ecological benefits are not sufficient to compensate for the negative environmental effects or for disproportionate economic costs. This can be the situation of scarcely populated areas or small islands; in this cases, a deep study of the local circumstances will define the better solution.

The collection calendar and routes as well as the type of vehicles and bins depend on the kind of scheme. Generally, the collected streams are:

- paper and cardboard;
- organic waste;
- multi-material polymeric waste (e.g. plastic packaging, bottles, containers);
- aluminum cans;
- glass;
- garden trimmings;
- Unsorted Residual Waste (URW).

The URW fraction mostly includes the wastes that escape the SC, plus textile, composite objects, some type of plastic packaging and ferrous metals. Separate paths of collection are disposed for textiles (e.g. used clothes), harmful waste (e.g. batteries, used oils, paints, solvents, big ferrous metals), bulky waste (e.g. white goods) and WEEE. The revised WFD allows the commingling of certain types of waste during collection (e.g. plastic and aluminum, glass and aluminum) providing that quality for recycling is not hindered.

The value of Global Selective Collection SC_{gl} is defined as the percentage of MSW that is separated and collected [8]. This is the weighted average of the mass flow of the separated material streams m_i (namely paper, plastic, organic matter, wood, metal, glass and textile), where the weight is the degree of selective collection of the single stream SC_i (Equation 1.1). The relation between the TUW, the URW and the value of SC_{gl} are expressed by Equation 1.2.

$$SC_{gl} = \frac{\sum_i SC_i \cdot m_i}{TUW} \tag{1.1}$$

$$URW = (1 - SC_{gl}) \cdot TUW \tag{1.2}$$

The average MSW recycling rate for municipal waste in Europe is 46% [6]. Among the European countries, Italy has a medium-high level of waste SC, corresponding to 58.1% of the national waste generation in 2018 [8]. The SC trend between 2005-2018 has been shown in Figure 1.3. These values are weighted averages of the single region degree of SC; in reality, the country picture is pretty heterogeneous. Differences can be identified between and even inside regions. Table 1.2 resumes data on SC in Italian regions, with details on material separation for the most and less virtuous regions and for Piemonte region.

It is important to underline that these data refer only to collected wastes and not to the effectively recycled ones. In fact, part of the collected material ends up in a different final disposition (e.g. landfill or energy recovery) [19, 20].

The efficiency of the recycling system is mainly linked to:

- the post-collection treatment operations (e.g. material loss during the transport);
- bureaucratic restrictions (e.g. absence of legal regulation for packaging recycling);
- technological limits (e.g. absence of recycling plants).

1.2.3 Alternative paths for treatment

After the collection, MSW are transferred to a transfer station, where the material flows are then sent to the specific treatment plants. A graphical overview of the alternative treatment paths is shown in Figure 1.5.

A brief definition of the main sections is reported below.

Table 1.2: Data on Selective Collection in Italian regions [8]

Region	**Population (people)**	**%SC**	**SC material composition (% on SCtot)**							
			Paper	Plastic	Organics	Wood	Metals	Glass	Textiles	Others
Piemonte	4,341,375	63.24	21.10	9.6	33.9	7.7	1.7	13.00	0.9	12.1
Veneto	4,907,704	74.7	16.7	7.1	42.8	4.9	3.1	13.2	0.8	11.4
Sicilia	4,968,410	38.52	21.2	8.4	45.3	2.7	0.7	12.4	0.6	8.7
Abruzzo	1,305,770	62.66								
Basilicata	556.934	49.37								
Calabria	1,924,701	47.91								
Campania	5,785,861	52.75								
Emilia-Romagna	4,467,118	70.56								
Friuli-Venezia Giulia	1,211,357	67.17								
Lazio	5,865,544	52.21								
Liguria	1,543,127	53.41								
Lombardia	10,103,969	72.03								
Marche	1,518,400	70.26								
Molise	302.265	50.44								
Puglia	4,008,296	50.58								
Sardegna	1,630,474	73.3								
Toscana	3,722,729	60.2								
Trentino-Alto Adige	1,074,819	73.1								
Umbria	880,285	66.07								
Valle d'Aosta	125,501	64.53								
Veneto	4,907,704	74.7								

- *Transfer station.* It is the intermediate step between the MSW collection and final treatment and disposal. In these facilities, wastes are discharged in the receiving area, and are then compacted and loaded into larger vehicles without long-term storage (usually some hours) [21]. The main advantages derived from a transfer station are: cost reduction for transporting wastes; screening and sorting of wastes before landfill or treatment; flexibility in terms of disposal options, giving the possibility to split and allocate the collected separated materials into the different plants. The size and location of transfer station must be chosen in order to provide the coverage of the collection area and guarantee the economic savings in transport; generally the maximum distance is between 20-30 km [22].

- *Mechanical Biological Treatment (MBT).* In many countries, URW and rejects from recycling processes must be treated before disposal in landfill or energy recovery (in Italy this is regulated by the Italian Law LD 211/2015 art.48). The MBT plants undertake a series of mechanical operations on the wastes aimed to: increase the calorific value of the main outlet stream by separating the light and dry fraction (e.g. paper, plastic, textiles, etc.) from the wet one (organic matter) [23, 24]; recover the ferrous and non-ferrous metal to be devolved to recycling plants; stabilize the organic part before the final disposal; reduce the volume of biodegradable waste to be disposed in landfill, limiting gas and

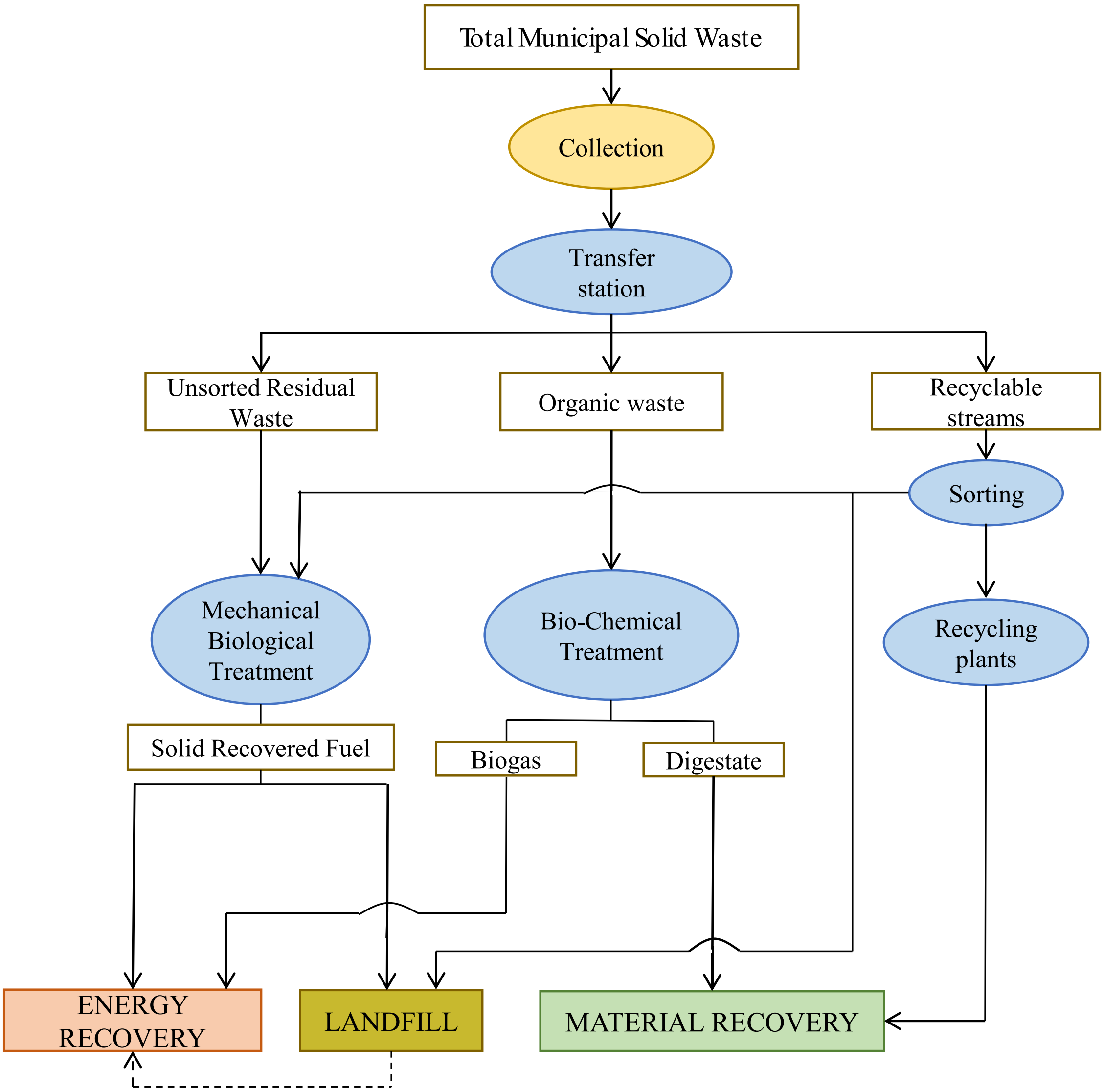


Figure 1.5: Municipal Solid Waste paths for treatment

leachate emissions. The main output is the Solid Recovered Fuel (SRF), which can be only used in incinerators, cement factories or thermal power plants of more than 50 MW, otherwise it is disposed in landfill (DM 22/2013). The resulting product from the biological treatment (stabilized organic matter) is not suitable for usage as a recycled product for land treatment or agriculture, due to the usually unacceptable level of contamination.

- *Sorting unit.* After transfer station, some separated material streams (e.g. the multi-material polymeric stream) are sent to sorting facilities. Here, the different materials (e.g. polymers) are divided using mechanical or optical techniques in order to obtain homogeneous recyclable streams for recycling plants. Sorting may also occur in facilities that are classified otherwise.

- *Energy recovery.* According to the definition of [25], energy recovery from waste is the conversion of non-recyclable waste materials into usable heat, electricity, or fuel through a variety of processes, including combustion, gasification, pyrolisis, anaerobic digestion and landfill gas recovery. This process is often also called Waste-to-Energy (WtE). The most diffused form of WtE is the incineration, which has to fulfil the energy efficiency criteria laid down in the Waste Framework Directive (2008/98/EC).

- *Composting/Digestion.* The composting/digestion processes are defined as the biological processes that submit biodegradable waste to aerobic or anaerobic (i.e. in absence of oxygen) bacterial decomposition, and that results in a product that is recovered [26]. The aerobic or anaerobic treatment generates compost or digestate which, after reprocessing, is used as a recycled product, material or substance for land treatment resulting in benefit to agriculture or ecological improvement. The anaerobic digestion also produces biogas, a mixture of fuel gases used for energy recovery.

- *Recycling.* It is defined as any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes [27]. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations.

- *Landfilling.* Landfill is defined as deposit of waste into or onto land, including specially engineered landfill, and temporary storage of over one year on permanent sites [28]. The adequate technique consists in an disposal of waste in the soil, minimizing the environmental impact and the injuries for public health and safety. This goal is reached using engineering solutions as soil waterproofing, fencing and draining of gases, rain water and leachate; at regular intervals of time the waste is covered with a dirt layer. In this way the area, the volume and the emissions of residues are reduced.

Figure 1.6 reports the percentage distribution of SW management and treatment alternative for the 2019 Italian scenario [8]. These are average data referring to the entire country. Waste treatment can occur in regions different from that of generation (e.g. considerable amount of waste from Centre ans South Italy are treated in the North). Data refer to the final destination, which means that not all the material sent to material recovery is effectively recycled. However, 74% of total waste is headed for some sort of recovery (i.e. energy or material recovery, composting or digestion, domestic compost) and only 22% is destined to landfill after treatment in MBT plant. The percentage of landfill disposal is constantly

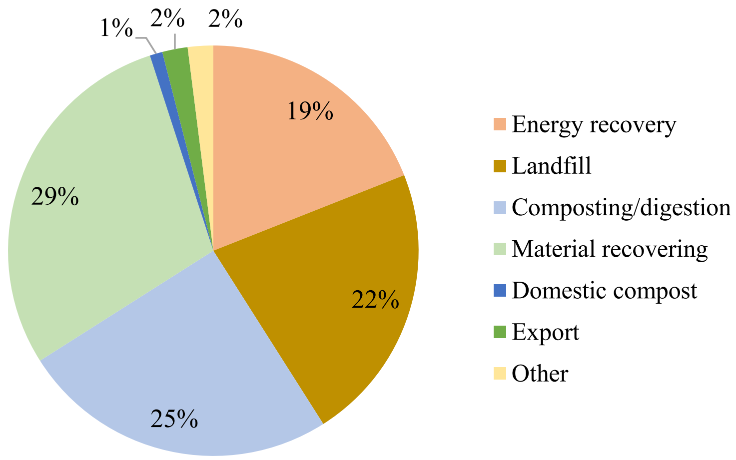


Figure 1.6: Solid Waste final destinations, Italy 2019 [8]

decreasing, and it must be halved in the next 15 years in order to reach the European directives. The exported wastes do not include the pre-treated materials (e.g. the SRF from MBT plant), since they are considered secondary materials. The term 'Other' include the wastes that are stocked in the treatment plants until the end of the year and the process losses.

1.3 Main issues

Some of the main issues related to ISWM systems and addressed in the present work are linked to:

- the management of the waste streams (i.e. URW and separated material streams) inside the system, which is normally influenced by economic and technical constraints;
- the physical and bureaucratic separation between the stakeholders (i.e. municipalities, collection companies, treatment and recycling plants operators, users of recycled materials);
- the aleatory factors (i.e. seasonal, geographical, technical) that can bring uncertainty in the system management;
- in a product-based perspective, the quantity and type of materials used for a product manufacturing are not usually designed for their recycling or considering the resources invested until its production.

The most common criterion for optimizing the waste flows management is the minimization of the monetary cost for each involved part. However, this usually does not imply the most rational waste disposal and resource utilization. For this reason, in this work, exergy analysis is used for resource assessment and it is coupled with economic criteria in the system optimization, as it will be illustrated in the next Chapters.

1.4 Objectives

The general objective of the present work is to use exergy criteria to assess the resource utilization into the Solid Waste (SW) treatment systems, including multiple scenarios and conflicting objectives. The accomplishment of this goal passes trough the following specific steps:

- to identify the best instruments within the exergy cost theory and mathematical methods for performing the analysis;
- to show the influence of various factors (e.g. population density, unit collection area, degree of SC) on the waste collection cost, considering a typical Italian C&T system, for obtaining a set of optimal combinations to use for the optimization of the entire SWM system;
- to evaluate the performance of the MBT plant under an Exergoeconomic perspective, considering the influence of aleatory variations of external and internal operating parameters and so reproducing the variety of operating conditions that can be faced;
- to use the Embodied Exergy criteria to follow the path of the inlet waste streams and to evaluate their allocation into the treatment system, testing its sensibility to uncertain working conditions;
- to develop exergy-based resource consumption indicators and to evaluate the effect of flow repartition between plants, including all the possible combinations from 0 to 100% of recycling of waste streams;
- to perform a multi-objective optimization on cost and exergy efficiency in order to find the trade-off points of system management;
- to define and assess the exergy life cycle of polymeric materials and to develop exergy-based indicators comparing polymers production from primary and secondary raw materials;

Chapter 2

The theory of Exergy analysis

Exergy is a thermodynamic quantity, whose definition derives from the Second Law of Thermodynamics. It represents the upper limit of the portion of a resource that can be converted into work, given the prevailing environmental conditions. Due to its characteristics, it results to be an useful tool to calculate the production cost of materials and energy vectors, identify the efficiency improvements of a system or a technology and perform resource assessment of production processes.

In this work, exergy analysis is applied for calculating the exergy-based costs and accounting for the irreversibility of a specific Solid Waste (SW) treatment plant. Moreover, the cumulative property of exergy cost is employed for a resource assessment of the entire SW collection and treatment (C&T) system, including the recycling options and the alternative scenarios of production. A product-specific application is also presented for evaluating the exergy life cycle of polymeric materials.

In this Chapter, an overview of the fundamentals of exergy analysis is offered. First, in Section 2.1, the principles of Exergoeconomics are summarized, starting from the definition and classification of exergy (Section 2.1.1) and the the methods for accounting the irreversibility of a system (Section 2.1.2), to the theory of the exergy-based cost formation (Section 2.1.3). Then, in Section 2.2, the exergy for resource accounting approach is explained. The Embodied Exergy concept and the boundary setting criteria are introduced in (Section 2.2.1). Finally, a comparison between the exergy life cycle approach adopted in this work and the widely diffused Life Cycle Assessment is proposed (Section 2.2.2).

2.1 The principles of Exergoeconomics

2.1.1 Exergy: definition and classification

The exergy of a system (i.e. energy form or portion of matter) is the maximum useful work obtainable when it is taken from its given state to the thermodynamic equilibrium with the environment, by only interacting with the environment [29] [30]. Thus, exergy can be seen as a measure of the existing disequilibrium with the surrounding environment [31], and so of the potential of a system to cause change and have an environmental impact [32].

From this definition, it is evident that the specific exergy of a system is a thermodynamic property function of two thermodynamic states (i.e. the actual state in which the system is and the state where it would be in thermodynamic equilibrium with the environment) [33]. For this reason, in order to perform exergy calculations, the definition of a common reference basis is necessary, as well as a reasonable idealized model for the Reference Environment (RE) [31]. Different RE have been proposed [34, 35], but the most used so far is the one proposed by Szargut [29]. The RE is physically stable at temperature T_0=298.15 K and pressure p_0= 1 atm. The chemical composition of RE consists of a number of reference substances to which null exergy is assigned. These substances are found in the three main natural subsystems, namely the atmosphere (i.e. oxygen, nitrogen and other gases), the hydrosphere (i.e. saturated liquid water) and the lithosphere composed by the most abundant and lowest value substances of solid crust (i.e. gypsum, calcite). The thermodynamic equilibrium is reached when temperature, pressure and chemical potential of the system are equal to the ones of the RE; this final state is called 'dead state'. From the definition of RE, it is evident that the natural environment has a not null exergy, since the subsystems are not in thermodynamic equilibrium between themselves.

The exergy of a matter stream is the sum of different components, namely physical, chemical, kinetic, potential and nuclear exergy. Figure 2.1 graphically reports the various contributions.

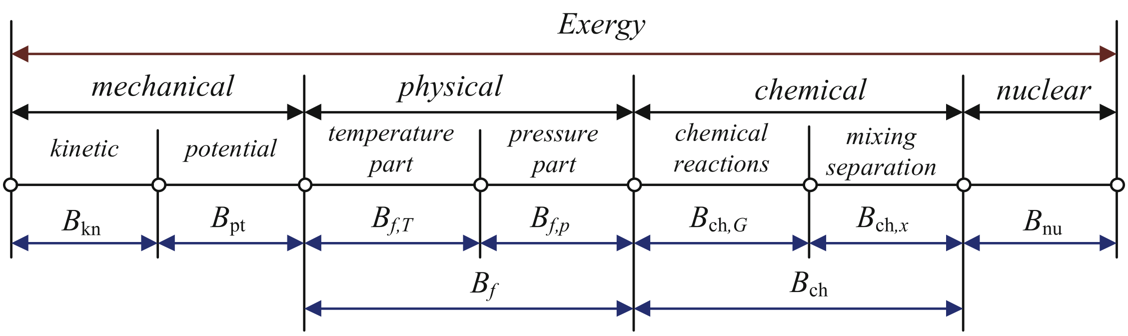


Figure 2.1: Exergy components [36]

- *Physical exergy*

The physical exergy is the maximum useful work that can be performed from a system or a flow rate that pass from a given state (T, p) to the environmental state (T_0, p_0), trough purely physical processes. In other words, it is the portion of exergy obtained when only thermal and mechanical equilibrium is reached. According to Equation 2.1, in order to calculate the specific physical exergy b_{ph} [kJ/kg] it is necessary to know the enthalpy and entropy of the stream both in the actual (h,s) and in the environmental state (h_0, s_0).

$$b_{ph} = (h - h_0) - T_0(s - s_0) \tag{2.1}$$

- *Chemical exergy*

When the stream composition is not in chemical equilibrium with the RE, the chemical exergy is defined as the maximum work obtainable passing from the environmental to the dead state, by means of chemical processes. The chemical exergy of a pure substance that is not part of the RE can be calculated as the result of a series of reversible processes. A reaction occurs at P_0 and T_0 between the substance and other coreactants of the RE for generating a product substance that exists in the RE. Before that, the concentration of coreactants is changed from the state they are in equilibrium in the RE to the one they assume at P_0 and T_0. After the reaction, the concentration of products is brought up to the one of the RE. Equation 2.2 gives the resulting molar chemical exergy $\overline{b_{\mathrm{ch}}}$ [kJ/kmol], where ΔG_0 is the free Gibbs energy of formation and x is the molar fraction [30].

$$\overline{b_{ch}} = -\Delta G_0 + [\sum_j x_j \overline{b_{chj}}]_{products} - [\sum_i x_i \overline{b_{chi}}]_{reactants} \tag{2.2}$$

For a ideal gas mixture and liquid solutions, the chemical exergy $\overline{b_{\mathrm{chmix}}}$ can be calculated by means of Equation 2.3. The logarithmic term accounts for the exergy destroyed during the mixing of different streams.

$$\overline{b_{chmix}} = \sum_i x_i \overline{b_{chi}} + RT_0 \sum_i x_i \ln x_i \tag{2.3}$$

The chemical exergy of a fuel stream is generally evaluated through empirical correlations with its Lower or Higher Heating Value (LHV or HHV), since it is difficult to know its exact composition. For liquid or organic solid fuels containing carbon (C), hydrogen (H), oxygen (O), nitrogen (N), the Szargut factor ϕ of LHV correction is calculated with different expressions depending on the O/C ratio. Trough the several expressions for the chemical exergy of solid fuels containing sulphur (S), one of the main used is reported in Equation 2.5, taking into account also the moisture content MC of fuel [30].

$$b_{chfuel} = \phi \cdot LHV \tag{2.4}$$

$$[b_{chfuel}]_S = \phi \cdot (LHV + 2442 \cdot MC) + b_{chwater} MC + 9683 \cdot S \tag{2.5}$$

- *Kinetic, potential and nuclear exergy*

Kinetic and potential exergy are the mechanical components of exergy. The kinetic part results from the velocity v of the system with respect to the reference environment ($b_{kin} = 1/2v^2$), while the potential part is related to the system height H ($b_{pot} = gH$). Since these energy forms can be completely converted into work, the energy and exergy values are the same. Nuclear exergy results from the energy of fission decreased by energy of emitted neutrino that are not interacting with the matter[36].

The exergy of non-matter streams can be reduced to the sum of energy of work and heat streams.

- *Work flow exergy*

By definition, exergy is the maximum obtainable potential work. Therefore, a work flow W has the same exergy content of the work in the flow (i.e. the energy and exergy value are the same, $b_{work} = w$). This also applies to electrical energy, since this energy form can be fully converted into work.

- *Heat transfer exergy*

The exergy content of a heat transfer q is related to the temperature T at which the heat is available, with respect to the reference temperature T_0, according to Equation 2.6. The more T is near to T_0, the lower is the exergy content. For $T < T_0$ the exergy and heat transfers have opposite signs: it means that, at temperature lower than the environmental temperature, an heat flow input causes an exergy output as greater as the temperature T is lower.

$$b_q = q(1 - \frac{T_0}{T}) \tag{2.6}$$

2.1.2 Accounting the irreversibility

According to the Second Law of thermodynamics, every time that an irreversible process occurs (e.g. heat transfer, chemical reaction, expansion, mixing, head loss), there is an entropy generation, which means that part of the work turns into internal energy [33]. Since exergy measures the capacity of a system to produce work, it follows that exergy is not conservative, except for ideal, reversible processes. Therefore, the irreversibility is the cause of the process inefficiency.

Equation 2.7 reports the exergy rate balance for a system in steady state conditions. The term $\dot{B}$ includes the physical, chemical, kinetic, potential and nuclear exergy of a material stream flow, while $\dot{B}_q$ and $\dot{W}$ are the heat transfer and work exergy flows, respectively. All terms are expressed in kW.

$$\sum_{in}[\dot{B} + \dot{B}_q + \dot{W}]_{in} = \sum_{out}[\dot{B} + \dot{B}_q + \dot{W}]_{out} + \dot{B}_{losses} \tag{2.7}$$

Therefore, the 'useful effect' and 'resources' of a process are defined as a linear combination of output and input streams, respectively. The exergy of the useful products $\dot{B}_{prod}$ resulting from a process (i.e. 'useful effect') is always lower than the exergy of the resources feeding the system $\dot{B}_{res}$; the exergy efficiency η_{ex} is defined as the ratio between these factors (Equation 2.8, also called degree of perfection by Szargut [29].

$$\eta_{ex} = \frac{\dot{B}_{prod}}{\dot{B}_{res}} \tag{2.8}$$

The term $\dot{B}_{losses}$ closes the exergy rate balance, being the exergy associated to internal or external losses, and it can be seen also as an irreversibility rate ($\dot{B}_{losses} = \dot{I}$). Thus, the exergy efficiency expression can be written highlighting the contribution of the $\dot{I}$, which is the sum of internal $\dot{I}_{int}$ and external $\dot{I}_{ext}$ irrevesibilities (Equation 2.9).

$$\eta_{ex} = 1 - \frac{\dot{I}_{int} + \dot{I}_{ext}}{\dot{B}_{res}} \tag{2.9}$$

External exergy losses $\dot{I}_{ext}$ are linked to waste products (e.g. flue gases) and can be partly recovered. The exergy destruction associated to the process internal irreversibilities $\dot{I}_{int}$ is proportional to the entropy generation according to the Gouy-Stodola Law (Equation 2.10) and represents an unrecoverable loss.

$$\dot{I}_{int} = T_0\dot{S}_{gen} \tag{2.10}$$

It results that the exergy method is useful for identifying the location, type and magnitude of process losses [32]. Calculating exergy efficiency gives the measure of the deviation from the ideality and so the margin to optimize the design of a system. However, it remains an upper limit, since practical applications show that a certain degree of exergy loss has to be accounted in order to reduce the investments costs.

2.1.3 Exergy cost formation

As already said, from the definition of exergy efficiency, it is clear the correlation between capital costs and thermodynamic losses for devices [32]. Moreover, high exergy values were often associated to expensive goods or materials. With these premises, it is understandable the reason that has lead to the integration of exergy in the economic analysis [32, 37–39].

When monetary costs are applied, the term Thermoeconomics is used, while it is called Exergoeconomics if exergy costs are employed [33]. The aim of an exergy-based cost analysis is to determine the products and irreversibilities cost according to the exergy content of each material and energy flow involved in the process. The main advantage is the possibility to design a system and optimize its operation, considering the allocation of resource consumption and efficiency degradation among the equipment. With respect to the simple economic analysis, the Thermoeconomic analysis introduces the concept of the quality of the energy conversion process and the thermodynamic value of each product in the determination of production costs. Therefore Thermoeconomics and Exergoeconomics are used in a wide range of applications [36, 40, 41]: global and local optimization based on the minimization of the production costs; plant diagnosis by detecting the inefficiencies and their effect on the plant operation [42]; comparing design alternatives basing on economic feasibility and profitability; energy audits.

The methodology is based on the combination of cost rate balances for the components of the system and exergy-based cost partition criteria. A detailed exergy and economic analysis of each component must have taken place a priori. If we consider a closed control volume, the internal expenses $\dot{C}_{equipment}$ are linked to capital, operational and maintenance costs of the equipment. The general cost balance equation is reported in Equation 2.11 and includes the costs of all the inputs $\dot{C}_{in}$(e.g. materials, fuel, energy) and outputs $\dot{C}_{out}$(e.g. products, waste) streams. The term C is expressed in dollars/sec in Thermoeconomic and kJ of exergy/sec in Exergoeconomics. The exergy-based average unitary cost is in Equation 2.12, where $\dot{B}_i$ [kW] is the exergy flow rate of the i-th stream.

$$\sum_{in} \dot{C}_{in} + \dot{C}_{equipment} = \sum_{out} \dot{C}_{out} \tag{2.11}$$

$$c_i = \frac{\dot{C}_i}{\dot{B}_i} \tag{2.12}$$

Additional equations have to be written if there is more than one product. The cost partition criteria are based on considerations on the nature of product, in particular if it is considered a primary product or a by-product of the process (as well as if the product is made for the market or for internal use of the plant). The main used methods of partition are the equality and the extraction methods. In the first one, all the products are supposed to have the same importance, so all products have the same exergy-based average cost; it means that the internal expenses are equally divided among the products as a function of their exergy content. In the case of extraction method, there is a specific function of the equipment and so a primary product, which is charged with all the internal costs.

2.2 Exergy for resource accounting

All human activities require material resources. What humans have always done was to transform the natural resources into something valuable for them, generally for allowing an improvement of living standards. In a modern economic system, this concept translates into the production process of a service (i.e. material or immaterial) that satisfies human needs [43]. The natural resources, also called primary resources or natural capital (i.e fossil fuels, minerals, water, solar energy, land), are the necessary input flows that allows the production of materials goods, energy carriers, immaterial services or profit [44]. Material resources can be re-used or not according to the type of process they are subjected to and the chemical and physical changes that occur. The case in which the resource is no longer available after use is called depletion, while degradation occurs when the initial characteristics are deeply changed. In any case, the natural resources supply, exploitation and recycling implies the utilization of other resources, resulting in a cumulative primary cost and repercussions on the environment.

In this context, exergy, as a measure of the distinction of a system from the environment, can help in the quantification of the environmental impact. In [32], three fundamental links between exergy efficiency and natural impacts are identified:

1. exergy is a measure of the degree of order and the destruction of order is a form of environmental damage;

2. the resources degradation is a form of environmental damage;

3. exergy of waste emission represents can be related to their potential to cause change and so the measure of their environmental impact.

These burdens can be reduced by increasing the efficiency (i.e. reducing the exergy necessary for a process or the waste emissions) and using external renewable exergy resources (e.g. solar energy).

Another advantage is that exergy is a common measure for streams of different nature, allowing their comparison on a single, rational basis. It follows that the possibility of quantifying the flows between and within systems and subsystems in exergy allows the development of sustainability criteria for industry [45]. The attempt to achieve a rational, efficient and organized industrial system that imitates the behaviour of a natural ecosystem falls in the field of the Industrial Ecology (IE) [46]. The aim of the IE is to obtain a sustainable industrial development by valuing the inclusion of every new or existing technology in the overall industrial metabolism. Many authors underlined in their studies the correlation between Second Law analysis and exergy concept and IE purpose [47]. For these reasons a certain amount of thermodynamics exergy-based methods for life cycle resource accounting have emerged.

2.2.1 Cumulative calculus and boundaries definition

As already said, the resource assessment is performed through the cumulative calculus of a physical properties, which can be energy, entropy or exergy in the case a thermodynamic method is used. In this context, Embodied Exergy (EE) is by definition "the sum of the actual exergy of the system plus the exergy previously used to produce and provide the resources" [48]. It has been also defined as the cumulative amount of commercial energy (i.e. fossil, renewable and nuclear), invested to extract, process and manufacture a product and transport it to its point of use, minus the part associated with the losses [49]. In any case, the EE term (Equation 2.13) includes the exergy physically $EE_{physical}$ or chemically $EE_{chemical}$ embodied in the materials (which can be eventually released) and the exergy invested in creating the i-th process conditions and bringing the materials together (including transport), $EE_{process}$.

$$EE = EE_{physical} + EE_{chemical} + \sum_{i}(EE_{process})_i \tag{2.13}$$

In general, there are two types of approach, according to the boundary setting (Figure 2.2): a product-specific and a process-based analysis. In the first one, an input material of an industrial process is chosen as a final product (e.g. cement, plastic); then, all direct and indirect energy or material inputs that contributed to its production are tracked backward, with an approach that can be defined "grave-to-cradle" [50]. The second approach is more an analysis of the entire supply chain, as extended as the limits of the boundaries. The analysis always starts from extraction of raw materials (i.e. "cradle") and can end up at different points: i)"cradle-to-inlet gate", which includes the first section until the inlet of factory gate; ii)"cradle-to-exit gate", where the exergy of product manufacturing is added; iii) "cradle-to-site", which includes the exergy until the point of use; iv)"cradle-to-grave", until the end of products' life cycle; v)"cradle-to-cradle", where the circle is hypothetically closed by re-obtaining starting materials by replacing the resources into the environment.

Various research groups have developed theories and indicators in the field of the exergy-based resource assessment. The main achievements with the relative differences are reported below.

- *Cumulative Exergy Consumption (CExC)/Exergy Cost*

  In 1986, Valero et al. [51] developed the Exergy Cost theory, as part of the general theory of exergy savings. Almost in the same years, in 1987 Szargut and Morris proposed the CExC concept [29]. Both concept are in fact the same of the already mentioned EE. In general, the approach of these two methodologies is "cradle-to-grave" or at least "cradle-to exit gate".

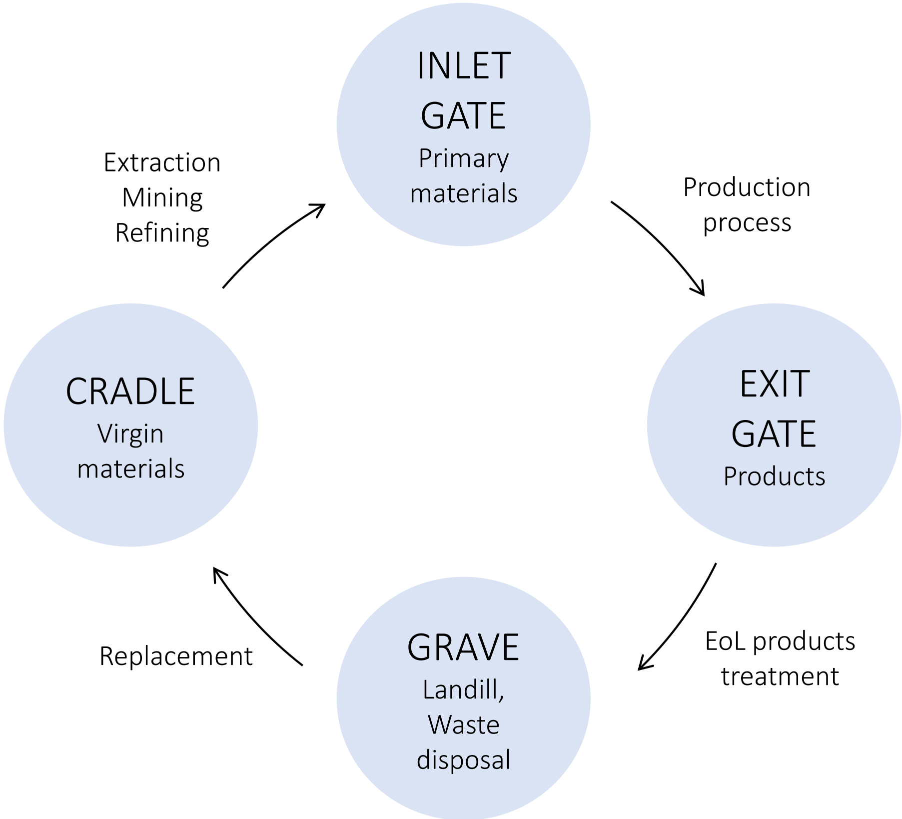


Figure 2.2: Boundaries limits in life-cycle assessment

- *Thermodynamic rarity*

  A particular "grave-to-cradle" product specific application is the one developed by Valero and Valero for mineral resources [52–54]. The analysis starts from the assumption that exergy represents the thermodynamic distinction of a system from the surrounding environment, measuring the degree of its rarity. The Thermodynamic rarity is by definition "the amount of exergy resources needed to obtain a mineral commodity from an accessible common rock, using the best prevailing technology". The rarity of minerals is composed by the sum of two contributions. The first is similar to the classical EE, taking into account the resources associated with conventional mining, beneficiation, smelting and refining processes, plus the chemical exergy of minerals. The second part is called Exergy Replacement Cost (ERC), namely the hidden cost linked to the natural bonus of having minerals concentrated in deposits, instead of dispersed in the Earth's crust. The ERC is defined as the total exergy required to concentrate the mineral resources from an hypothetical degraded planet where all resources have been extracted and dispersed (which they called Thanatia), using the best available technologies. The work needed to separate a substance from a mixture follows a negative logarithmic pattern with the concentration (i.e. ore grade).

- *Thermoecological Cost (TEC)*

  The theory of TEC was first developed by Szargut [55] and carried out by Stanek et al. [36, 56]. TEC is defined as a cumulative consumption of non-renewable exergy connected with the fabrication of a particular product,including the consumption resulting from the compensation of environmental losses caused by the rejection of harmful substances. In the case of renewable energy (e.g. biomass), only the external non-renewable exergy contributions (e.g. fuel) are accounted, excluding the specific exergy. The addition of the resources expenses to compensate human health, industrial and environmental losses is a peculiarity of TEC indicator.

- *Cumulative Exergy Extraction from the Natural Environment (CEENE)*

  The CEENE methodology was developed by Dewulf et al. and aims at quantifying all the exergy that is taken away from the natural environment in order to be released in a production process [57]. It is calculated considering all the resource reference flows and their contribution to the product, using conversion factors. The reference resources are fossil fuels, metal ores, nuclear energy, biomass, land occupation, renewable energy flows, minerals, atmospheric and water resources. Volume occupation and land transformation are not considered because no exergy is deprived from the natural ecosystem.

- *Extended Exergy Analysis (EEA)*

  The EEA method was first ideated by Sciubba [58] and it can be considered a further extension of CExC theory. The main novelty is the inclusion of the side-effects that externalities (i.e. human labor, capital and environmental pollution) have on primary exergy requirements.

2.2.2 Differences with traditional Life Cycle Assessment

Life Cycle Assessment or Analysis (LCA) is a methodology used for assessing the environmental impact associated to a product, process or service during its lifetime [52, 59]. Generally a "cradle-to-grave" approach is used, but the boundary setting can varies as explained in Section 2.2.1. After the definition of the goal and scope of the analysis, a functional unit is chosen as reference for evaluating input and output flows and comparing alternative products or systems.

Back in 1997, Ayres et al. underlined the potential advantages of using exergy in LCA; above all, the fact that exergy is a rational basis for the comparison of flows of different nature and the possibility to estimate exergetic efficiency, giving indication of the theoretical potential of future improvements [47]. The prosecution of this theory has led to the development of the aforementioned methodologies (Section 2.2.1), where the functional unit is always expressed in kW of exergy. One of the main differences between these methods and the classic LCA is precisely that the aim is uniquely defined according to the chosen indicator. On the contrary, the goal and scope of LCA, the boundary conditions and the functional unit are defined case by case according to the authors, resulting in a difficult comparison of results and subjective conclusions.

In this type of analyses, the quality of data is essential, since the more accurate is the information, the more reliable are the results. Traditional LCA generally relies on public or proprietary databases, which cover a huge number of industrial processes and sections. Even if databases are periodically updated, data are given as average values and they may not be accurate for reproducing specific situations, leading to too generic results. The analyst criteria in data comparison should always be preferable whenever possible.

Moreover, in LCA the environmental effects are evaluated by a wide range of impact categories, each with its own unit of measure. With exergy analysis all the adverse effects on the environment are evaluated with the same basis, allowing an unambiguous determination and comparison of the impacts.For these reasons, exergy is a powerful tool to identify the benefits and economics of energy technologies.

Chapter 3

Mathematical methods

Apart from the already described Exergy Analysis tools, the study of SW treatment systems can require additional instruments for modelling realistic scenarios and obtaining reliable information. In this work, Uncertainty modelling and Multi-Objective Optimization are used for deepening and completing the analysis of the SW system.

In real working conditions, the operation of SWM systems involves political choices other than technological, social and geographical factors (Figure 3.1). The heterogeneity of these conditions and their variability results in a high degree of uncertainty for the global system. The uncertain factors can be external (site-dependent) or internal. External factors can be linked to the structure of collection system and the degree of Selective Collection, which influence the waste composition, or the market demand of end-products that affects their production. Internal factors can regard the structure of each treatment chain or malfunctions in equipment, which lead to variable energy consumption. Some example of uncertainty inclusion in the analysis of ISWM systems are present in the literature [60, 61]. In general, stochastic and probabilistic tools are adopted for generating simulation scenarios, such as crude Monte Carlo methods.

The Multi-Objective Optimization is used when conflicting objectives are present, in order to find the best trade-off solutions. In case of SW treatment the general decision making criteria is the economic one, which means that the best solutions is usually found for cost minimization only. However, most of the time this is not a sufficient criteria for ensuring a rational use of resources and final disposal of waste. For this reason, one of the scope of this work is to integrate the resource utilization efficiency with the economic criteria, using a double objective optimization.

In this Chapter the fundamentals of these mathematical methods are presented. Section 3.1 starts with the definition of uncertainty analysis, focusing on Monte Carlo simulation methods (Section 3.1.1). In Section 3.2 an overview of Multi-Objective optimization is proposed (Section 3.2.1), including solutions techniques based on scalarization (Section 3.2.2) and evolutionary methods (Section 3.2.3).

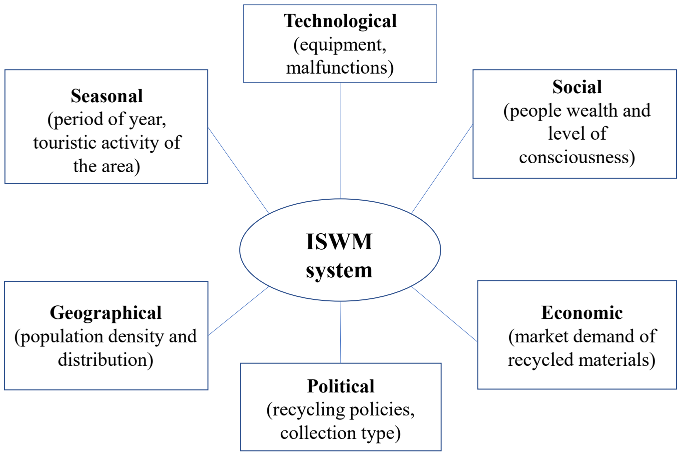


Figure 3.1: Influencing factors potentially causing uncertainty in ISWM systems

3.1 Uncertainty Analysis

Uncertainty is a constant in real-world issues. It can arise from difficulties in obtaining secure information, hypothetical conjectures on future scenarios or random events occurring. Even experimental or real data can be affected by errors and variability. Therefore, uncertainty quantification and impact analysis is fundamental in the performance assessment of complex engineering systems. The major sources of uncertainty that can be found in a model are listed below [62].

- *Uncertain physical variables.* These uncertainties are linked to the natural or random variability inherent to the process. They can regard the internal system properties (e.g. mechanical or chemical characteristics) or the external variables (e.g. environmental or operational conditions).
- *Data uncertainty.* The acquired data can be sparse, imprecise or qualitative (i.e. epistemic uncertainty). In some cases, the uncertainty can be reduced by obtaining more data while other times data are available only in a range of values. In experimental procedures, data measurements are always affected by errors.
- *Scenario uncertainties.* Scenario uncertainties derive from the different modeling conditions used for performing the simulation. They can be linked to system boundaries, technologies, time horizon or products allocation [60].
- *Model bias.* The modelling assumption and computational approximation lead to errors inherent to the model. This represents a source of uncertainty for the output values.

The knowledge of the uncertainty sources is the first step of the uncertainty analysis, which aims at quantifying the impact on the solutions for a more conscious and realistic decision-making process. The main steps of an uncertainty analysis can be summarized as follows [63].

1. *Uncertainty evaluation.* Uncertain parameters are usually quantified as random variables using statistical analysis (i.e. spectral representation, Karhunen-Loeve expansion, polynomial chaos expansion). Data sets that present a time or space variability can be analysed with regressive methods. Sparse or uncertain data can be represented with confidence intervals or Bayesian statistics. This approach is based on the utilization of probability distributions for reproducing the behaviour of uncertain parameters. The distribution can be clear from the data dispersion or can be built with all the obtainable information about a phenomenon (i.e. literature data, scarce measurements, personal or expert opinions).

2. *Sensitivity analysis.* After the identification of the input uncertain parameters, a necessary step is the evaluation of their influence on model outputs by performing a sensitivity analysis using their mean values. It gives an idea of the critical parameters, namely the ones that cause largest instability in the solutions.

3. *Uncertainty propagation.* Once the input uncertainties have been identified and quantified, their propagation to the model results should be considered. In order to do so, various probabilistic methods are adopted, such as first and second order analytic approximations and Monte Carlo simulation.

4. *Results analysis.* The last step may include the model validation, calibration and performance assessment based on the results of uncertainty propagation. Another investigation is linked to the assessment of the contribution of each uncertain parameters to the overall uncertainty.

3.1.1 Monte Carlo methods

The most common and fast method for uncertainty propagation evaluation is the one based on Monte Carlo simulation. From a physical point of view, Monte Carlo method is used for the simulation of natural stochastic processes. It consists in the generation of a large number of random values used for sampling the probability distributions of the uncertain parameters. With this procedure, the probability distributions of the model outputs can be built and the influence of the input uncertainty can be assessed [60, 64].

A random variable x_i is defined as the numerical outcome of a random i-th event with an associated probability p_i, such that $0 \leq p_i \leq 1$. The distribution of all the random values x with a given probability function *f(x)* in the range [a,b] is described by a statistical function, namely the Probability Distribution Function (PDF) (Equation 3.1). The PDF is identified by two main factors: the mean value

μ (or first moment, Equation 5.17) and the variance σ (Equation 5.18), which is a measure of the fluctuation of the random variable. Other parameters can be used for characterizing a PDF, such as the mode, the median and the skewness or kurtosis factors.

$$P(a \leq x \leq b) = \int_a^b f(x)dx \tag{3.1}$$

$$\mu = \overline{x} = \sum_{i=1}^{n} x_i p_i \tag{3.2}$$

$$\sigma = var(x) = \frac{\sum_{i=1}^{n} |x_i - \mu|^2}{n-1} \tag{3.3}$$

Another related statistical function is the Cumulative Distribution Function (CDF) (Equation 3.4), which is a non-decreasing function which expresses the probability that the random variable X takes a value less or equal to x. Many probability distributions have already been studied (e.g. uniform, binomial, geometric, exponential, normal or Gaussian, Lorentz, Poisson, Weibull).

$$F_X(x) = P(X \leq x) \tag{3.4}$$

The most diffused method for generating samples from PDF with Monte Carlo approach is the inversion method. It can be used when a clear expression of the CDF is available; then, a uniform distribution of random values U between 0 and 1 is generated and their inverse images on the CDF curve (Figure 3.2) are found in the x-axis [65](Equation 3.5).

$$X = {F_X}^{-1}(U), U \in \{0,1\} \tag{3.5}$$

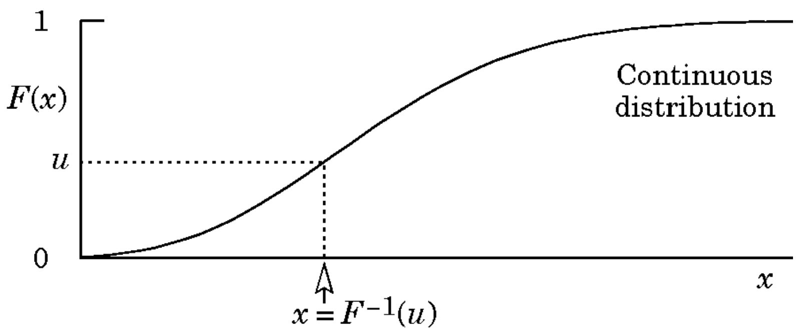


Figure 3.2: Inversion method for sampling probability distributions [65]

3.2 Multi-objective Optimization

3.2.1 Overview

Real-world problems are complex because they are influenced by heterogeneous factors (e.g. social, economical, technological, environmental, ethical). It means that their solution will not be uniquely defined by the optimization of a specific function since there is no feasible solution guaranteeing the best value in all evaluation aspects. Multiple Objective Functions (MOFs) models allow to expand the range of solutions, showing the trade-offs between the conflicting objectives according to specific decisions parameters.

The idea of multi-criteria decision making was born at the end of the XIX century in the field of economic applications. Professors Edgeworth and Pareto developed the first theories of optimum research in presence of conflicting objectives [66]. These ideas spread into the scientific community in the 80's, leading to the deepening and consolidation of theory and resolution methods [67, 68]. Nowadays, multi-objective optimization procedures have found fertile ground for a large range of applications: from the economic and financial field to social problems, from medical to logistic and engineering problems [69, 70].

The general formulation of a Multiobjective Optimization Linear Problem (MOLP) is reported in Equation 3.6, where $\boldsymbol{F} = \{F_1, F_2, ..., F_M\}$ is set of M objective functions that have to be minimized or maximized.

$$
\begin{aligned}
&Minimize/Maximize\ F_m(\boldsymbol{x}), \quad \{m = 1, ..., M\} \\
&subject\ to = \begin{cases} g_j(\boldsymbol{x}) \leq 0, & \{j = 1,2, ..., J\} \\ h_k(\boldsymbol{x}) = 0, & \{k = 1,2, ..., K\} \\ {x_n}^L < x_n < {x_n}^U, & \{n = 1, ..., N\} \end{cases}
\end{aligned}
\tag{3.6}
$$

The problem is subjected to J inequality and K equality constraints, and upper and lower limits for the N decision variables $\boldsymbol{x} = \{x_1, x_2, ..., x_N\}^T$. For each solution x in the feasible decision variable space $\boldsymbol{X} \subset \boldsymbol{R}^n$ there is a corresponding vector z in the multi-dimensional Objective Functions (OF) space $\boldsymbol{Z} \subset \boldsymbol{R}^m$. Differently from the single objective function problem, in MOLP there is no feasible solution simultaneously improving all OF. A gain in a given target implies accepting a degradation in, at least, one of the other. For this reason the result of a MOLP is a non-dominated or non-inferior set of solutions $\boldsymbol{Z}_E$ in the objective function space $\boldsymbol{Z}$. A vector $\boldsymbol{x}_E$ is called an efficient solution in $\boldsymbol{X}$ if it is feasible and no worse than another $\overline{\boldsymbol{x}}$ in all objectives and is strictly better than $\overline{\boldsymbol{x}}$ in at least one objective (Equation 3.7). The image of an efficient solution is a non-dominated solution.

$$
\begin{aligned}
&\boldsymbol{Z}_m(\overline{\boldsymbol{x}}) \leq \boldsymbol{Z}_m(\boldsymbol{x}_E), \forall m \\
&\boldsymbol{Z}_m(\overline{\boldsymbol{x}}) < \boldsymbol{Z}_m(\boldsymbol{x}_E), for\ at\ least\ one\ m
\end{aligned}
\tag{3.7}
$$

The non-dominated points are graphically visualized as a front, also called Pareto-optimal front, with corresponding vectors in the decision variable space (Pareto-optimal solutions), as shown in Figure 3.3.

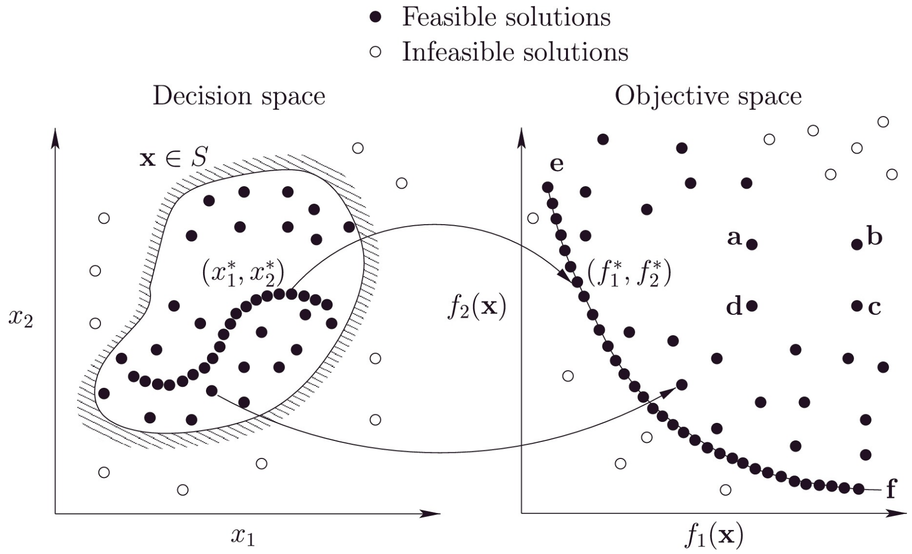


Figure 3.3: Matching between the decision variable and the objective function space [71]

Since all the non-dominated solutions can be selected to be the final solution of the MOLP problem, the second step consists in interpreting, ranking and eventually choosing a solution, according to the Decision Maker (DM) preference. The DM criteria can be decided *a priori* (e.g. setting an expected value function) or may evolve throughout the decision making process (i.e. interactive methods). The DM can interact in order to reduce the area of the search until a stop condition is met. The process ends when the final solution satisfies the DM criteria. The other alternative is not choosing one configuration but analyzing the entire solutions space, obtaining information on the extent of trade-offs. In any case, it is never a definitive decision, but can be used as reference for planning choices.

In case on Multiobjective Integer (MOIP), Mixed-Integer (MOMIP) or Non-Linear problems (MONLP), it is necessary to add some specifications on efficient solutions. In particular, in MONLP improper efficient solutions may occur, i.e. solutions presenting unlimited trade-offs between the OF values. In all the three cases, unsupported efficient solution may exist, namely a solution that is dominated by an infeasible convex combination of points.

3.2.2 Scalarization Techniques

The main issues arising in the solution of MOFs problems are linked to the heterogeneity and incommensurability between the OF (i.e. no common measure can be used) and the uncertainty in the DM preferences [72]. The MOFs problems decision support methods are generally divided into two groups: the generating and the preference-based methods. In the generating methods, no preference is expressed or is expressed *a posteriori*, in the moment of selection of an alternative; the aim is to estimate the entire Pareto set by using approximation methods of the non-dominated set (e.g. weighting or constraint methods). However, generating algorithms can be complex and require high computational cost. Preference-based methods are based on the quantification in a structured way of the DM preference and the research of a solution that satisfies it. Preference-based techniques reduce the computational effort, but require an huge effort from the DM in terms of knowledge and experience of the problem in order to have adequate information. For these reasons the Pareto optimal solutions would be presented *a priori* or with interactive methods. Scalarization techniques are employed in the resolutions of MOFs problems in order to aggregate multiple OF and generate efficient solutions for DM evaluation (in generating methods) or to include the DM's preference parameters. They basically consist in optimizing a surrogate scalar function. The most used scalarization methods are reported below [73].

- *Weighting method.* It consists in optimizing a weighted sum of the M OF (Equation 3.8). The individual optima of each objective represent the extreme points of the non-dominated surface. Varying the weights w_m allows navigating in the optimal solution domain. For applying this method, it is important that the scales of the OF are comparable. The major limitation is the lack or robustness: a small change in the weighting coefficients may lead to big differences in the OF values.

$$\mathit{Optimize}\;\; F(\boldsymbol{x}) = \sum_{m=1}^{M} w_m F_m(\boldsymbol{x}), \;\; w_m \geq 0 \tag{3.8}$$

- *Constraint method.* It consists in optimizing a given OF considering the others as constraints (Equation 3.9). The DM decides the most important n-objective and assign lower bounds ϵ_m to the other *m-1* OF. The Pareto set is generated by changing the value of ϵ.

$$\begin{aligned} &\mathit{Optimize}\;\; F_n(\boldsymbol{x}) \\ &\mathit{subject\ to}\; F_m(\boldsymbol{x}) \leq \epsilon_m,\; m = \{1,2,...,M\},\; m \neq n \end{aligned} \tag{3.9}$$

- *Weighted metric method.* It can be defined an *a priori* preference-based method. The aim is to find an efficient solution near to the one desired by the DM according to a given metric p. Therefore, it is based on the minimization of a distance from a reference expected goal z_m, as expressed by Equation 3.10.

This method requires the independent calculation of the ideal value of OF. For small p, not all Pareto-optimal solutions may be obtained, while for high p the problem becomes non-differentiable.

$$Optimize \;\; l_p(\boldsymbol{x}) = (\sum_{m=1}^{M} w_m |F_m(\boldsymbol{x}) - z_m|^p)^{1/p} \tag{3.10}$$

- *Interactive methods.* In interactive methods, the DM's preference information are incorporated into the parameters of the surrogate scalar function. After the computation of the solution, a dialog session with the DM is included. The stopping criterion is generally linked to the degree of satisfaction with the obtained information.

3.2.3 Evolutionary methods

Another set of MOFs problems solution methods is the one linked to heuristic technique. Evolutionary algorithms are part of these, being very popular in optimization procedures due to their flexibility and ease of application [74]. They are based on the generation of populations of solutions at each iteration. Since the first aim of a MOFs problem is to find a feasible set of Pareto optimal solutions, the use of an Evolutionary Optimization (EO) procedure appears to be suitable and profitable. In fact, an entire Pareto set can be found in a single simulation, highlighting the multiple non-dominated and isolated solutions. The information of the valuable solutions pass from a generation to another, until finding all the trade-off solutions. The second step is always the evaluation of these solutions basing on qualitative or experience-driven criteria for comparing them and eventually make a choice.

The Elitist Non-dominated Sorting Genetic Algorithm (NSGA-II) is one of the most used EO procedures [75]. It is based on an elitist principle and diversity preserving methods, which means that the members in each population (i.e. a set of points on the design space) can be limited according to a rank; these elite members are controlled in order to include individuals that are relatively far on the front. The initial population is randomly generated, while the next generation of population is chosen using the non-dominated rank and a distance measure (i.e. crowding distance) of the individuals in the current generation. Individuals of the same rank with a higher distance have a higher chance of selection for maintaining diversity. The usual stopping criteria is the spread calculation, as a measure of the changing in the Pareto set.

The general NSGA-II flow is reproduced in Figure 3.4.

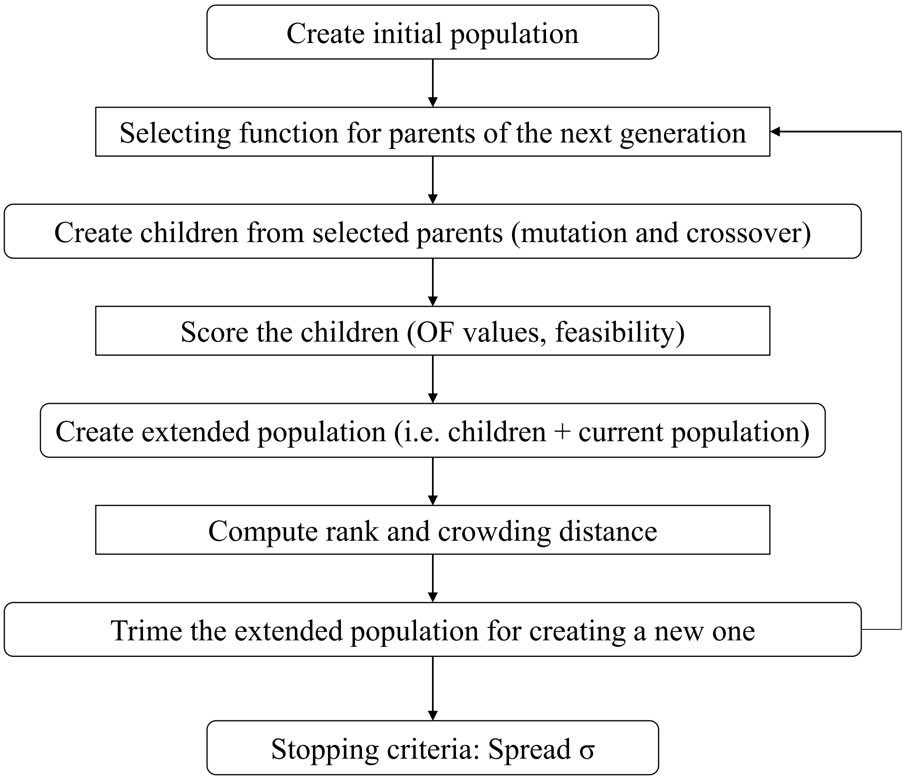


Figure 3.4: NSGA flow

Chapter 4

A material based view: Exergy Life Cycle of polymers

In this chapter, an example of an exergy-based resource accounting is presented for evaluating the life cycle of polymeric materials. A grave-to-cradle path for polymers is identified and thermodynamic recycling indexes are developed (Section 4.2). Then, the production and recycling routes are identified in detail for nine polymers of commercial interest, including material and energy flows (Section 4.3 and Section 4.4). The nine polymers are thus compared and ranked according to the global EE and the values of the thermodynamic indexes (Section 4.6.1 and Section 4.6.2). The results are then applied in a specific application for a thermodynamic assessment of vehicle plastic components (Section 4.5 and Section 4.6.3). The content, the methodology and the results of the present Chapter are largely based on the following work:

- Russo, S.; Valero, A.; Valero, A.; Iglesias-bil, M. Exergy-Based Assessment of Polymers Production and Recycling: An Application to the Automotive Sector. Energies 2021, 14, 363. https://doi.org/10.3390/en1402036

The data on polymers production and recycling collected in this Chapter are then used in the system analysis of Chapter 5, hence the decision to put this section first.

4.1 Introduction

Nowadays, polymeric materials are widely diffused in the everyday life of people all around the world. In the last decades, they have become a milestone of the industry and the economy, with a production of 57.9 million of tons in Europe in

2019. This constitutes only 16% of the global production, being Asia the major producer (51%) [76]. The spread of the worldwide use of plastic is strictly linked to the growth of the petrochemical industry. Currently, the major feedstock for polymers production is still coming from by-products of oil and gas refineries: heavy hydrocarbons (e.g., kerosene and naphtha) or saturated hydrocarbons (e.g., ethane and propane) [77]. According to an estimation of Hamman [78], between 1.3% and 2.1% of primary hydrocarbon resources consumed each year are diverted to hydrocarbon feedstock for the production of plastics world-wide. It corresponds to an average energy consumption (e.g., energy in the feedstock) of 45 MJ/kg of plastic. Moreover, the additional energy for processing the polymers ranges from 36 to 54 MJ/kg of plastic. Considering the European 2019 production, it means that between 0.531 and 0.797 Gtoe of primary energy have been invested for polymer manufacturing.

Despite polymeric materials are usually referred to as plastics, they are composed by a great variety of materials designed to cover the different needs of the end products. More than 350 different types of polymers are currently commercially available [79]. All polymers can be classified in one of the following two categories, depending on the polymerization process [80]:

- thermoplastics: a family of polymers that can be melted when heated and hardened when cooled in a reversible way;
- thermosets: include plastics that change their chemical structure with heat and so they cannot be reshaped.

As reported by a PlasticEurope survey [76], 29.1 Mt of plastics were collected as post-consumer waste in EU countries in 2018. Of these, 42.6% were sent to energy re-covery, 32.5% to recycling and 24.9% ended up in landfills. However, according to Crippa et al. [19], only 13% of the total volume collected for recycling reaches European converters, while 30% is exported without certified information on its final destiny. In general, the level of substitution of virgin material is low and often recycled plastics are used in applications requiring lower material quality [81].

Even if the major demand of plastic is for packaging (40%), about 10% of the produced polymers in Europe is used in the automotive sector [76, 82]. In the last 15 years, an impressive enhancement of End of Life Vehicles (EoLVs) occurred, due to the shortening of the cars average life, estimated in 1012 years [83]. According to a survey delivered by the EU commission [84], the EoLVs legally deregistered produce every year between 7 and 8 million tonnes of wastes; however, considering also the number of estimated unknown whereabouts vehicles, the total increases to 13 and 15 million tonnes of wastes. Furthermore, in the last 10 years, the percentage of plastic in vehicle increased, since the reduction in weight is justified by a decrease in fuel consumption; the current amount is between 15 and 17% of the car total weight and 50% of its volume [85]. Plastics in EoLVs are not recycled, apart from the amount that is incidentally reused during the pre-shredding phases of depollution and dismantling (e.g., tyres, bumpers, tanks), which does not exceed 25% of the total [86]. Considering an average weight of vehicle of 1250 kg, it means that 150 kg of mixed plastics per vehicle are discarded, shredded, and ultimately landfilled. Therefore, only in EU about 2 million of tonnes of plastic are dispersed every year due to the automotive sector, approximately 4 kg per person. For comparison, the average production of plastic packaging per year in EU is 31 kg per person [6].

Various examples of energy and environmental impact analysis of polymers production and recycling are present in literature. Results of Cumulative Energy Demand and CO_2 emissions are reported in [87] for many products of organic chemical industry, including a large number of polymers, starting with the extraction of resources and ending with the saleable material. In [88] a Life Cycle Assessment (LCA) and environmental impact of polymeric products is presented. An important contribution is represented by the PlasticEurope Eco-profiles [89] which include Life Cycle Inventory (LCI) datasets and Environmental Product Declarations (EPD) for plastics. LCA methodology has been widely used also for evaluating the polymers recycling chain. Environmental impact of PET bottle-to-fibre recycling is assessed in [90], comparing four recycling cases. A life-cycle impact of recycling PVC window frames is presented in [91]. An application of LCA to the products and processes involved in mechanical recycling of black HDPE is also re-ported in [92]. An application of LCA for quantifying the overall environmental performance of mechanical recycling of plastic containers in Italy is presented in [93]. Besides, examples of resource assessment analysis applied to the automotive sector are present. In [94] a resource efficiency comparison between a plug-in hybrid vehicle with a conventional combustion engine is carried out using a methodology that considers the pollution of the environment as well as the physical and socio-economic availability of resources. An assessment of strategic raw materials in the automotive sector is presented in [**Ortego2020**], including supply risk analysis. An interesting application is found in [95, 96], where thermodynamic rarity is used to rank the critical metals used in passenger car and as a weighting factor for assessing their downcycling. A comprehensive metal assessment of two passenger cars (conventional and battery electric models) in terms of mass and thermodynamic rarity is also presented in [97].

Research gap and objective

Currently, no examples are present of use of exergy for comparing the resources invested in producing polymers from virgin (i.e. primary) material with those from secondary materials through recycling. Besides, no applications are present for the thermodynamic assessment of vehicle plastic components. The aim of the analysis presented in this Chapter is to define and assess the exergy life cycle of polymeric materials and to develop exergy-based indicators comparing polymers production from primary and secondary raw materials. Besides, a thermodynamic assessment of the vehicle plastic components is performed with for obtaining useful information to develop recycling practices. The general scheme of the adopted methodology which will be detailed in the next Sections is presented in Figure 4.1.

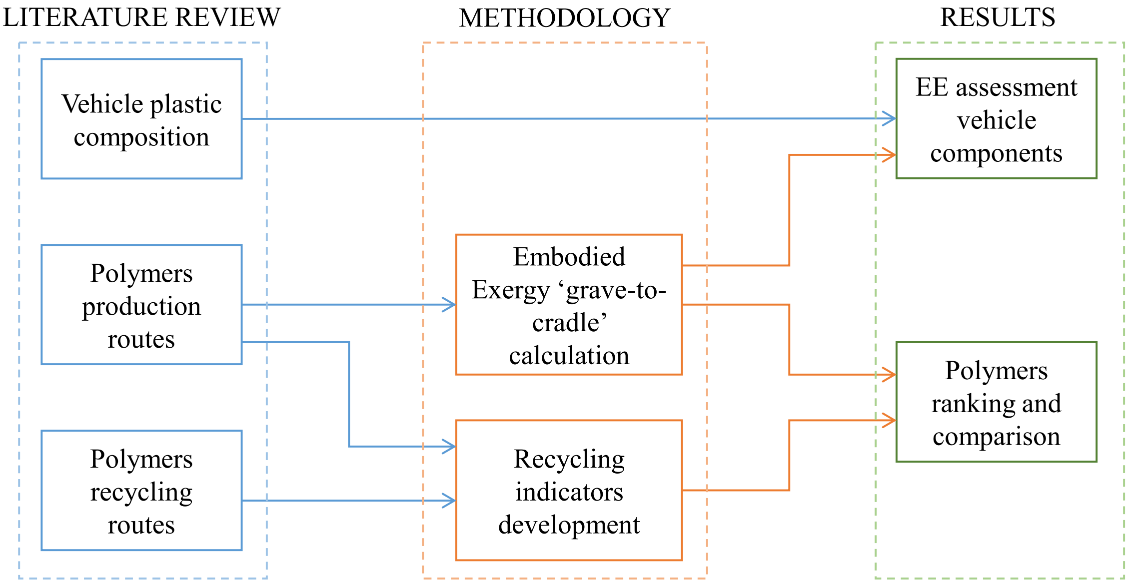


Figure 4.1: Research stages

4.2 Polymers production routes

As already said, the main feedstock for plastics production is still found in by-products of oil and gas refineries. Most of these hydrocarbons (e.g., naphtha, ethane, propane, gas oil) have little commercial value and must be separated and processed in order to obtain lightweight unsaturated olefins [77]. To this end, the most common process is the steam cracking [98]; the process energy demand is consistent and depends on the feedstock characteristics. Ethylene, propylene, butadiene, benzene, toluene and xylene are the main building blocks for creating the macromolecules of polymers and are mainly obtained by steam cracking of naphtha, gas oil or light hydrocarbons [87]. The creation of polymers from monomers is accomplished through the polymerization process. Temperature, pressure, catalysts and energy requirement vary in order to create the conditions for the building blocks to combine and bond. Catalysts can be used to start or speed up the reaction [99]. The most common mechanisms of polymerization are by addition or condensation. In addition polymerization (e.g., PE, PP and PVC) the growth of polymer occurs by reaction between a monomer and a reactive site; no by-products are generated. In condensation polymerization (e.g., PET, PA and PC), the reaction between the repeating unit and the growing chain produces by-products.

A brief description of the production routes identified for the 9 polymers analyzed in this work is reported below. Information are taken from an extent literature review [26, 87, 98, 100–102]. The selected polymers are among the most commercially diffused; they are also the ones with the highest weight percentage in the vehicle plastic composition presented in the next Sections.

- *Polyethylene/Polypropylene (PE/PP)*. Addition polymerization of ethylene (C_2H_4) for PE and propylene (C_3H_6) for PP, obtained from steam cracking of naphtha.

- *Polyvinyl Chloride (PVC)*. Chlorine (Cl_2) is extracted from salt (NaCl) by electrolysis and it reacts with ethylene for producing Ethylene Dichloride (EDC); cracking of EDC produces Vinyl Chloride Monomer (VCM) and HCl, which is used to produce additional EDC by oxychlorination. Polymerization of VCM occurs by addition in aqueous medium.

- *Acrylonitrile Butadiene Styrene (ABS)*. Emulsion polymerization of acrylonitrile, polybutadiene and styrene. Acrylonitrile (C_3H_3N) is obtained by the reaction between propylene and ammonia (derived from natural gas); polybutadiene comes from polymerization of butadiene (C_4H_6) from naphtha cracking; styrene is produced from ethylbenzene dehydrogenation.

- *Polyurethane (PU)*. Condensation polymerization between a diisocyanate (e.g., MDI) and a polyol. MDI production starts with a condensation reaction between aniline (C_6H_7N) and formaldehyde (CH_2O) for producing MDA, which reacts with phosgene ($COCl_2$) to produce MDI. A polyol is the result of an alkoxylation (ethylene oxide EO + OH group), with glycerine as initiator.

- *Polyamide 6.6 (PA6.6)*.Polycondensation between adipic acid and hexamethylene diamine (HMD). Adipic acid proceeds from benzene, KA oil and nitric acid, while HMD is produced from hydrogenation of adiponitrile (from benzene).

- *Polyethylene Terephthalate (PET)*. Polymerization of terephthalic acid (PTA) (or dimethyl ter-ephthalate DMT) and ethylene glycol (EG). PTA is obtained by oxidation of p-xylene (C_8H_{10}) with acetic acid as solvent, while EG ($C_2H_6O_2$) comes from hydrolysis of EO.

- *Styrene Butadiene Rubber (SBR)*. Polymerization of styrene and butadiene, followed by vulcanization with sulphur (S).

- *Ethylene Propylene Diene Rubber (EPDR)*. Solution polymerization of ethylene, propylene and diene (e.g., hexadiene C_6H_{10}), followed by vulcanization with S or peroxide.

The sum of all the contributions in terms of materials and exergy invested in the different steps of polymer production chain gives the Embodied Exergy (EE) of the materials, as reported in Table 4.1. The exergy data are expressed in MJ of exergy/kg of final product (i.e., polymeric material). The energy consumption is divided into direct fossil fuel use, electricity and heat. The chemical exergy of fossil fuel is calculated by means of the Szargut correction factor ϕ of Lower Heating Value (LHV) (Equation 4.1) [29]. The method is applied also for calculating the feedstock exergy of polymers, namely the primary exergy of the initial fossil fuel embodied in the final product. The value of ϕ is 1.06 for oil fuel and 1.04 for natural gas, while for each polymer it is evaluated for fuels with $O/C < 0.667$, according to the ultimate analysis (carbon C, hydrogen H, oxygen O and nitrogen N). Heat refers to steam consumption and its exergy is evaluated as the sum of the physical exergy at the given T and p conditions and the chemical exergy of liquid water, namely 50 kJ/kg. If the conditions are not specified in literature, steam is considered saturated at 16 atm.

$$\phi_{dry} = 1.0437 + 0.1882\frac{H}{C} + 0.061\frac{O}{C} + 0.0404\frac{N}{C} \tag{4.1}$$

4.3 Polymers recycling routes

Recycling methods are usually referred to as primary, secondary, tertiary and quaternary recycling [110]. Primary and secondary recycling techniques are based on mechanical treatment of discarded polymers in order to obtain the starting material. The primary recycling is usually performed by the manufacturer itself for post-industrial waste (closed-loop recycling) [81]. The secondary recycling is the most common and involves a series of steps after collection, namely cleaning, drying, shredding, contaminant separation, addition of additives, agglomeration, pelletization and extrusion. The mechanical characteristics of recycled polymers can be degraded, so that they are commonly used in manufacturing less value products [19]. Only thermoplastic polymers can undergo mechanical recycling because they can be remelted and reprocessed into end products [111]. Tertiary recycling consists in the recovering of monomers through depolymerization processes, such as solvolysis, thermolysis and pyrolysis (thermal recycling) or glycolysis and methanolysis (chemical recycling). Many thermosets plastics can be chemically recycled in order to recover their constituent molecules [110]. The expression quaternary recycling is used to indicate the energy recovery from plastics through incineration [111].

Due to the variety of existing recycling processes, an extent literature review has been performed in order to identify the most suitable considering the hypothetical application to vehicle plastic recycling. A brief description of the recycling processes and the associated exergy consumption (expressed in MJ of exergy per kg of recycled material) are reported in Table 4.2.

Table 4.1: Material and exergy flows in polymers production processes

Polymer	**Yield of products**	**Ratio[(5)](kg/kg)**	**Process phases**	**Exergy consumption (MJ_{ex}/kg_{pol})**				**Ref.**
				Fuel	**Electricity**	**Heat**	**Water**	
	Naphtha/Ethylene	3.34	Ethylene production	21.7	0.3			
PE							0.145	[87, 98, 100, 103]
	Ethylene/PE	1.02	Polymerization		1.2			
			Feedstock	48				
	Naphtha/Propylene	5.74	Propylene production	37.2	0.6			
PP							0.115	[87, 98, 103]
	Propylene/PP	1.02	Polymerization		1.2			
			Feedstock	48				
	Naphtha/Ethylene	3.34	Ethylene production	11.1	0.16			
PVC	Chlorine/VCM	0.64	Chlorine extraction		9.34		0.155	[26, 87, 103, 104]
	Ethylene/VCM	0.49	VCM production	0.045	0.77	1.7[(1)]		
	VCM/PVC	1.065	PVC polymerization		0.83	1.5		
			Feedstock	20.5				
	Propylene/Acrylonitrile	0.75	Acrylonitrile production	14.2	0.19			
							0.2	[26, 87, 101]
ABS	Naphtha/Polybutadiene	27.7	Polybutadiene production	12.6	0.2			
	EB/Styrene	1.066	Styrene production	35	0.61	3.52[(2)]		
	Styrene/ABS	0.56	Polymerization	0.95	2	0.56		
			Feedstock	47.2				
	Benzene/MDI	0.407	MDI production	20.3	0.45	0.75[(3)]		
PU	PO/Polyol	0.8	Polyol production	17.7	0.15	0.19[(3)]		[102, 105]
	PO/PU	0.39	Polymerization		1.5			
	MDI/PU	0.62						
			Feedstock	42.3				
	Benzene/Adipic acid	0.7	HMD and adipic acid production	79.1				
							7	
PA66	Adipic acid/HMD	0.93						[103, 106]
	Adipic acid/PA	0.65	Polymerization		4	9.26[(3)]		
	HMD/PA	0.52						
			Feedstock	33				
	Ethylene/EG	0.63	EG production	5.71	0.43	0.9[(3)]		
PET	p-xylene/PTA	0.54	PTA production	63.5	1.3	1.1[(3)]		[87, 100, 103, 107, 108]
	PTA/PET	0.85	Polymerization	3.5				
	EG/PET	0.33						
			Feedstock	25.2				
	EB/Styrene	1.066	Styrene production	17.6	0.37	1.6[(2)]		
							0.18	
SBR	Naphtha/Butadiene	27.7	Butadiene production	45.05	0.7			[87, 101, 103]
	Styrene/SBR	0.25	Polymerization	1.9	1.9	3.9[(2)])		
	Butadiene/SBR	0.75						
			Feedstock	45				
	Naphtha/Ethylene	3.34	Ethylene production	9.04	0.14			
	Naphtha/Propylene	5.74	Propylene production	15.5	0.24			
	Ethylene/Hexadiene	0.715						
EPDM	Butadiene/Hexadiene	0.715	Hexadiene production	21.2	0.32			[87, 103, 109]
	Ethylene/EPDM	0.68						
	Propylene/EPDM	0.273	Polymerization		3.9	5.56[(4)]		
	Hexadiene/EPDM	0.047						
			Feedstock	45.5				

(1) Steam at saturated conditions at 13 atm. (2) Steam at 720 C and 42 atm. (3) Steam at saturated conditions at 16 atm. (4) Steam at saturated conditions at 18 atm (5) kg of products/kg of reactant

4.4 A grave-to-cradle approach for polymers

In order to calculate the exergy invested along the entire polymer production chain, some assumptions are made on its structure. According to the grave-to-cradle path [50], polymers production phases are considered as follows: (i) polymerization;

Table 4.2: Recycling processes for polymers.

Polymer	Type of Recycling	Process description	Exergy Consumption (MJex/kg)	Ref.
PE/PP	Secondary	Compacting, sorting and reprocessing phases are included. The reprocessing generally occurs by conventional melt filtration extrusion into granules. The temperature of extrusion will fall between the melting point of the polymer and the onset of any thermal degradation to prevent excessive damage to the plastic.	• Fuel 0.71 • Electricity 2.2 • Water 0.09	[80, 93, 111]
	Tertiary	Polyaddition polymers cannot be recycled on its monomer content. As a consequence, feedstock recycling is performed by low temperature pyrolysis in fluidized bed reactor. Process products include heavy fractions, naphtha, C3/C4 compound, sand, CaO, CaCl.	• Fuel 0.23 • Electricity 0.42 • Water 0.1 • CaO 2.3	[93, 111]
PVC	Secondary	An example of recycling of post-consumer PVC window frames is assumed as reference process. The waste is first shredded, manually sorted, granulated into chips and then converted into powder in order to allow blending with other grades of PVC for extrusion.	• Fuel 0.14 • Electricity 1.1	[91]
	Tertiary	Among the others, the NKT process is chosen as reference. The chemical and thermal degradation of the PVC waste takes place in a reactor at low pressure (23 bar) and moderate temperatures (maximum 375 C). The products of the process are: calcium chloride, coke, metal concentrate, organic condensate.	• Fuel 0.11 • Electricity 0.13	[112]
ABS	Secondary	Only few applications of ABS recycling are reported in literature; secondary re-cycling via injection moulding appears a viable solution.	• Fuel 2.3	[113]
PU	Tertiary	A closed-loop recycling for PU foam is taken as reference, which consists in a split-phase glycolysis. The compacted PU foam pellets are charged into a stirred batch reactor containing diethylene glycol (DEG) in presence of catalysts at a temperature of 200 C. Then the DEG and the polyols are separated and are used as raw materials for new polymers.	• Fuel 5.3	[114]
PA6.6	Tertiary	Applications mainly relates to carpet recycling. The most common techniques are ammonolysis and hydrolysis in concentrated sulfuric acid.	• Fuel 10.3	[113]
PET	Secondary	PET reprocessing process consists in a first section to remove impurities (pre-washing, magnetic separation, x-ray separation of PVC) and in a second to recover PET and by-products (HDPE and fines) by flotation. The material is then dried, screened and stored.	• Fuel 2.7 • Electricity 1.3 • Water 0.15	[93]
	Tertiary	The considered depolymerisation process is methanolysis for DMT recovery. The reaction occurs in presence of catalysts and the DMT is recovered by precipitation, centrifugation and crystallization.	• Fuel 16.8 • Methanol 22	[90]
SBR/EPDM	Tertiary	Devulcanization is the most delicate phase, because a selective rupture of sulphur bonds (S-S or C-S) must be achieved without breaking the hydro-carbon bonds. The most common method is a thermal process carried out in steam-heated autoclave at a certain temperature (225 C) and pressure (2830 bar) in presence of catalysts.	• Fuel 11.4	[115]

(ii) production of monomers or building blocks from oil and gas heavy by-products (referred as naphtha); (iii) production of naphtha from fossil fuel (referred as coal); (iv) fossil fuels from organic matter (referred as wood). Figure 4.2 offers a visual representation of the various steps. The first two phases have been described in

Section 4.2; details on phase (iii) and (iv) are reported below.

- *Naphtha from coal.* Naphtha is produced from the processing of fossil fuels [116]. Although the most common commercial route is the one from petroleum refinery, there are historical examples of naphtha production from coal through direct liquefaction or Fisher Trops (FT) reaction as well as from destructive distillation of biomass [117]. In this work fossil fuel is modelled as coal since it appears inclusive of all the characteristics of the generic fossil fuel. Therefore, direct liquefaction from coal is assumed, resulting the most efficient process in terms of yield of naphtha (i.e., 10%, considering that the black sub-bituminous coal and the lignite are more suitable for this process). The invested fossil energy for naphtha production (excluding the feedstock energy) is 38 MJ/kg of naphtha [116].

- *Coal from wood.* Coal is chosen in the model also for its convenience at the time of calculating the Exergy Replacement Cost (ERC), presenting a more stable composition than oil. In its general definition, the ERC corresponds to the natural bonus of having resources concentrated in a deposit. The ERC of fossil fuels has not been previously considered by Valero and Valero due to the impossibility of reproducing the photosynthetic process that once created the resource [52]. This makes sense if oil, coal and natural gas are considered strictly as fuels, which are destined to be finally burned. Anyway, if fossil fuels are used as raw materials, as in the case of polymer production, it becomes theoretically possible to come back to the cradle with recycling. According to Whiting and Carmona [117], the ERC of fossil fuels can be evaluated considering the cumulative exergy cost of equivalent fossil fuels (first generation bio-fuels) production (e.g., bioethanol for gasoline, biogas for natural gas, biochar for coal); furthermore, they extend the boundary of the analysis including the solar radiation to crop factor to ERC calculation. In this work, only the crop to fuel part of the described ERC is taken, which represents the exergy invested in processing and concentrating the natural primary resources into viable deposits. In line with [117], charcoal produced from timber is considered as the alternative bio-fuel for ERC evaluation; the invested exergy is composed by the feedstock exergy of the biomass, 54.5 MJ/kg of coal, and an external contribution for the process amounting to 28.1 MJ/kg of coal. All the previously reported values of invested energy refer to the main product unit (i.e., by-products are not included in the calculation).

4.4.1 Thermodynamic recycling indexes

In order to evaluate the recycling process, exergy-based recycling indexes are developed, depending on the final product, namely the new crude polymeric material

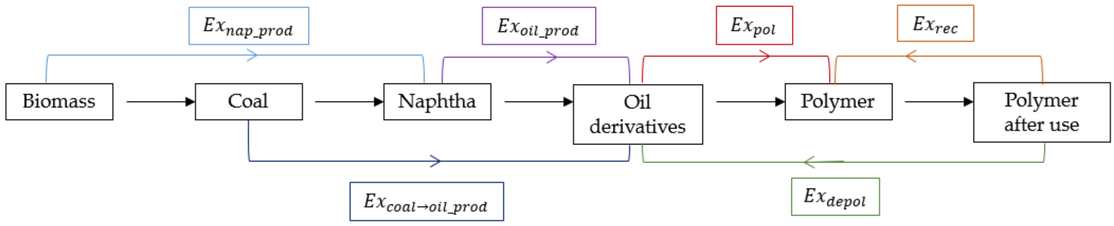


Figure 4.2: Exergy flow chart of polymer life cycle

(i.e. primary product) or the oil derivatives (i.e. secondary products). Examples of developing exergy-based indicators for products life cycle are present in [118].

Figure 4.2 can be useful for understanding the exergy flows. A new polymer can be obtained by mechanical recycling (as in the case of PE, PP, PVC, ABS and PET) or via chemical recycling through decomposition into the constituent macro-molecules and consequent re-polymerization (as for PU, PA6.6, PET, SBR, EPDM). According to this, different recycling indexes are adopted:

- REC_{mec}. The mechanical recycling index (Equation 4.2) is defined as a comparison between the embodied exergy of the mechanical recycling ($\mathrm{Ex_{rec}}$) and the exergy of the production from virgin material, starting from naphtha, ($\mathrm{Ex_{oil\ prod}}$+$\mathrm{Ex_{pol}}$).

- REC_{ter}. The tertiary recycling index (Equation 4.3) is defined as the ratio between the exergy necessary for re-obtaining the polymer via depolymerization ($\mathrm{Ex_{depol}}$+$\mathrm{Ex_{pol}}$) and the one for producing it from naphtha.

- REC_{gl}. The global recycling index (Equation 4.4) is calculated as the ratio between the embodied exergy of the recycling (secondary or tertiary) and the one of the entire production chain starting from the biomass, in order to give a broader order of magnitude.

- REC_{ch}. The chemical recycling index (Equation 4.5) compares the embodied exergy of the production of oil derivatives from polymers ($\mathrm{Ex_{depol}}$) with the one from fossil fuel ($\mathrm{Ex_{coal \to oil\ prod}}$). This indicator is introduced since, for some polymers (PE, PP, PVC), the chemical recycling consists in a decomposition into secondary products (hydrocarbon molecules).

$$REC_{mec} = \frac{Ex_{rec}}{Ex_{oil.prod} + Ex_{pol}}$$

$$REC_{ter} = \frac{Ex_{depol} + Ex_{pol}}{Ex_{oil.prod} + Ex_{pol}}$$

$$REC_{gl} = \frac{Ex_{rec}(or\ Ex_{depol} + Ex_{pol})}{Ex_{nap.prod} + Ex_{oil.prod} + Ex_{pol}}$$

$$REC_{ch} = \frac{Ex_{depol}}{Ex_{coal \to oilprod}}$$

It has to be considered that these indexes are strictly relative to the processes of materials manufacturing and recycling; they do not take into account the exergy invested in dismantling the end-of-life products or collecting and transporting the waste materials. The values of the indexes are given in percentage; low values mean that the recycling process is advantageous in terms of invested exergy compared to production from virgin materials.

4.5 Polymers in vehicles

Data on polymeric composition of vehicles are provided by SEAT S.A. They refer to a 2017 SEAT Leon model of approximately 1270 kg, of which 16.6% are non-metallic materials (i.e., glass, polymers and ceramics). As reported in Table 4.3, 21 polymers are identified, composed by 14 thermoplastics and 9 thermosets. Adhesives and resins are not included (even if they can be polymer-based materials). The vehicle plastic composition is compared with data found in the literature, showing good accordance for typology and quantity of polymers. Only the polymers with a weight percentage higher than 2% were chosen for the analysis, namely PE, PP, PVC, ABS, PU, PA6.6, PET, SBR and EPDM. They also occur to be between the most commercially diffused and with existent recycling practices.

4.5.1 Vehicle components

The developed thermodynamic concepts and values are used for the analysis of the plastic content of a vehicle. In addition to the data on the total polymeric material contained in a SEAT Leon, the composition of some vehicle components has been provided by SEAT S.A., as reported in Table 4.4.The analysed car parts are chosen between the ones with significant plastic content as well as for their facility at the time of being eventually removed for recycling.

Table 4.3: Polymers in 2017 SEAT Leon vehicle according to category

Polymer	**kg**	**% on Total Plastic**
Thermoplastic		
Polypropylene (PP)	72.3	34.2
Polyamide 66 (PA66)	22.9	10.9
Polyethylene Terephthalate (PET)	15	7
Polyethylene (PE)	12.1	5.7
Acrylonitrile Butadiene Styrene (ABS)	10.9	5.2
Polyvinyl Chloride (PVC)	4.8	2.3
Polycarbonate (PC)	4.1	1.9
Polyoxymethylene (POM)	2.3	1.1
Polysulfone (PES)	1.7	0.8
Polystyrene (PS)	1.1	0.5
Polyvinyl butyral (PVB)	1	0.5
Poly(methyl methacrylate) (PMMA)	0.7	0.3
Polyphenylene Sulfide (PPS)	0.4	0.2
Ethylene vinyl alcohol (EVOH)	0.1	0.1
Thermosets		
Styrene-Butadiene Rubber (SBR)	31.4	14.9
Polyurethane (PU)	17.2	8
Ethylene Propylene Diene Rubber (EPDM)	12.2	5.8
Vinyl Methyl Silicone (VMQ)	0.45	0.2
Fluoroelastomer (FKM)	0.28	0.1
Polyacrylic rubber (ACM)	0.17	0.1
Epichlorohydrin rubber (ECO)	0.11	0.05
Total	211.2	
% on total car weight	16.6	

Many vehicle polymers incorporate additives for enhancing mechanical characteristics, strength, fire resistance or for colouring [119]. The composition of some of these chemical substances is not declared by producers, which only report the weight content. The most common declared additive are the ones reported in Table 4.5; their feedstock exergy has to be included in the calculation of the EE of the corresponding polymer.

The global EE of each car part is calculated, in order to account for the distribution among the various polymers. In case of no recycling and total shredding, the EE is totally dispersed. Therefore, the evaluation is useful also to give information at the time of planning recycling practices, together with the developed recycling indexes.

Table 4.4: Details on plastic composition of SEAT Leon components

Vehicle Part	Polymer	Weight (g)	Additive	Weight (g)
Rear bumper	PP	2627.3	-	-
	EPDM	1409	Talc	162.2
	PET	39.6	Titanium dioxide	0.3
	ABS	26.8	-	-
	PE	18.9	-	-
	PA6.6	3.3	-	-
	tot	4124.8	tot	162.5
	% on component weight*	78.5		
Dashboard	PP	3228.6	Talc	296.6
			Glass fibre	2865.4
	PE	618.2	-	-
	PU	611.2	-	-
	PVC	511.6	-	-
	PET	6.6	-	-
	tot	5035.9	tot	3162
	% on component weight*	90.5		
Floor covering	PET	1808.4	-	-
	PP	581.3	-	-
	PE	219.1	-	-
	SBR	48.6	Glass fibre	105.2
	PA6.6	23.9	Glass fibre	3.2
	tot	2681.2	tot	108.4
	% on component weight*	86.9		
Instrumental cluster	ABS	237	Carbon black	1.19
			Glass fibre	0.27
	PP	53.3	Talc	38.4
	PET	5.9	Titanium dioxide	0.58
			Glass fibre	1.55
			Carbon black	0.04
	PA6.6	4.2	Glass fibre	0.78
	tot	300.4	tot	42.8
	% on component weight*	46.5		

(*)It refers to polymers with additives

Table 4.5: Composition of the major additives in vehicle polymers

Additive	Chemical Formula	Chemical Exergy (MJ/kg)	Ref.
Talc (Magnesium silicate)	$Mg_3H_2(SiO_3)_4$	0.096	[29]
Titanium dioxide	TiO_2	0.28	[120]
Glass fibre	Combination of SiO_2, CaO, Al_2O_3, B_2O_3, Na_2O, MgO, FeO, TiO_2, F_2	0.97	[29, 119, 120]
Carbon black	C	34.2	[29]

4.6 Results

4.6.1 Comparison of Polymer Production EE

First, the global EE of the polymers production chain (from Biomass to Polymer in Figure 4.2) is calculated (Figure 4.4), evaluating the contribution of each step of the process (Figure 4.3). Results show a wide range of values of EE for the analyzed polymers, ranging from 0.036 toe/kg of PVC to 0.479 toe/kg of SBR.

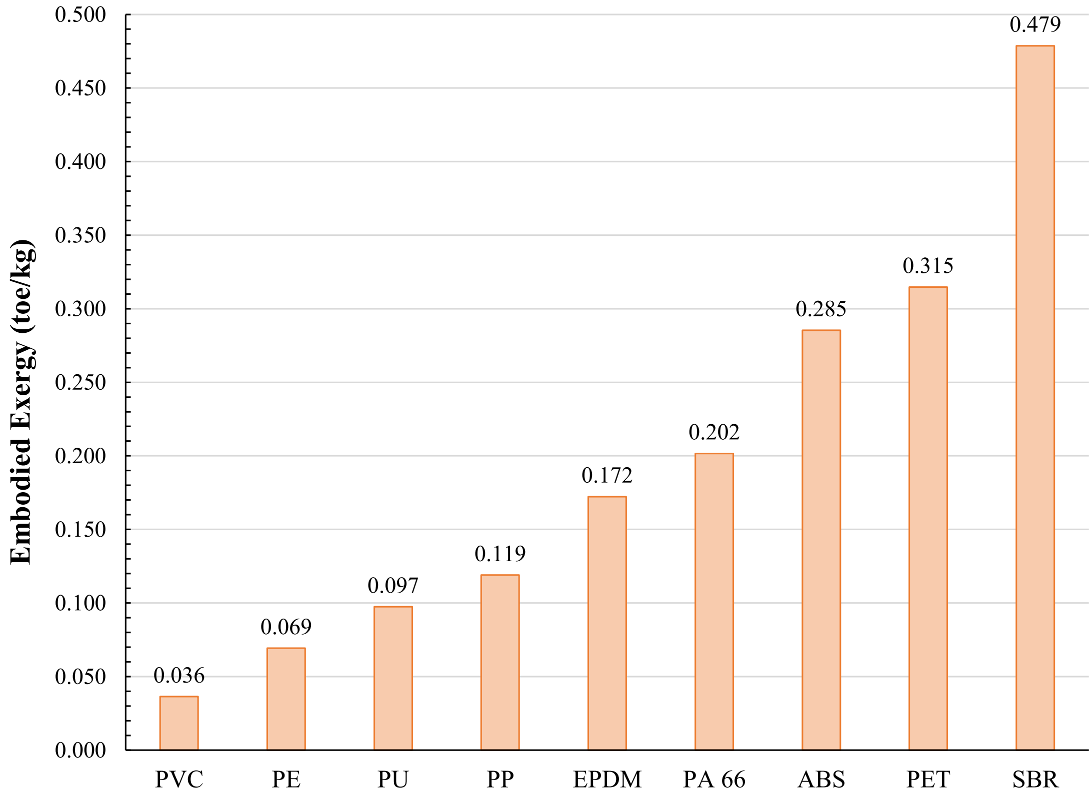


Figure 4.3: Global Embodied Exergy of polymers

The average values of percentage contribution of each step to the global EE are reported in Figure 4.4. The repartition is similar for all polymers, with approximately 60% of exergy embodied in the biomass for coal production, 32% in the external contribution to the biomass-to-coal process, 4% in naphtha production from coal and the remaining 4% in polymerization process and feedstock. The major differences between polymers are linked to feedstock and process exergy, which strongly influence the global balance. The polyolefin (PE, PP, PVC) and the PU have the lowest values of EE, since the production processes are quite plain and the major constituent hydrocarbons (ethylene and propylene) have high yield from naphtha. An increase in the complexity of the molecules lead to a growth in the process exergy as well as in the quantity of required primary fossil fuel. This is the case of ABS, SBR and PET and, to a lesser extent, of PA6.6 and EPDM. The use of butadiene represents the major burden in the production of ABS (20 wt% of butadiene) and SBR (75 wt%), since it has a particularly low yield from naphtha (1:27); butadiene is present also in EPDM, even in lower quantities (10 wt%). The second more influencing factor is the presence of benzene (yield from naphtha 1:12) for styrene production. Despite its large commercial use, PET is the second most important in terms of global EE; in fact, the production of PTA requires para-xylene, which is extracted from heavy reformate of naphtha with very low yield (4 wt%).

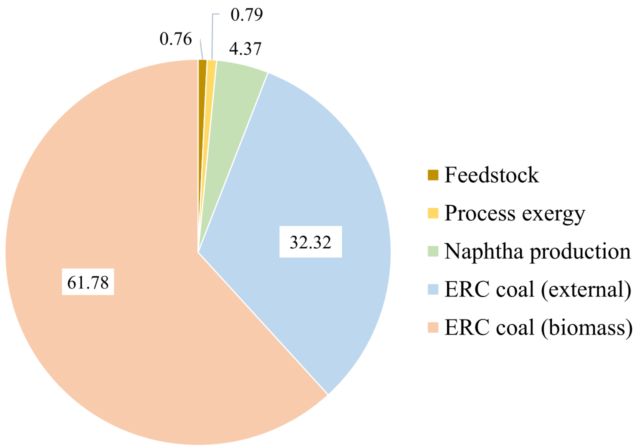
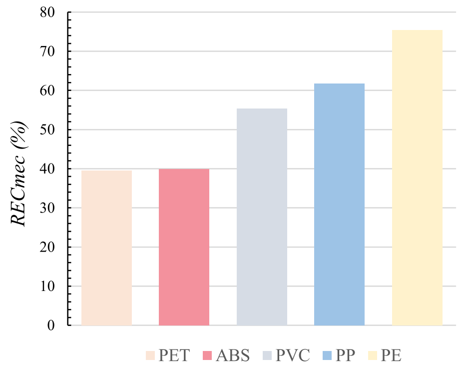


Figure 4.4: Incidence of each step of the production chain

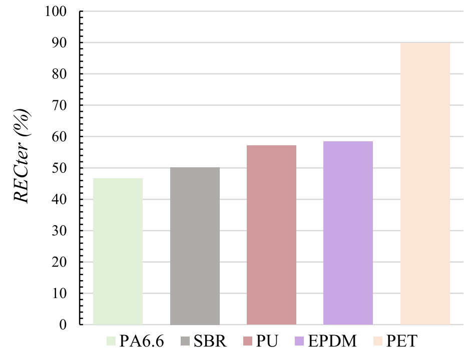
4.6.2 Comparison of Recycling Indexes

According to the data reported in Section 4.6.1, the thermodynamic recycling indexes are calculated for each polymer. Results are graphically reported in Figure 4.5.

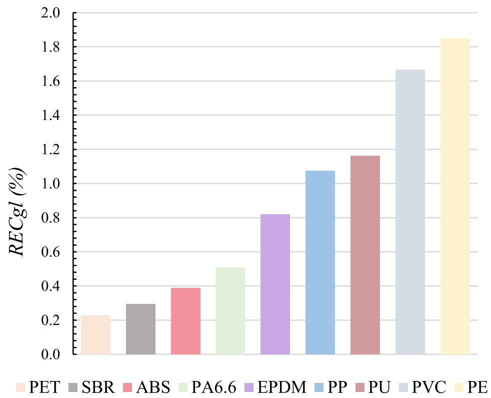
Among the polyolefin, PE is the one with the highest REC_{mec}(75%), followed by PP, PVC and ABS. Mechanical recycling is the most convenient option for PET, with an exergy saving of about 60% with respect to production from virgin materials; on the other hand, recycling through depolymerization appears not so convenient, since the value of REC_{ter} is about 89%. This picture is confirmed by the real practice since PET is one of the most mechanically recycled polymers (other than one of the most diffused). In terms of tertiary recycling, PA6.6 has the lowest value of REC_{ter}, less than 50%. This should encourage the recycling of polyamide, better if in closed loop, which is not so diffused so far. Even the values of REC_{ter}



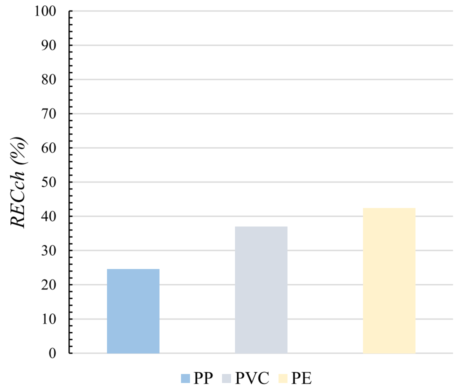
(a) Mechanical recycling index



(b) Tertiary recycling index



(c) Global recycling index



(d) Chemical recycling index

Figure 4.5: Exergy-based recycling indexes for polymers

of rubbers (50% for SBR and 58% for EPDM) appear not as high as for justifying the almost total absence of recycling practices in the world. Looking at the broader vision, the values of REC_{gl} are quite low as expected. In fact, the exergy invested in the recycling process is less than 2% of the total exergy necessary for obtaining the polymer from virgin material, starting from the primary exergy of the biomass. Finally, it is interesting to notice the values of REC_{ch} of the polyolefin (24.6% for PP, 42.4% for PE and 37% for PVC). Considering this quite low exergy cost of the petrochemicals production, the depolymerization could be a promising solution for obtaining secondary products to sell in the market if the mechanical recycling is not possible. It has to be considered that all these values refer to the processes only, excluding the collection and transport exergy cost of waste polymers as well as raw materials.

4.6.3 Thermodynamic Assessment of Vehicle Plastic Components

Comparison between plastics and metals

A first thermodynamic assessment of the vehicle is conducted by calculating the global EE in the vehicle polymeric content. Results are reported in Table 4.6, where a comparison with the rarity of the metals is presented [96]. It is evident that the exergy embodied in the polymeric materials is several orders of magnitude greater than the metals rarity. However, the analysis of the contribution of the single steps highlights that the exergy associated to the processing from raw materials is pretty similar. The real difference is represented by the ERC of fossil fuel. In fact, the grave-to-cradle path for theoretically reintroducing the fossil fuel derivatives into their dead state (so in the condition where they are organic materials) is much more complicated and exergy intensive than the re-concentration of minerals from the Thanatia′s grave.

Table 4.6: Contribution of plastic to the embodied exergy of the entire vehicle

Polymers	Global EE (GJ)	EE of Vehicle (GJ/Ton)	Feedstock and Processing (from Naphtha to Polymer) (GJ)	ERC of Fossil Fuel (from Wood to Naphtha) (GJ)
	1715.9	1351.1	18.3	1697.6
Metals	Total rarity (GJ)	Rarity of vehicle (GJ/ton)	Beneficiation, smelting and refining (from mine to market) GJ	ERC of minerals (GJ)
	148.7	117.1	19.7	129

EE distribution

According to the material composition reported in Table 4.3, the total EE of the four vehicle components plastic content is calculated (the EE of additives is included). A comparison with the specific values (referred to the total amount of polymers) is reported in Figure 4.6. The highest value (0.8 toe) associated to the floor covering is due to the presence of a large quantity of PET (83.5% of the total EE), which is the polymer with the highest values of EE together with SBR (also present in this component). Floor covering is the third component in terms of weight between the analyzed, so its specific EE value (0.29 toe/kg) is higher than the one of dashboard (0.07 toe/kg) and rear bumper (0.16 toe/kg). On the other hand, the instrumental cluster has the lowest value of global EE (0.09 toe), since its weight is considerably lower than the others; this also implies that its EE specific value is high (0.26 toe/kg) since the resources are more concentrated. The dashboard has the highest weight and the smallest EE specific value (0.07 toe/kg), but its total EE (0.6 toe) is lower than the one of the floor covering and the rear bumper, since it is mainly composed by PP.

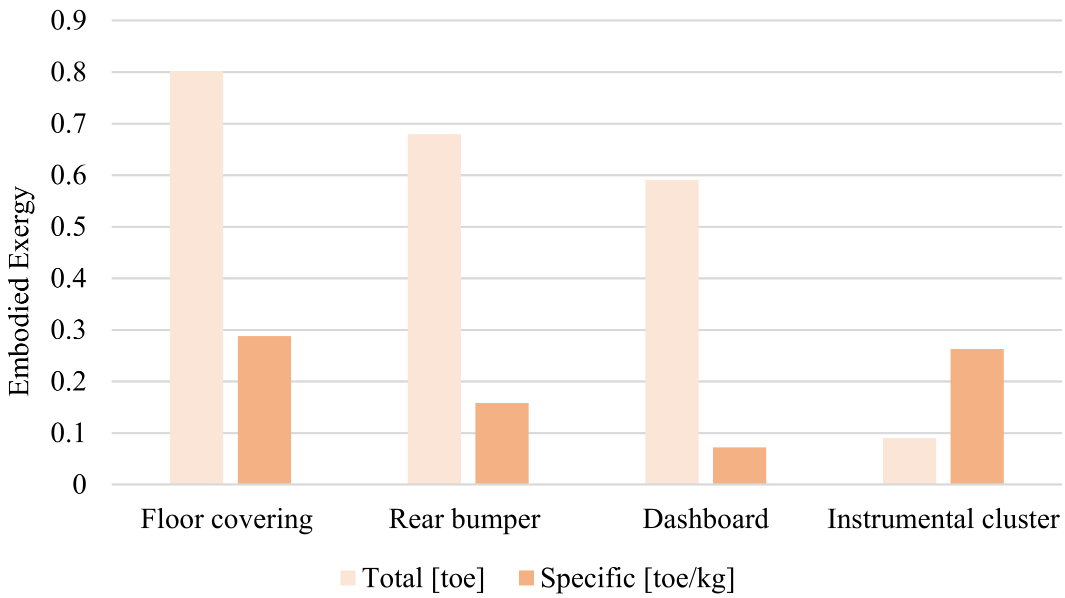


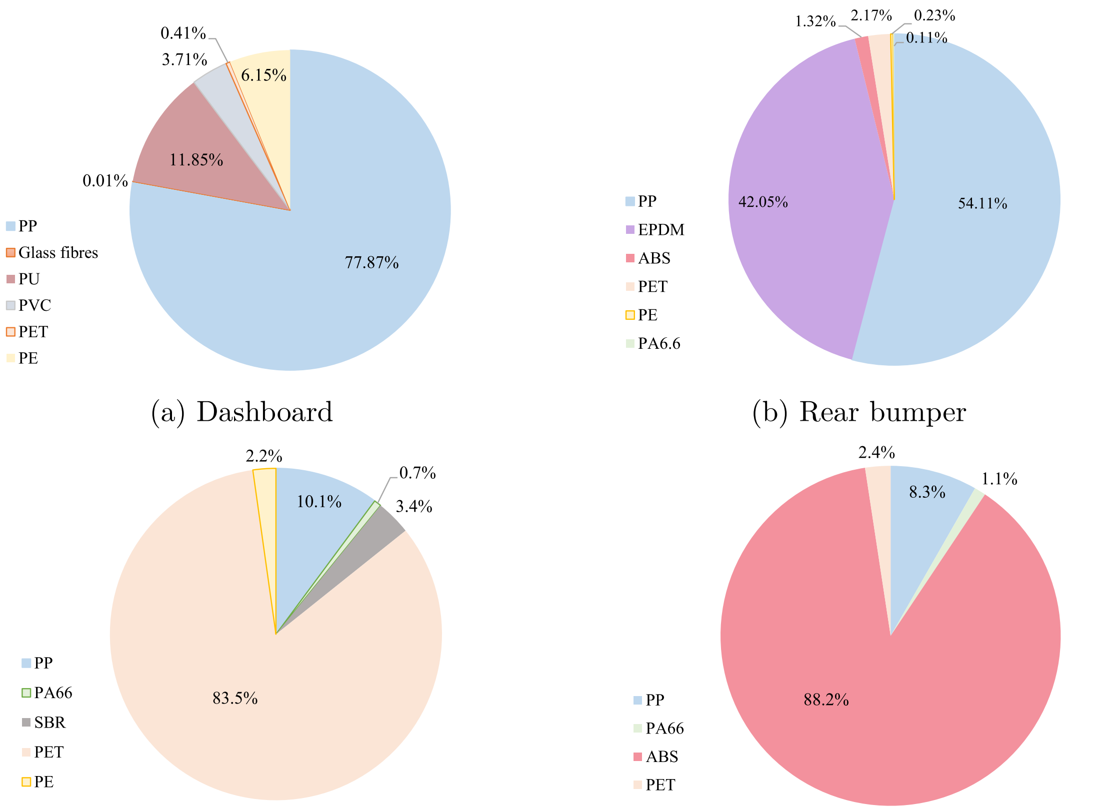
Figure 4.6: Comparison between total and specific EE values of vehicle components polymeric content

Figure 4.7 reports the detailed distribution of the EE between the constituting polymers of the components.

4.7 Conclusions and discussion

An exergy-based assessment of polymeric materials has been performed in order to compare the resources invested in producing polymers from virgin material with those from secondary materials through recycling. Besides, the calculated data have been used to analyze the plastic composition of vehicle components with the aim of obtaining useful information for recycling practices.

First, the global Embodied Exergy of 9 different polymers has been calculated tracking back the exergy invested in the production process, considering polymerization, naphtha production from fossil fuel and Exergy Replacement Cost of coal. The set of analyzed polymers have been chosen between the most commercially diffused ones with a weight percentage higher than 2% basing on the plastic composition of a 2017 SEAT Leon vehicle. Data on the best available production and recycling processes have been collected and exergy-based recycling indicators have been defined and calculated for each polymer, according to the type of recycling



(a) Dashboard (b) Rear bumper (c) Floor covering (d) Instrumental cluster

Figure 4.7: EE distribution between constituting polymers of vehicle components

(secondary or tertiary) and the nature of the final products (new polymer or secondary materials). Finally, a thermodynamic assessment of the plastic content of some vehicle components is presented. The main conclusions and outcomes are discussed below.

- Enlarging the system boundaries so as to include the entire production chain (i.e. until the 'cradle') has given its benefits in terms of understanding the resources allocation. In facts, it shows that the major exergy investment occurs in the first steps where the primary natural resources (e.g. biomass) are concentrated in form of fossil fuel to be further utilized. Of course, it is an 'hidden cost' since no one has to practically pay for it, being thus a natural bonus. However, quantifying this natural process in energy terms gives the measure of how precious fossil fuels are and which is the cost that would be paid if they will disappear from the Earth's crust. Then, during the strictly polymers production phases, the complexity of the processes for obtaining the constituent molecules is what distinguishes and determines the polymers total EE.

- The scenario resulting from the recycling indexes comparison confirms as quite convenient some practices that are already in use, such as the mechanical recycling of PET or of some polyolefin (PP, PVC) over the chemical one. Besides, it also suggests that some scarcely diffused recycling processes are not so prohibitive from an exergy perspective, at least considering the comparison with the production process from virgin materials. Even if the transport and collection of waste polymers is not accounted for in the calculation of the EE, the fact that all the recycling indexes are lower than 100% (some of them even significantly) leaves a positive margin for a possible additional exergy consumption, remaining advantageous the recycling path. This is even more marked in the comparison of the recycling process with the entire production chain (i.e. starting from the biomass up to the polymer), being the values of REC_{gl} in the order of 2%. All these factors are an encouragement not only to pursue and improve recycling technologies, but also to optimize the connection between the waste companies and the recycling plants and in general all the intermediate producers. The idea, confirmed also by real practices and experts interview, is that most of the times polymers recycling is hindered by logistical, bureaucratic and regulatory issues that not allow all the stakeholders to benefit from the real savings derived from recycling. Of course the matter is mostly, but not only, economic: the end use of recycled products can be limited also by technological issue (e.g., degradation of mechanical characteristics; required products design; necessity of different equipment for specific polymer recycling). However, the research of practical solutions for overcoming these limits is strictly linked to the presence of regulation and incentives to recycling practices.

- A controversial issue concerns the choice between chemical recycling and incineration with energy recovery. At the moment, chemical recycling is not a largely adopted alternative for its high costs and complexity since it requires dedicated plants, energy, reactants and systems for emission abatement. At the same time, the large diffusion of WtE plants makes them an easier and more convenient treatment alternative for not recycled plastics. The specificity of the context plays a fundamental role in defining the right choice. For certain polymers (e.g. thermosets) chemical recycling is the only option for recovering the macromolecules and it may be a good solution in the case their supply is difficult; it can be also an alternative for producers for initiating closed-loop recycling practices. The fact is different for polyolefins, for which the mechanical recycling is well developed and convenient and the depolymerization produces hydrocarbons (e.g. naphtha) that are quite common on the market.

- The application of a thermodynamic-based methodology to the practical field of EoLVs has given some interesting insights. In the first place, the calculation of the total exergy embodied in the vehicle plastic components gives an idea of the order of magnitude of the resources (expressed in MJ of exergy) that are definitively dispersed in case that the materials are not reused or recycled (i.e. landfill disposal or incineration). This means that the same amount of resources (i.e. EE of polymers) are needed in order to re-obtain the plastic parts; the aim of recycling is to recover the value and to spend only a percentage of the total resources for having the final products. The exergy-based methodology applied to the single component can be useful to reveal which polymer can be critical with respects to the others at the time of recycling. The polymeric composition is a fundamental factor in defining recycling practices. In theory, all the analyzed polymers are recyclable, in the sense that at least one recycling industrial process exists. In real practice the most recycled are PP, PE and PET. It allows the car producers to justify the inclusion of an increasing number and quantity of polymers in vehicles, complying with the normative on EoLVs. In reality, many factors influence the practical implementation of recycling of vehicle components:

- the compatibility with the other polymers and the difficulty in separating them;
- the presence of additives that can affect the recycling process;
- the form on which the polymer is present (e.g., PET in the floor covering is in form of fibre, which is not commonly recycled differently from the bottle PET material);
- the recycling volumes that can be achieved.

All these qualitative elements (together with the developed recycling indexes) have to be considered in order to better define the meaning of 'recyclability' for vehicle components.

Limitations and future developments

The presented values of EE for polymers can be useful for a first comparison of different options. For some polymers (i.e. PA6.6,PU, ABS,SBR) only limited information and aggregated data have been found in the literature for production and recycling process. An integration with practical knowledge from industries would be recommended. Moreover, an extension of the methodology to other commercial diffused polymers (e.g. PS, PPS, PC, PMMA) may enlarge the data set available for comparison. In any case, a more precise assessment of specific case studies should include strictly boundary definitions, plants layout and transport modeling. It is possible that, in a comparison between two or more polymers, the ranking will be different from the one presented in this work, since it depends from the peculiarity of the scenarios (e.g. presence of recycling plants, materials supply capacity, economic burdens).

Further investigation should concern the quantification of material degradation on an exergy basis. In fact, even if the recycled polymers have the same chemical exergy, their mechanical characteristics can change due to contamination and variation of molecular weight during recycling. Maintaining the same properties requires the use of stabilizers or fillers in the recycling process. Material degradation is the main factor hindering the market of recycled products. The integration with the exergy methodology could start from an extension of the exergy definition: not only the capacity of producing work, but also the possibility to be transformed into something valuable computing the downcycling with respect to a initial condition.

In the field of thermodynamic assessment of vehicle components, further investigation should concern about the integration of the obtained information with eco-design principles. The author has already been started to work on the topic, developing a quantitative scale of eco-design points for polymers in vehicle components, combining qualitative information on recyclability limitations and numerical data on EE of polymers and recycling indexes.

Chapter 5

A system-based view: Exergy-based assessment of Solid Waste treatment alternatives

5.1 System boundaries

As already said in Chapter 1, an ISWM is based on the optimal integration of the different subsystems (e.g. collection, transport, treatment). In this Chapter, a reduced MSW treatment system is analysed, whose boundaries start from the waste after generation and end with the manufacturing of secondary products (Figure 5.1). It includes the collection and transport to a transfer station, and the further transport to the various treatment plants, namely: a Mechanical Biological Treatment plant for the Unsorted Residual Waste, a paper recycling plant for cardboard production, a plastic sorting and recycling unit for the mixed plastic packaging waste. The decision of including only these two material streams is linked to their high weight percentage in SC and subsequent strong influence on the overall system balance. In order to include in the calculations the burden due to the resource consumption associated to substituting products, the alternative process of coal supply (substituting SRF in cement kiln combustion) and virgin production of paper and plastic are modelled too. The analysis is performed in various steps, modelling the different parts of the system and analysing them with the instruments of exergy-based analysis, MOFs optimization and uncertainty inclusion. Data on the polymeric stream are the same reported and calculated in Chapter 4; here, only three polymers (i.e. PE, PP, PET) are considered, which are the most diffused in plastic waste and whose recycling is well industrially assessed.

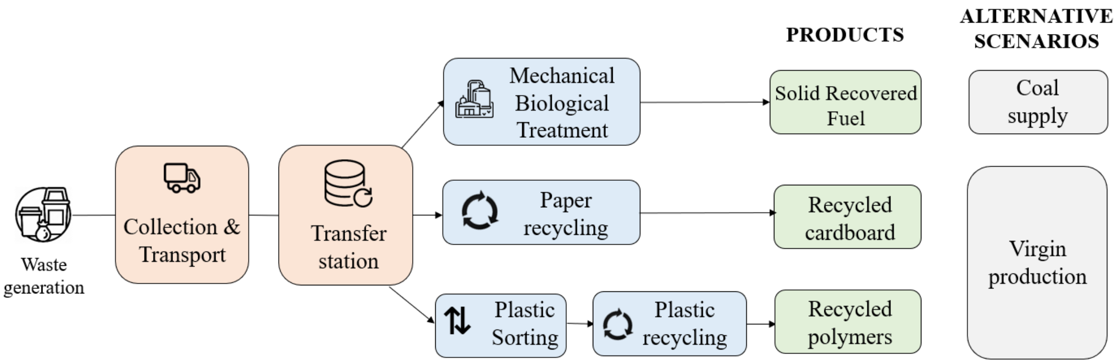


Figure 5.1: Reduced Solid Waste treatment system analysed in Chapter 5

A brief description of the contents of each section is reported below.

- Section 5.2 reports the description of the Collection and Transport (C&T) model (Figure 5.2) and the analysis of the effect of influencing parameters on collection cost. The content, the methodology and the results of this Section are largely based on:
  - Russo,S., Verda V., Influencing factors of Solid Waste Management global cost and efficiency: a multi-objective optimization focusing on the collection system, 2020, Proceedings of The 75th National ATI Congress 7 Clean Energy for all (ATI 2020);

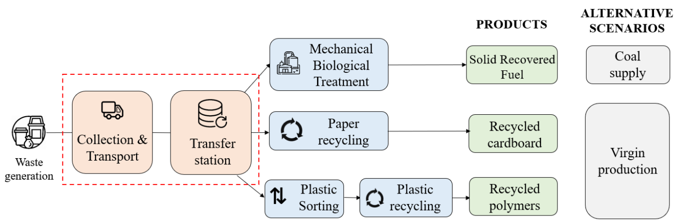


Figure 5.2: System boundaries in Section 5.2

- Section 5.3 focus on a detailed analysis of a Mechanical Biological treatment plant (Figure 5.3), comparing different chain structures with Exergoeconomic analysis principles. The content, the methodology and the results of this Section are largely based on:
  - Russo,S., Verda V., Exergoeconomic analysis of a Mechanical Biological Treatment plant in an Integrated Solid Waste Management system including uncertainties, Energy, vol. 198, p. 10, 2020;

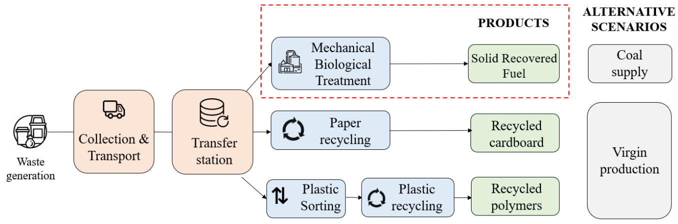


Figure 5.3: System boundaries in Section 5.3

- Section 5.4 includes in the analysis the paper recycling chain (Figure 5.4), using the Embodied Exergy instrument for comparing different Selective Collection scenarios. The content, the methodology and the results of this Section are largely based on:
  - Russo,S., Verda V., Embodied exergy-based analysis of a municipal solid waste treatment system with uncertainty inclusion, Int. J. Exergy, Vol. 34, No. 3, p.17, 2021;

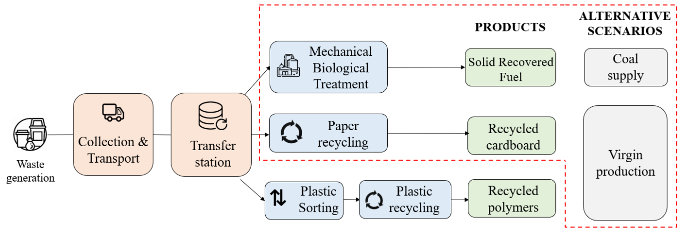


Figure 5.4: System boundaries in Section 5.4

- In Section 5.5 the boundaries are enlarged to the entire system (Figure 5.5), which is optimized in a MOFs optimization between monetary cost and exergy-based efficiency. The content, the methodology and the results of this Section are largely based on:
  - Russo,S., Verda V., Exergy-based assessment and multi-objective optimization of a Solid Waste treatment system including recycling routes, 2020, Proceedings of CPOTE 2020 - The 6th International Conference on Contemporary Problems of Thermal Engineering.

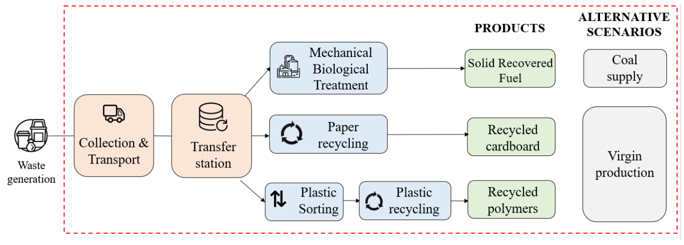


Figure 5.5: System boundaries in Section 5.5

5.2 Solid Waste collection system

Among all the constituting parts of an ISWM, the SW Collection and Transport (C&T) system surely has a crucial role. In fact, it represents the first economic burden associated to the waste after generation. Besides, it has a strong influence on SW treatment plant location and operation. For these reasons, a deep understanding of SW C&T mechanisms and influencing factors is essential. The analysis of waste C&T is widely diffused in literature, even with different approach and goals. Many works deal with the vehicle routing optimization [121, 122], or plant location-allocation based on GIS systems [123, 124]. Other studies are focused on finding correlations between the influencing variables through mathematical models and real data collection. In [125], the impact of SW source segregation on the fuel consumption and collection cost is evaluated. In [126, 127], different methods are developed for analysing the drivers of the SW collection cost and efficiency, basing on Italian data. Techno-economic performance indicators of SW collection strategies are developed in [128].
The analysis reported in this Section falls into the second category of studies, since the aim is to show the correlation of various factors (e.g. population density, unit collection area, degree of Selective Collection) and their influence on the collection cost, considering a typical Italian C&T system. The goal is also to obtain a set of optimal combinations to use for the optimization of the entire SWM system.

5.2.1 The model

Regarding the SW C&T, there are two main collection schemes: i) kerbside (or "door-to-door") collection, when the waste is daily collected from every housing unit, according to the type of material; ii) traditional (or "bring point") collection, when the waste is dropped off in separated street bins. In Italy, the recent trend is to gradually change in favour of the kerbside collection, since it allows to reach higher degree of SC, with moderate cost increment. According to [18], citizens that practice kerbside separation have a higher recycling conscience and are more satisfied with the city waste management system. In this work, a typical Italian kerbside collection system is modelled. Small rear-loader trucks handle the door-to-door collection; when they reach their collection capacity V_{st}, the wastes are unloaded into bigger trucks (with V_{bt} capacity) and transported to the transfer stations where they are displaced to the various treatment plants. The first action in order to plan the SW collection scheme consists in the estimation of the number of small and big trucks, N_{st} and N_{bt} respectively. It depends from various factors, as follows.

- *Route time.* The time of an entire route t_{st} (Equation 5.1) for the small rear-loader truck is calculated as the sum of the collection time t_{coll} (Equation 5.2), which depends on the picking time t_p and the waste volume V_p at the collection point, and the dropping off time into the big truck t_{drop}. A recovery time factor W (between 0 and 1) takes into account the distance between the collection points and it is strongly linked to the population density. The route time increases if W increases and it corresponds to lower population density for equal amount of collection. The maximum number of rounds in a working day of $H_{day} = 8$ hours is $N_d = H_{day}/t_{st}$.

$$t_{st} = \frac{t_{drop} + t_{coll}}{1 - W} \tag{5.1}$$

$$t_{coll} = \frac{t_p \cdot V_{st}}{V_p} \tag{5.2}$$

- *Weekly SW generation.* The collection routing is planned on a weekly basis, setting a number of weekly removal N_w. To this end, the generated volume of the i-th waste stream V_{w_i} is calculated as in Equation 5.3 by the product of the per-capita generation V_{pc_i} and the unit collection area U_b , which is the reference district used for designing the collection scheme.

$$V_{w_i} = V_{pc_i} \cdot U_b \tag{5.3}$$

Considering these factors, the number of small trucks necessary for the collection in U_b is given by Equation 5.4. The number of small trucks serving the entire urban center ${N_{st}}^{tot}$ is then calculated in Equation 5.5, considering the total population P_{tot} and the fact that the same trucks can be used in different days (D_w=7) and districts during the week, depending on their availability. From author considerations and literature review, the number of big trucks N_{bt} is estimated to be the half of the small ones N_{st}.

$${N_{st}}^{U_b} = \sup\left(\frac{V_{w_i}}{V_{st} \cdot N_w \cdot N_d}\right) \tag{5.4}$$

$$N_{st}{}^{tot} = \sup\,(N_{st}{}^{U_b} \frac{P_{tot} \cdot N_w}{U_b \cdot D_w}) \tag{5.5}$$

The trucks estimation allows the calculation of the specific costs, namely: the fixed cost associated to the vehicles purchase and maintenance; the operation cost associated to fuel consumption; the labour cost.

- *Purchase cost.* The annual depreciation of the j-th vehicle C_{a_j} (Equation 5.6) is calculated given the purchase cost C_{fix_j} and the percentage of insurance (Ins) maintenance ($Maint$) and taxation (Tax) on the annual cost. The actualization factor f_{a_j} (Equation 5.16) depends on the interest rate i_j and the annual recovery period Y_{rec_j}. Equation 5.8 gives the specific cost per unit volume of waste due to the purchasing.

$$C_{a_j} = (1 + Ins_j + Maint_j + Tax_j) \cdot f_{a_j} \cdot C_{fix_j} \tag{5.6}$$

$$f_{a_j} = \frac{i_j \cdot (1 + i_j)^{Y_{rec_j}}}{(1 + i_j)^{Y_{rec_j}} - 1} \tag{5.7}$$

$$c_{v_{fix}} = \frac{N_{st}{}^{tot} \cdot C_{a_{st}} + N_{bt}{}^{tot} \cdot C_{a_{bt}}}{V_{w_i} \cdot week_{year}} \tag{5.8}$$

- *Fuel cost.* The cost associated to fuel consumption depends on the vehicle hourly productivity P_{h_j} (Equation 5.9), which accounts for the equivalent kilometres K_j travelled by the vehicle during a working day. For small trucks $K_{st} = t_{st} \cdot \overline{v_{st}}$, where $\overline{v_{st}}$ is their average velocity, namely 30 km/h, while for big trucks $K_{bt} = 2d_{ts}$, where d_{ts} is the distance between the last drop point and the transfer station. The specific cost per unit volume of waste due to the fuel consumption is given by Equation 5.10, which includes the fuel cost c_{fuel} and the specific fuel consumption $cons_{fuel}$.

$$P_{h_j} = \frac{N_d \cdot K_j \cdot N_j{}^{tot}}{H_{day}} \tag{5.9}$$

$$c_{v_{fuel}} = \sum_j \frac{c_{fuel} \cdot P_{h_j} \cdot H_{day} \cdot N_w}{cons_{fuel_j} \cdot V_{w_j}} \, , j \in \{st, bt\} \tag{5.10}$$

- *Labour cost.* Equation 5.11 gives the cost per unit volume of waste due to the personnel cost, in the hypothesis of one employee for each vehicle. The average salary Sal is chosen according to Italian survey.

$$c_{v_{lab}} = \frac{(N_{st}{}^{tot} + N_{bt}{}^{tot}) \cdot Sal}{H_{day} \cdot D_w \cdot week_{year}} \tag{5.11}$$

The total specific cost per unit of volume of the i-th waste stream is the sum of the three contributions, namely ${c_v}^{tot} = c_{v_{fix}} + c_{v_{fuel}} + c_{v_{lab}}$. The specific cost per unit of mass ${c_m}^{tot}$ is then calculated considering a URW density ρ_{URW}= 80 kg/m^3. When planning the collection scheme, removal efficiency is supposed to be the maximum achievable. To this end, data on recent years per-capita generation are gathered [8] and degree of primary source segregation (i.e. material separation by the end-users) are supposed. In order to understand the relation between the influencing factors on the specific cost, sensitivity of the system is tested according to the variation of key parameters, namely: the population density W, the number of weekly removal N_w, the unit collection area U_b and the total population P_{tot}. Among them, N_w and U_b are project variables, since they can be decided during the design phase, while W and P_{tot} are linked to the local context. All the other fixed parameters are specified in Table 5.1.

Table 5.1: Parameters used in the SW collection model, based on [22] and Italian municipalities reports on SW collection

t_{drop} [hours]	0.1	V_{st} [m^3]	10		
t_p [hours/point]	0.015	H_{day} [hours/day]	8		
V_p [m^3/point]	0.2	d_{ts} [km]	25		
$V_{pc_{URW}}$ [kg/day]	1.3	$week_{year}$	48		
c_{fuel} [€/L]	1.55	Sal [€/year]	40,913		
	st	bt		st	bt
Y_{rec} [year]	5	7	Ins [%]	0.72	1.7
$cons_{fuel}$ [l/km]	7	2	Tax [%]	1.03	0.4
C_{fix} [€]	50,000	145,000	$Maint$ [%]	8.9	9.3

5.2.2 Results

Influencing factors

First of all, a sensitivity analysis is performed to test the influence of external factors (i.e. P_{tot} , N_w, W, U_b and SC) on the collection system. As a general consideration, the total specific cost decreases with an increment in the number of inhabitants (P_{tot} and U_b), until reaching a constant value. In practice, there are step fluctuations around a mean constant value due to the influence of an integer number of vehicles.

The inhabitants of U_b are varied between 1000 and 8000 and the influence of the other parameters is tested one at a time. The main hypothesis is that the characteristics of waste generation (i.e. SC and V_{pc_i}) of each area are the same. A description of the main results is reported as follows.

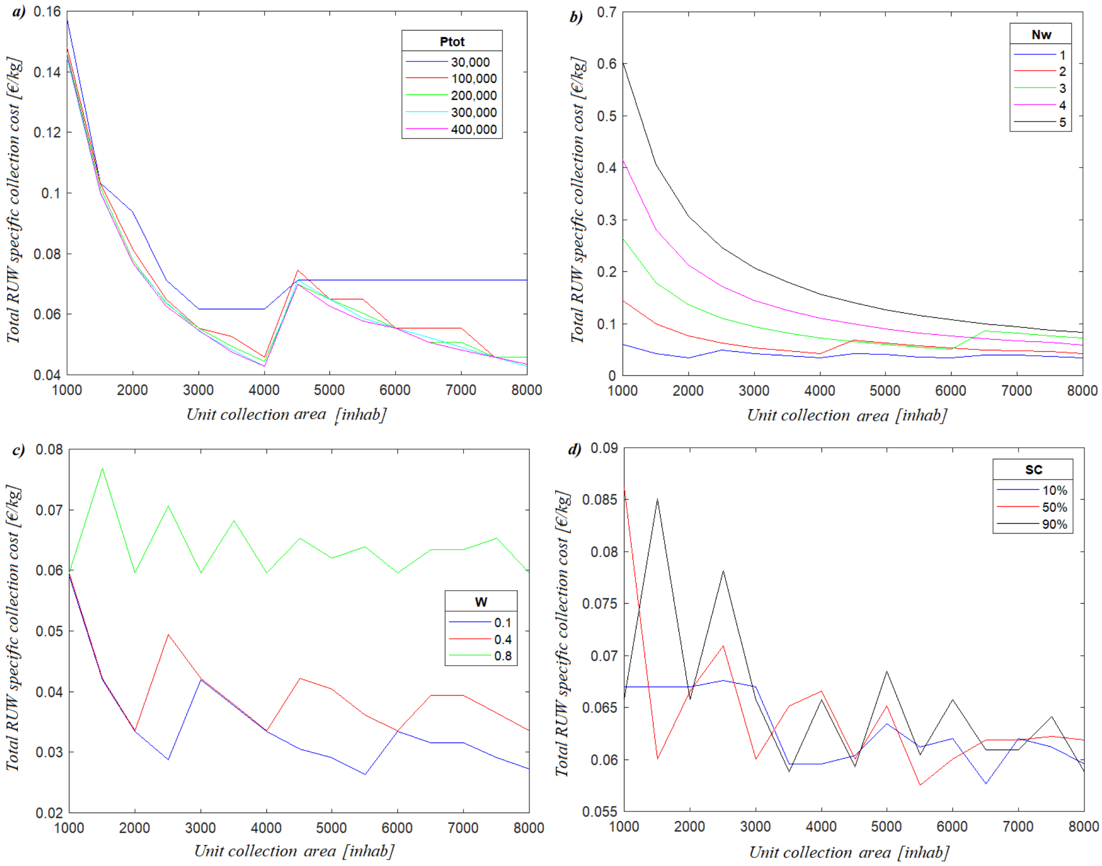


Figure 5.6: Influence of various parameters on URW specific collection cost: a) total population; b) number of weekly removals; c) population density; d) degree of selective collection.

- *Total population* (Figure 5.6a). For a given N_w and W, the specific cost decreases with an increment in the total population. The trend of ${c_m}^{tot}$ with U_b tends to become the same as P_{tot} increases (this effect is more evident for P_{tot} higher than 100,000 inhabitants); it means that the optimal collection units are almost independent from the total population of the area.

- *Number of weekly removals* N_w (Figure 5.6b). An intensification in the waste removal frequency leads to an increment in the specific cost. In fact, the growth in the operation costs (fuel and personnel) is not compensated by the decrements associated with the reduced number of vehicles. The increment is more evident for small U_b, while the values tend to become more similar for high U_b.

- *Population density* W (Figure 5.6c). Lower population density (associated with higher values of W) implies longer collection times, which means more vehicles for a given waste generation. Therefore, the specific cost increases with W. It can be noticed that the optimal combinations (i.e. values of U_b for which the cost is minimum with a given W) increase with W.

- *Degree of selective collection* SC (Figure 5.6d). The global SC parameter is the one that causes more fluctuations for the URW fraction cost. This effect is more marked for smaller U_b. In general there are a lot of optimal values of the collection area for a certain SC degree.

Optimal parameters

Results from the sensitivity analysis show a deep interconnection between all the parameters influencing the total specific cost. The operation variables that can be actually chosen during the design phase are N_w and U_b. Results of optimal parameters clustering derived from a minimization of collection cost are shown in Figure 5.7.

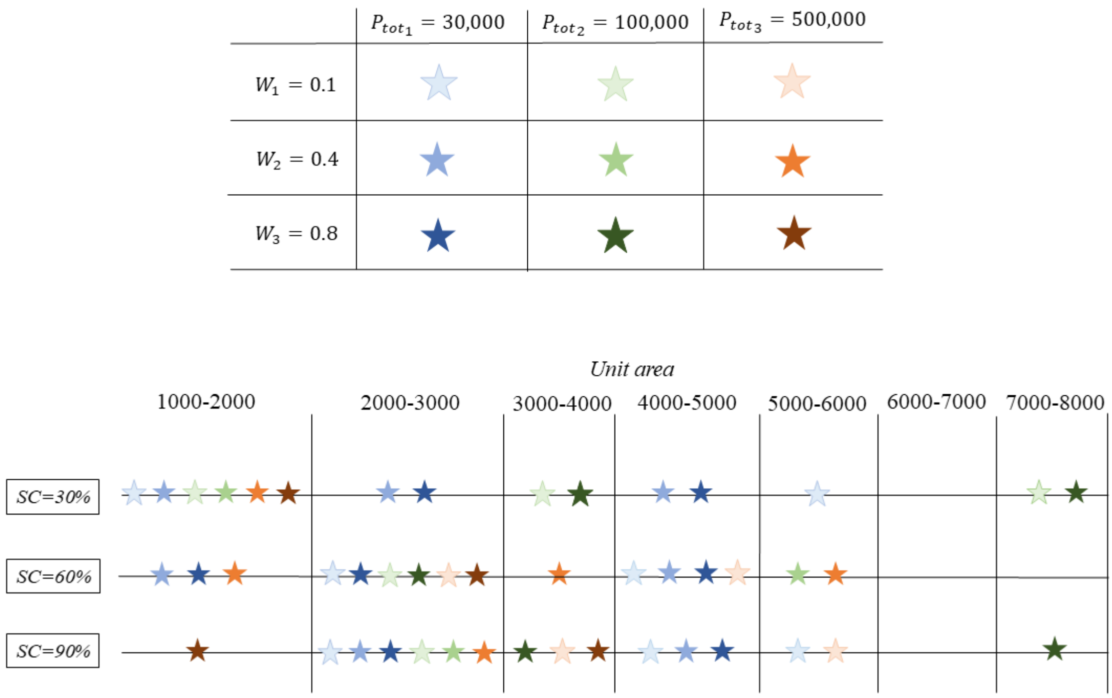


Figure 5.7: Clustering of optimal solutions according to SC_{pap} and U_b and relative legend of scenarios according to total population and population density

The optimization is performed with a classical GA algorithm and it is repeated for 3 values of P_{tot}, W and SC; results are clustered for ranges of U_b population. All the values are obtained in the hypothesis of a collection efficiency of 100%. This assumption is consistent with the fact that the system management will guarantee the complete waste removal. Since URW stream generally has the highest share in weight, its cost minimization results to be the best choice for design purposes. All the optimal solutions result to correspond to only one weekly removal,N_w=1, which is coherent with the outcomes of the sensitivity analysis. The majority of solutions are found in the range between 1000 and 3000 inhabitants for all the possible combinations of P_{tot}, W and SC; for low population (i.e. P_{tot}=30,000 inhab) greater values of U_b are included. In general, the cluster shows that the majority (83%) of optimal solutions are associated to U_b<5000 inhabitants. The fact that one configuration appears in more clusters is because more than one solution is present for the same value of minimum ${c_m}^{tot}$. This effect comes from the fluctuating trend of the cost, as already shown in Figure 5.6.

5.2.3 Conclusions and discussion

The design of a typical 'door-to-door' or kerbside collection scheme starts with the definition of the main external parameters: the total population of the area, the average per-capita waste generation and the expected degree of selective collection for the single material streams (from historical datasets). At this point, the main design variables are two: the number of weekly removals, which depends from the type of waste and the number of purchased trucks; the unit collection areas of collection, i.e. the smaller districts in which the total area is divided for a better collection management.

The performed sensitivity analysis has shown that the combination of external parameters (W, SC and P_{tot}) and design variables (N_w and U_b) has a strong influence on the waste specific collection cost. Therefore, it is strongly recommended to take into consideration all these factors when designing the collection scheme, choosing an appropriate collection unit area according to their combination. In the case of minimization of the URW ${c_m}^{tot}$ a set of possible configurations are found where the optimal weekly removal is always once a week (N_w=1), which is the actually more common frequency for URW.

The range of optimal U_b is restricted to values between 1000 and 5000, with preference for solutions between 1000 and 3000 inhabitants. The advantage of having smaller collection areas is the reduction of the downtimes in the collection and the possibility to cover the entire collection using the same number of trucks in different days of the week. The global effect is the reduction of operating and fixed costs. Therefore, it is also important to proper chose U_b, and eventually redesign it if significant changes occur in the external variables.

This first analysis on the collection system has been necessary to understand the first step of the SW path and to collect a set of optimal solutions and values to be used for the simulation of the entire treatment system presented in the next sections.

5.3 Mechanical Biological Treatment plant analysis

The collected waste material streams are directed to the recycling plants. The rejected material from the recycling processes and the collected URW have to be treated before being disposed into landfill or burned in an incinerator for energy recovery, according to the Italian law LD 211/2015 art. 48. For this reasons, in many countries, the Mechanical Biological Treatment (MBT) plants have became important elements of the ISWM system [24, 129]. These plants undertake a series of operations on the URW aimed to:

- increase the calorific value of the main outlet stream by separating the light and dry fraction (paper, plastic, textiles, etc.) from the wet one (organic matter)[130];
- recover the ferrous and non-ferrous (NF) metal to be devolved to recycling plants [131];
- stabilize the organic part before the final disposal [23, 132];
- reduce the volume of waste to be disposed in landfill [133, 134].

Currently in Italy, there are 130 MBT plants, which treat more than 10 million of MSW per year, 90% of which are URW [8]. There are different types of MBT plants depending on the type of flow repartition: single-flow, separated-flow and mechanical [135, 136]. In most cases, the main final product is the Solid Recovered Fuel (SRF) (or Refused Derived Fuel, RDF, according to the old nomenclature), whose utilization in Italy is regulated by the Law D.L. 205/2010 in accordance with the standard UNI EN 15359 [**DiLonardo2015**, 137]. SRF can only be used in incinerators, cement factories or thermal power plants of more than 50 MW, otherwise it is disposed in landfill. The SRF can be fluff, densified or dust, depending on the procedure that is used for its production [138].

In the literature there are various examples of works focused on the modelling and analysis of MBT plants. A Material Flow Analysis (MFA) is conducted in [139] with the goal of valuating its effectiveness in removing hazardous substances. The influence of input waste and processing technologies on SRF characteristics is studied in [133]. Experimental analyses are conducted with the aim to show the environmental advantage of insert a MBT plant before landfill [132]. Mass, energy and material balances are validated with laboratory analysis in [140], where different types of wastes are compared. In [131], a Life Cycle Assessment (LCA) approach is used for evaluating the energy and environmental performance of a MBT plant producing SRF for cement kiln co-combustion. Results of a LCA are also presented in [23], comparing eight European MBT plants.

Research gap and objective

In a MBT plant, mechanical processes involve electric energy consumption and generate rejected materials. According to the Second Law of Thermodynamics, the sources of irreversibility of the system are linked to material losses and exergy destruction. Exergy based performance indicators can provide a measure of the irreversibility distribution trough the equipment and so of the recovery degree of exergy potential. Currently, no examples of Exergoeconomic analysis applied to specific waste treatment plants (such as MBT plant) are found in literature.

Moreover, in real working conditions, the operation of the waste treatment systems is strongly influenced by social, political and economic conditions, which entail a high degree of uncertainty. The uncertain factors can be external (site-dependent) or internal. External factors are the structure of collection system and the degree of selective collection, which influence the waste composition, and the market demand of end products that affects their production. Internal factors are the structure of each treatment chain or malfunctions in equipment, which lead to variable energy consumption. Some example of inclusion of uncertainty in the analysis of ISWM systems are present in [60, 61], however the literature is not very extensive so far.

In summary, the aim of this work is to evaluate the performance of the MBT plant under an Exergoeconomic perspective, considering the influence of aleatory variations of external and internal operating parameters and so reproducing the variety of operating conditions that can be faced.

5.3.1 Model structure and methodology

The following Sections reports the description of the steps for modelling and simulating the MBT plant, including the parameters used for the evaluation. The model is validated with data declared by real MBT plants, by comparing the values of LHV and Moisture Content (MC) of SFR. All the modelling and simulation are performed in Matlab environment.

Mass balance

Since the relation between the inputs and outputs of each equipment is linear (no chemical or nuclear reactions occur), mass balances are performed using transfer matrices. For the MBT plant, the Recovery Factor Transfer Function (RFTF) matrix [141] introduced by Diaz [142] is used. According to this methodology, transfer coefficients are assigned to each equipment of the treatment chain for each inlet material stream, for the wet and the dry part respectively. Equation 5.12 expresses the relation between the input and output flow of the i-th material stream through the j-th component of the chain. The reference process chains are the ones depicted in Figure 5.8.

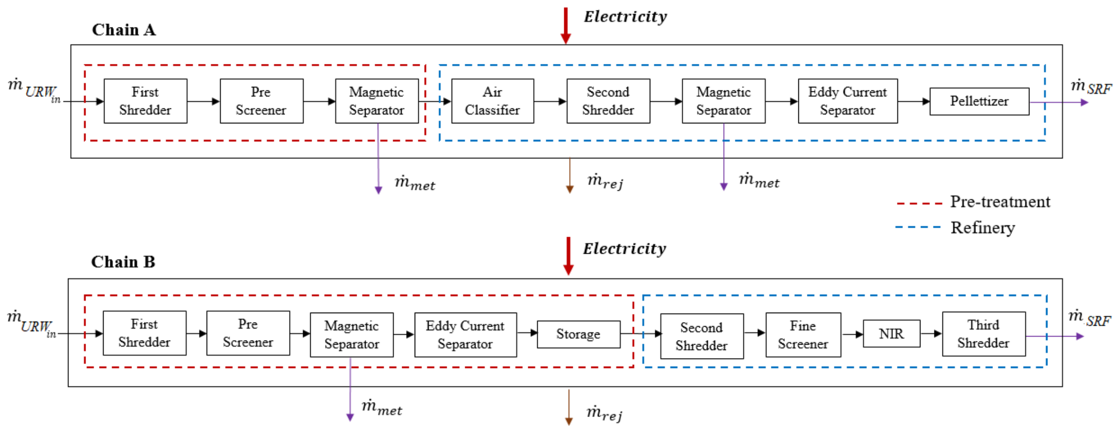


Figure 5.8: Different chain structures considered in the analysis

$$m_{i_{out}} = m_{i_{in}} \cdot RFTF(j) \tag{5.12}$$

The RFTF matrix used for the MBT plant is shown in Table 5.2. In order to perform the calculation, some assumptions are made on the repartition of the inlet material streams: Organic Matter (OM) stream is composed by organic waste and garden trimmings; Other Plastics (OP) stream includes PVC and hard plastics; diapers are divided in 50% of organic matter, 35.5% of cellulose (paper) and 14.5% of plastic [143]; Other Inorganics (OI) include mostly inert and a small percentage of batteries and dangerous waste. Wet and dry part and ultimate analysis are calculated according to the values in Table 5.3.

Energy balance

In a MBT plant, the main energy consumption is the electric one. According to literature review, a range of energy consumption (kWh/Mg) is indicated for each equipment. The variation are due to the diversity in the inlet material characteristics (i.e. sizing, moisture content, density, mass flow) or to random malfunctions [22]. Table 5.4 resumes the energy consumption of the equipment included in the treatment chains considered in this analysis.

For calculating the Lower Heating Value (LHV) of the inlet material and the outlet fuel, the Mendeliev equation is adopted (Equation 5.13) [147], where the coefficient of Carbon, Hydrogen, Oxygen, Sulphur (C, H, O, S) and the MC are on wet basis.

$$LHV[kJ/kg] = 4.187 \cdot [81C + 300H - 26(O - S) - 6(9H + MC)] \tag{5.13}$$

Table 5.2: RFTF matrix factors, elaborated by the author based on [131, 143, 144]

j-th component		*i-th material stream*										
		Paper	Plastic	OP	OM	Wood	Leather	NF metal	Ferrous metal	Glass	Textile	OI
Storage	Dry	1	1	1	1	1	1	1	1	1	1	1
	Moisture	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Shredder	Dry	1	1	1	1	1	1	1	1	1	1	1
	Moisture	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
Magnetic separator	Dry	0.98	0.98	0.98	0.95	0.98	0.98	1	0.2	1	0.98	0.95
	Moisture	0.98	0.98	0.98	0.95	0.98	0.98	1	0.2	1	0.98	0.95
Eddy current separator	Dry	0.98	0.98	0.98	0.98	0.98	0.98	0.1	1	1	0.98	0.98
	Moisture	0.98	0.98	0.98	0.98	0.98	0.98	0.1	1	1	0.98	0.98
Preliminary screening	Dry	0.785	0.69	0.69	0.166	0.73	0.73	0.52	0.52	0.198	0.73	0.468
	Moisture	0.785	0.69	0.69	0.166	0.73	0.73	0.52	0.52	0.198	0.73	0.468
Fine screening	Dry	0.97	0.96	0.96	0.46	0.96	0.96	0.91	0.91	0.08	0.96	0.7
	Moisture	0.97	0.96	0.96	0.46	0.96	0.96	0.91	0.91	0.08	0.96	0.7
Air classifier (shredded refuse)	Dry	0.98	0.98	0.98	0.7	0.98	0.98	0.5	0.1	0.7	0.98	0.2
	Moisture	0.882	0.882	0.882	0.63	0.882	0.882	0.45	0.09	0.43	0.882	0.18
Air classifier (un-shredded refuse)	Dry	0.98	0.98	0.98	0.4	0.98	0.98	0.5	0.1	0.02	0.98	0.15
	Moisture	0.882	0.882	0.882	0.36	0.882	0.882	0.45	0.09	0.018	0.882	0.135
Near Infrared Removal (NIR)	Dry	1	0.94	0.01	1	1	1	1	1	1	1	0.7
	Moisture	1	0.94	0.01	1	1	1	1	1	1	1	0.7
Pelletizer	Dry	1	1	1	1	1	1	1	1	1	1	1
	Moisture	1	1	1	1	1	1	1	1	1	1	1

Table 5.3: Ultimate analysis of URW stream, elaborated by the authors based on [144]

		% by mass, dry basis						
	%MC	C	H	O	N	S	Cl	Ash
Paper	16.7	43.3	5.8	44.2	0.3	0.2	0.2	6
Plastics	6.5	59.2	7.1	22.5	-	-	1.3	9.8
OP	2	54.9	6.6	20.8	-	-	8.5	9.2
OM	69.6	47.7	6.4	37.4	2.6	0.4	0.5	5
Wood	48	45.9	5.9	37.9	3.4	0.3	0.3	6.3
Leather	10	59.8	7.9	11.5	10	0.4	0.4	10
NF Metal	3.7	4.5	0.6	4.3	0.1	-	-	90.5
Ferrous metal	2	4.5	0.6	4.3	0.1	-	-	90.5
Glass	2	0.5	0.1	0.4	0.1	-	-	98.9
Textile	10	47.8	6.4	39.8	2.2	0.2	0.4	3.2
OI	8	-	-	-	-	-	-	-

Exergy and cost balance

The exergy of the mixed waste $\dot{B}_{URW_{in}}$ (kW) is evaluated by considering the organic, inorganic and water content separately. The organic part includes the

Table 5.4: Equipment characterization, elaborated by the authors based on [22, 23, 142, 145, 146] and data declared by plant managers

Equipment	Description	Energy consumption		Cost(1) $keuro$
		Range (kWh/Mg)	Chosen value (kWh/Mg)	
Primary shredding	First shredding after the delivery of the material. The energy consumption depends from the dimensional reduction following the Kicks Law $E = C \cdot \ln \frac{F_0}{X_0}$ with F_0=170 mm and X_0=80 mm and C=8.2216.44	6.2 -12.4	9.3	51.9
Secondary shredding	The air-classified light fraction requires more energy for shredding than the mixed waste	15 - 25	20	51.9
Magnetic separator	Removal of ferrous metal. The energy consumption is due to the movement system of the conveyor belt.	0.2 - 2.4	1.3	36.15
Eddy current separator	Removal of non-ferrous metal.	0.7 - 1.2	0.8	7.23
Pre-trommel	First screening for the primary separation of the organic wet fraction from the light one; the size of the screening is generally 80 mm. Energy consumption is due to the movement of the grid.	0.7 - 1.5	1.1	51.65
Fine screening	Secondary screening from removal of fines and residual organic part after the shredding. The size of the screening can be 50 mm or less.	0.7 - 1	0.8	51.65
Air classifier	Light fraction (paper, plastic, textile) separation. The specific energy consumption depends from the inlet moisture content and increases if a dust collection system is included.	1 - 4.1	3	41.3
Pelletizer	Increase in final product density and quality. The energy consumption increases when the production and the moisture content decreases	25 - 35	30	206.58
NIR	Removal of hard plastic (PVC) trough optical separation with an infrared generator.	3.3 - 6.1	4.7	50
Rocket shredding	Hard shredding with hammer mill. High energy consumption and maintenance but good quality of SRF.	33.6 - 62.4	48	51.9
Auxiliary				
Conveyor/Raising	Empirical relation for a belt length L=20 m and a raising height H=2 m.		6.722e-03/ 5.46e-03	15.49
Fan	It is associated to storage and air classifier.		3.8	
Press	It can be included at the end of the chain or between the first and second treatment section.		1.5	

(1) The costs refer to a plant capacity of 5 tons/hour

streams that contains mainly carbon (C) and hydrogen (H), namely paper, organic matter, wood, leather, plastics and textiles. The chemical exergy content of these materials b_{ch_i} is calculated using the Equation 2.5. Regarding the inorganic part, the exergy of pure iron and aluminium is assumed respectively for ferrous and non ferrous metal; the exergy of glass is calculated considering the solid mixing of the glass components (1.5% Al_2O_3, 10.8% CaO, 13.2% Na_2O,73.3% SiO_2) [47]; the exergy of inert material can be disregarded, as demonstrated by [148]. For the water W, only the chemical exergy $b_{ch_{wat}}$ is considered, since ambient temperature (T_0) and pressure (p_0) are assumed. All the values of LHV and exergy of the material stream and the relative ϕ coefficient are reported in Table 5.5.

Table 5.5: Chemical exergy and ϕ coefficient for material stream, elaborated basing on [22, 144]

Material stream	LHV_i **(kJ/kg)**	**Exergy content**	ϕ
Organic part			
Paper	15815	19278.3	
OM	4175	6750.1	$\frac{1.044+0.016\frac{H}{C}-0.3493\frac{O}{C}[1+0.0531\frac{H}{C}]+0.0493}{1-0.4124\frac{O}{C}}$
Leather	18515	20148.9	
Textile	17445	20375	
Plastic	32000	34800.6	$1.0437+0.014\frac{H}{C}+0.0968\frac{O}{C}+0.0467\frac{N}{C}$
OP	32000	34682.1	
Wood	15444	18770.8	$\frac{1.0412+0.216\frac{H}{C}-0.2499\frac{O}{C}[1+0.7884\frac{H}{C}]+0.045}{1-0.3035\frac{O}{C}}$
Inorganic part			
Ferrous metal (Fe)		6740	
Non-ferrous metal (Al)		32926	
Glass		885.7	
Water		50	

Furthermore, an exergy cost balance [33] is written for each equipment of the chain (Equation 5.14). All terms are expressed in €/sec.

$$c_{URW_{in}} \cdot \dot{B}_{URW_{in}} + c_{el} \cdot \dot{B}_{el} + \dot{C}_{eq} = c_{rej} \cdot \dot{B}_{rej} + c_{pr} \cdot \dot{B}_{pr} \tag{5.14}$$

The cost of electricity c_{el} (€/kWh) is fixed to the one of Italian market (0.1 €/kWh [149]). If we consider the MBT plant only, the inlet cost of URW, $c_{URW_{in}}$, is negative since it corresponds to the disposal fee paid from the municipalities, assumed as 0.067 €/kg [8]. The cost of the rejects c_{rej} is supposed to be the same, but it is positive for the plant [150]. The SRF and recovered metal are considered as the two products of the plant. An additional equation is written for the magnetic separator in order to find the cost of the products c_{pr}. According to the equality method, the same unit exergy cost is assigned to all products, therefore the additional equation is $c_{pr} = c_{met} = c_{SRF}$. Equation 5.15 is utilized for calculating the cost rate of the equipment C_{eq}. The operation and maintenance factor $f_{O\&M}$ is 10% of the global cost, the actualization factor f_a is given by Equation 5.16 considering an interest rate i of 7.5% and a capital recovery period N of 10 years [151]. The annual equivalent hours h_{year} are evaluated considering 8 working hours per day for 6 days a week. The actual costs of the equipment are reported in Table 5.4 for a reference plant capacity of 5 ton/hours.

$$\dot{C}_{eq} = \frac{C_{eq} \cdot f_{O\&M} \cdot f_a}{3600 \cdot 7800} \tag{5.15}$$

$$f_a = \frac{i}{1-(1+i)^{-N}} \tag{5.16}$$

Model validation

The model is validated by testing the RFTF matrix with some real MBT chain structures and comparing the characteristics (MC and LHV) of the final SRF with the data declared by the plants. Results of the validation are reported in Table 5.6. URW composition used for the validation is calculated from the values reported in Table 5.7, according to waste gravimetric composition of Torino metropolitan city. The discrepancies in SRF MC and LHV from the real plants data are reasonably due to the fact that the real URW composition entering each plant is different from the one used for the validation. The exact waste composition is not declared and is difficult to predict, since it depends from aleatory factors and no average values are given. For this reason, percentage differences until 10% are accepted as good values for the validation.

Table 5.6: Results of the validation with different Italian MBT chains: I) Pinerolo plant, II) A2A ambiente plant, III) Sommariva del Bosco plant

	SRF MC (%)	**SRF LHV (kJ/kg)**
MBT plant-I	14.5	16036
Model	15.3	15716
Difference (%)	+5.6	-1.9
MBT plant-II	18	16636
Model	17.2	16025
Difference (%)	-4.4	-3.6
MBT plant-III	14.9	21212
Model	13.3	21080
Difference (%)	-10.7	-0.62

Table 5.7: Base case scenario according to the TUW gravimetric composition of the city of Torino (IT) [151] (w.b.: wet basis)

Material Stream	**Gravimetric composition of TUW** %wg (w.b)	**SCi (%)** w.b.	**Internal repartition of SC (%)** w.b.
Paper	26.97	52.6	27.45
Plastics	17.16	50.27	16.7
OP	0.94	0	0
OM	33.8	58.4	38.2
Wood	6.13	73.46	8.7
Leather	0.26	0	0
NF Metal	1.08	27.84	0.585
Ferrous metal	1.49	20.19	0.585
Glass	6.29	56.29	6.85
Textile	3.05	15.97	0.94
OI	2.8	0	0

Sensitivity analysis

In order to show the effect of the equipment position on efficiency, two different structures of chain are considered, based on real plants layout, as reported in Figure 5.8. The main differences consist in the presence of the pelletizer and the NIR, since the final product is utilized in two different plants (an incinerator in case A and a cement factory in case B). The auxiliary energy consumption (Table 5.8) is calculated considering a proper number of conveyor belts and raisings according to the number of equipment. A fan is associated to each Air Classifier and Storage. In addition, a press is collocated after the pelletizer in chain A.

A sensitivity analysis is performed in order to evaluate the influence of the main external and internal parameters. The values of TUW composition, SC_i percentage and SC internal repartition for the base case scenario are reported in Table 5.7. The SC_i of paper, plastic and organic matter are varied linearly in a range between -30/+30% with respect to the base case. The global energy consumption is varied between the minimum and maximum values found in the literature (Table 5.4) (the auxiliary consumption is assumed constant).

Table 5.8: Auxiliary consumption calculated for the two chains, by calculation from [22]

Auxiliary consumption (kWh/Mg)		
	Chain A	Chain B
Conveyor belts	0.087	0.074
Raisings	0.01	0.01
Fan	3.8	3.8
Press	3	-
Total	6.897	3.884

Uncertainty inclusion

External uncertainties are associated to variations in inlet waste composition, due to fluctuations in SC. Uncertainties are included by means of random sampling on uniform distributions of SC_i values using a crude Monte Carlo simulation. The ranges of variation of SC_i are defined after an extent review of data available in the Italian scenario. The minimum and maximum values are about the same obtained by varying SC_i of 50%. According to each random generated scenario, the percentage composition of URW as well as the internal repartition of the separated waste are calculated. The percentage composition of the TUW before the collection is assumed as constant. The output parameters are evaluated according to their probability distribution, considering the mean value μ and the Relative Standard Deviation (%RStD) (Equations 5.17, 5.18, 5.19) [152].

$$\mu = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{5.17}$$

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n} |x_i - \mu|^2} \tag{5.18}$$

$$RStD[\%] = \frac{\sigma}{\mu} \cdot 100 \tag{5.19}$$

The μ value represents the central tendency of the n generated values x_i, while the RStD is the ratio between the Standard Deviation σ and μ and it gives a measure of the dispersion of values around μ and so of the sensibility to the uncertainty. The distribution of output values can be discretized by dividing the range of existence in a number of equidistant k intervals each one containing n_k values. In this way, the relative frequency or probability p_i associated to the values in the k-th range is defined as in Equation 5.20. This is not an absolute value, since it depends on the arbitrary choice of n and k, but it can be useful at the time of comparing different distributions of the same parameter.

$$p_i = \frac{n_k}{n} \tag{5.20}$$

The internal uncertainties are associated with the energy consumption of the equipment, which can present an aleatory behavior due to the characteristics of the inlet material (e.g. sizing, moisture content, density, mass flow) or random malfunctions. According to the ranges of electric consumption indicated in Table 5.4, a normal probability distribution is supposed for each equipment consumption. In order to simulate the plant considering the uncertain internal factors, a discrete probability distribution following the normal one is created, according to the percentage repartition of the standard curve [152], and the μ value and RStD are calculated. These values are then used to simulate the Cumulative Distribution Function (CDF) of a continuous normal distribution, which is sampled using the Inversion method with a Monte Carlo simulation [65]. Even in this case, the simulation is performed considering the two different chain structures, by fixing the inlet composition of the waste to the base case.

Evaluation parameters

In order to evaluate the efficiency of the treatment chains with the variation of external and internal variables, some evaluation parameters are considered. First of all, the Yield (%) of SRF is calculated as the ratio between the outlet SRF and the inlet URW flows (Equation 5.21), being a measure of the global material recovery [139]. The quality of SRF is expressed by its MC (%), LHV (kJ/kg) and exergy content $B_{ch_{SRF}}$(kJ/kg).

$$Yield[\%] = \frac{SRF\,flow\,rate}{URW\,flow\,rate} \tag{5.21}$$

The Global Energy Consumption (GEC), namely the direct sum of the electric consumption of every equipment plus that of auxiliaries, is calculated to account for the influence of internal uncertainties. According to the exergy balances, Second Law Efficiency η_{ex} (Equation 5.22) is evaluated for the entire plant: the exergy of the two products (i.e. SRF and metals) is compared with the global exergy invested in the plant, namely the exergy of URW and the electric energy. In order to allocate the irreversibility ψ_{I_j} due to material and energy losses, lack of efficiency δ_j (Equation 5.23) and specific irreversibility y_j of j-th component (Equation 5.24) are calculated for each equipment. In case of δ_j the exergy destroyed in each equipment is related with the global exergy consumption, while in y_j with the exergy of the product of the same equipment [153].

$$\eta_{ex} = \frac{B_{SRF} + B_{met}}{B_{URW_{in}} + B_{el}} \tag{5.22}$$

$$\delta_j = \frac{\psi_{I_j}}{B_{URW_{in}} + B_{el}} \tag{5.23}$$

$$y_j = \frac{\psi_{I_j}}{B_{pr_j}} \tag{5.24}$$

5.3.2 Results

Sensitivity analysis

Table 5.9 reports the results of the sensitivity analysis performed on the two treatment chains. The SRF unit exergy cost c_{SRF} as well as the exergy efficiency refer to a scenario with recovery of ferrous metals. The metal unit exergy cost c_{met} of the chain A refers to the second Magnetic Separator; the value associated to the first Magnetic Separator is the same of the chain B.

Table 5.9: Results from sensitivity analysis

		SC paper		SC plastic		SC organic		Energy consumption		Base case values
		-30/+30%	%Diff	-30/+30%	%Diff	-30/+30%	%Diff	Min/Max	%Diff	
Yield (%)	A	43.9/33.7	+11/-15	41.8/36.9	+5.5/-7	36.7/45.1	-7.3/+14	-	-	39.6
	B	40.9/29.1	+14/-19	38.1/33.3	+6/-7	33.2/41.1	-7.5/+14.5			35.9
LHV (kJ/kg)	A	14933/16337	-3.5/+5	16643/13846	+7.5/-10.5	16199/14362	+4.7/-7.2	-	-	15473
	B	15113/16295	-3.9/+3.6	16887/14095	+7.4/-10.4	16521/14524	+5/-7.6			15728
$c_{SRF}10^{-4}$ **€**$/kJ_{ex}$	A	0.087/0.102	-5.4/+10.8	0.08/0.114	-13/+24	0.095/0.089	+3.3/-3.3	0.091/0.093	-1.1/+1.1	0.092
	B	0.092/0.113	-7/+14	0.086/0.123	-13/+24	0.102/0.096	+3/-3	0.098/0.101	-1/+2	0.099
$c_{met}10^{-4}$ **€**$/kJ_{ex}$	A	0.08/0.093	-2.4/+13.4	0.074/0.104	-17/+15.8	0.087/0.081	+6/-1.2	0.084/0.086	-1.2/+1.2	0.085
	B	0.074/0.085	-2.6/+11.8	0.068/0.095	-12.8/+18	0.081/0.074	+3.8/-5	0.078/0.079	0/+1.3	0.078
Exergy efficiency (%)	A	62/57.3	+3/-4.8	60.8/59.1	+1/-1.8	59.3/61.7	-1.5/+2.5	60.5/59.9	+0.5/-0.3	60.2
	B	58/51.6	+5/-6.5	56/53.8	+1.4/-1.8	54.6/56.3	-1.1/+2	55.6/54.8	+0.7/-0.7	55.2

With regard to the effect of the SC parameters, the behaviour of the output parameters in the variation range (±30%) is linear. SRF Yield presents the highest variations when SC of paper is varied (+11/-15% for chain A and +14/-19% for chain B). The yield increases (+14%) with an increment in SC of organic matter, since this implies a major percentage of plastic and paper in the inlet URW stream. The LHV of SRF has an increment (+5% for chain A and +3.6% for chain B) only for high values of SC of paper. In the other cases, when the quantity of plastic and organic matter diminishes, the reduction of MC is not compensated by an increase in carbon content and so the LHV decreases. The unit exergy cost of the products and the exergy efficiency are linked in the sense that a decrease in η_{ex} leads to higher exergy costs for producing the same amount of products, which is reflected in an increase of the unit exergy costs. The major variations are associated to the degree of SC of plastic, both for c_{SRF} (-13/+24%) and c_{met} (-17/+15.8%). The unit exergy cost of ferrous metal depends on the position of the magnetic separator, as expected; c_{met} increases of 9% when the magnetic separator is in the sixth position instead of third, because it is affected by all the exergy cost (in terms of exergy invested and destroyed) until that equipment. The exergy efficiency behavior depends on the combined effect of Yield and LHV of SRF; decreasing LHV can lead to increment in η_{ex}, only if it is balanced by a consistent increase in Yield, as in the case of variation of SC of organic matter. A comparison between the two chains shows that the structure B presents a lower Yield (-7%) and exergy efficiency (-8%) with respect to A, while the SRF unit exergy cost is higher (+7%). The energy consumption has no influence on the Yield and the LHV of SRF. A variation between the minimum and maximum value leads to minor fluctuations from the base case, with percentage differences in the order of 1% for cost of products and exergy efficiency. There are no significant differences between the responses of the two chains. In general, it is evident that the influence of the internal variable is definitely lower than the external one, with percentage differences more than 90% lower, at least in the considered SC variation range.

Irreversibility distribution

The distribution of irreversibility y_j among the equipment and the lack of efficiency δ_j due to material and energy losses are shown in Figure 5.9 and 5.10 respectively. Material losses are the primary source of irreversibility and are mainly concentrated in the pre-screening phase; it means that an average of 70% of the global input exergy (75% for chain A and 65% for chain B) is lost in this equipment. The metal separation and fine screening have similar values of y_j for both the structures, in the order between 5 and 10%, while the contribution of the shredding is less than 1%. The NIR separator has an important effect on chain B exergy losses (12%), higher than air classifier for chain A (6%). The distribution of the lack of efficiency confirmed this interpretation, underlining the differences between the energy and the material losses. Figure 5.10 shows that some equipment (i.e. shredder, pelletizer and storage) are almost only energy destructive.

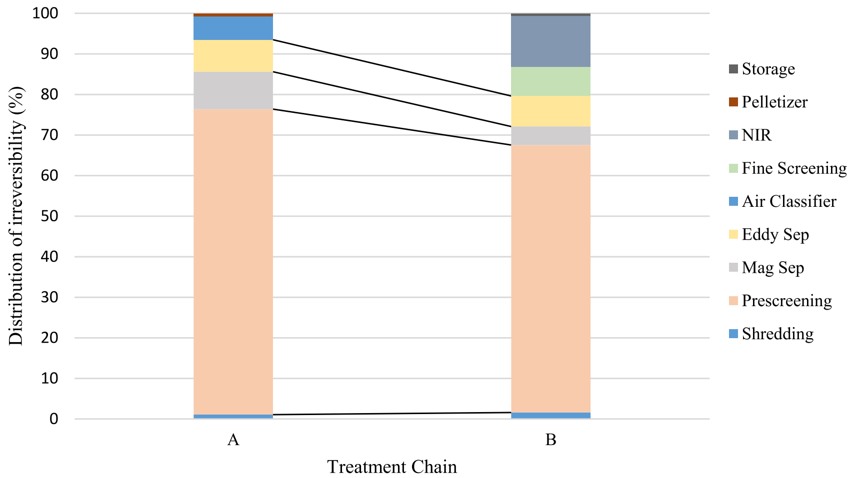


Figure 5.9: Distribution of irreversibility y among the equipment: comparison between the two chains

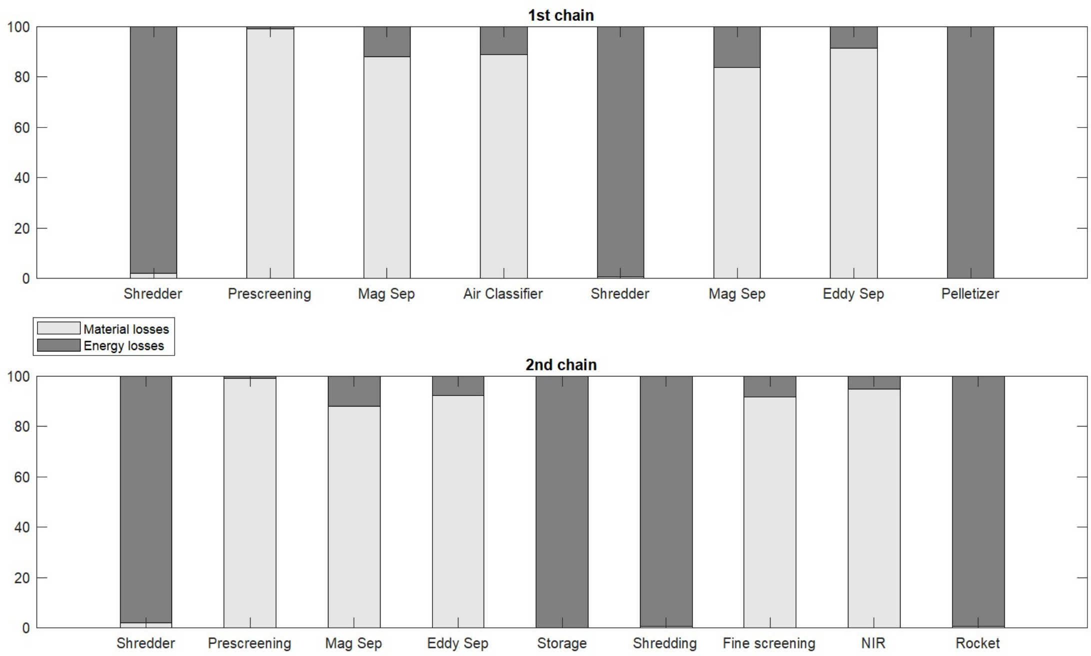


Figure 5.10: Lack of efficiency δ due to material and energy losses: comparison between the two chains

Uncertainty

The results of the random sampling using the Monte Carlo method are reported in Table 5.10, which contains the μ values and RStD of the output parameters. First of all, it is interesting to notice the μ value of SC_{gl}, since it represents the most probable value obtained by a random variation and combination of the values of SC_i. The SC_{gl} values follow the behaviour of a normal probability distribution (Figure 5.11), since it is the weighted sum of a number of independent random variables, each having a uniform distribution. The resulted theoretical probability distribution is the Irwin-Hall distribution with n=8 random variables [**E.Marengo2017**].

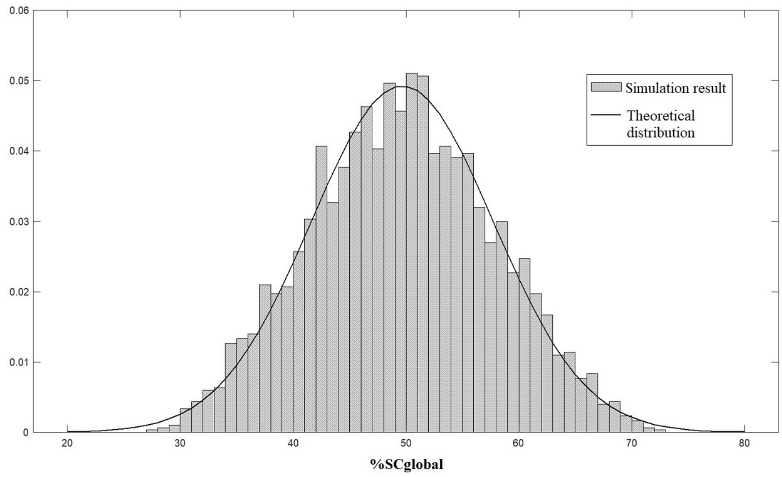


Figure 5.11: SC_{gl} distribution resulting from Monte Carlo simulation on waste composition

Regarding the evaluation parameters, the unit exergy cost of products is the most influenced by the uncertainties, showing an RStD of about 16%, while the exergy efficiency is the less affected (about 3%). As a general consideration, the dispersion of values around μ diminishes for the output parameters (i.e. Yield, LHV of SRF, exergy efficiency and cost of products). It means that the values of RStD of these parameters are considerably lower than the fluctuations of the input random variable (in this case the SC_i values and the energy consumption). This is an effect of the transformation operated by the treatment process, which tends to homogenize the inlet material. A comparison between the two chains shows that Chain A presents better performances with respect to Chain B, as already noted in the sensitivity analysis. The Yield has higher values (+7.7%), as well as the LHV of SRF (+0.2%) and the exergy efficiency (+8.5%), which leads to lower SRF exergy costs (-7.8%). Besides, Chain B is more sensitive to the uncertainties, as demonstrated by the values of RStD, which are from 1.7%

to 39% higher than Chain A, depending from the parameter. The trend of the probability distributions of evaluation parameters after Monte Carlo simulation on waste composition is graphically shown in Figure 5.12. The Yield presents a behaviour similar to the normal one, while the unit exergy cost and exergy efficiency are markedly not centred, following approximately an inverse Weibull distribution more than a normal one.

Table 5.10: Mean values μ and standard deviations of evaluation parameters resulting by uncertainty analysis

	External uncertainties				Internal uncertainties			
	μ		RStD (%)		μ		RStD (%)	
	A	B	A	B	A	B	A	B
SC_{gl} (%)	49.7		16.3		-	-	-	-
Yield (%)	42	39	11.8	13.3	-	-	-	-
LHV (kJ/kg)	15462	15432	5.8	5.9	-	-	-	-
SRF Unit Exergy cost (10^{-4} €/kJ_{ex})	0.089	0.096	16.1	16.8	0.086	0.092	0.09	0.27
Metal unit exergy cost (10^{-4} €/kJ_{ex})	0.082	0.076	15.8	15.5	0.08	0.074	0.02	0.02
Exergy efficiency (%)	60.8	56	2.8	3.9	62	55.2	0.07	0.14
GEC (kWh/Mg)	-	-	-	-	73.3	93.8	3.7	5.5

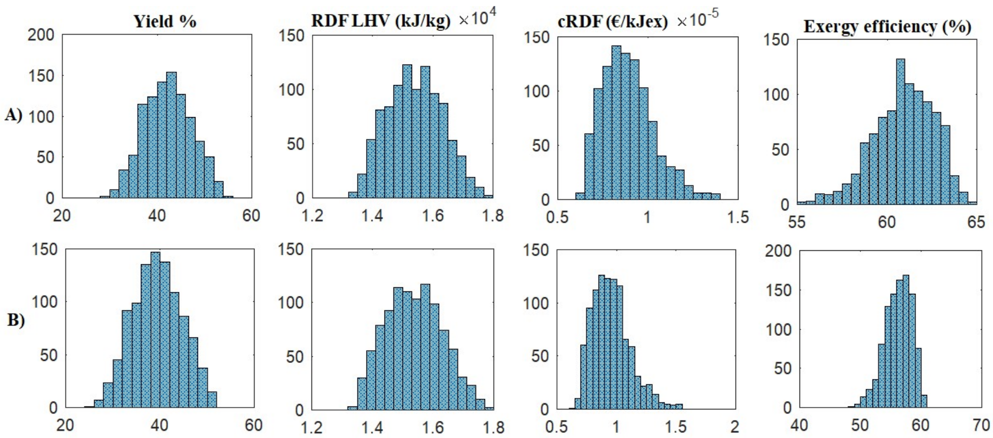


Figure 5.12: Probability distributions of evaluation parameters after Monte Carlo simulation on waste composition for the two chains

With respect to the internal uncertainties, the only evaluation parameters affected by the random variation of energy consumption are the exergy efficiency, the unit exergy costs of products and the GEC. As it can be seen in Table 5.10, the RStD of c_{SRF} and c_{met} and of η_{ex} is about two orders of magnitude lower than the one of the GEC. Besides, a comparison with Chain A shows that the RStD values are more generally lower for chain B and about 90% lower with respect to the external uncertainties ones. This result confirms the small impact of energy consumption of the equipment on the global performance of the system. Besides, as in the case of external uncertainties, it shows that the effect of fluctuations of energy consumption are absorbed and reduced within the system. As expected, the discrete probability distributions of the values follow the behaviour of the normal distributions, as can be seen in Figure 5.13. This is a consequence of the fact that the input variable varies in the assigned range according to a normal probability distribution.

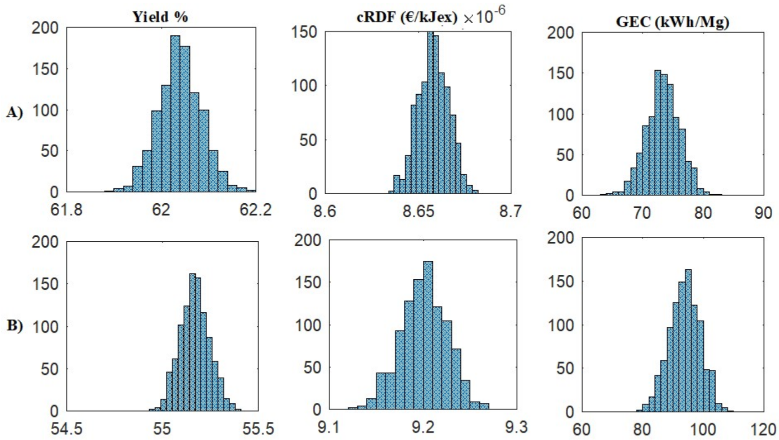


Figure 5.13: Probability distributions of evaluation parameters after Monte Carlo simulation on energy consumption for the two chains

Combined effect

In real working conditions, the system will be influenced at the same time by external and internal factors. For this reason, the combined effect is analyzed and the results are reported in Figure 5.14. The predominant influence of the external variables is even more evident, since the mean values of η_{ex} and c_{SRF} (red line in Figure 5.14) are very close to the ones obtained by performing the Monte Carlo simulation on waste composition only (see Table 5.10). Regarding the discrete probability distributions, it is interesting to notice that only for the η_{ex} of chain A, the p_i of the μ value is in the range of maximum probability. For the other parameters, the ranges are not the same, as can be seen by the values reported in Table 5.11.

Table 5.11: Comparison of the probability of the mean value with the range of maximum probability in case of combined effects

	Chain A		**Chain B**	
	η_{ex}	c_{SRF}	η_{ex}	c_{SRF}
p_i of μ value (%)	12.04	11.88	10.94	11.87
Maximum p_i (%)	12.04	12.28	12.28	12.94

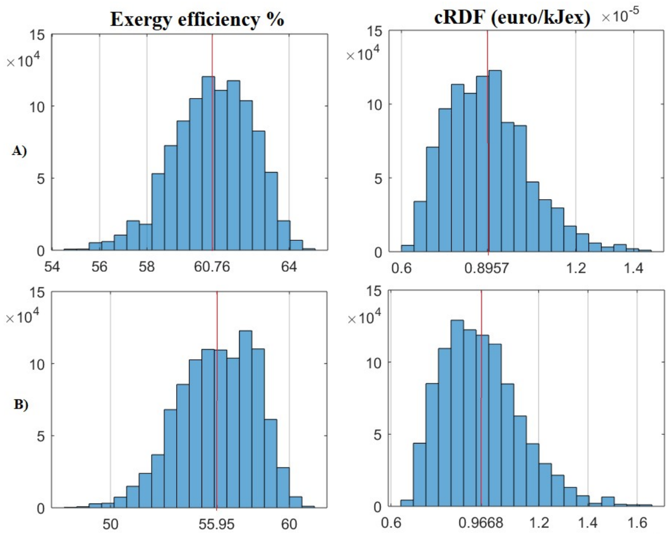


Figure 5.14: Probability distributions of evaluation parameters after Monte Carlo simulation on combined effects of uncertainty for the two chains

5.3.3 Conclusions and discussion

In this Section, a MBT plant for SRF production and metal recovery is modeled considering mass, energy and exergy balances. The aim is to evaluate the performance of the plant under an Exergoeconomic perspective, considering the influence of aleatory variations of external and internal operating parameters. The main conclusions are discussed below.

- The inclusion of a MBT plant into the ISWM system has been often a consequence of legislation modifications that force to treat the URW fraction before landfill disposal. The advantages of this intermediate step on the overall system performance are due to the possibility of removal of hazardous substances or recyclable material after the collection. In particular, the separation and stabilization of the organic part reduce the contamination due to gas and leachate emissions in landfill. Moreover, the MBT plant results to be a buffer for the variations in waste composition due to changes in degree of SC.

- The use of exergy in this context appeared to be particularly useful since material and non-material streams are involved. Besides, Exergoeconomics results a valuable approach for allocating the cost of the products considering the exergy invested and destroyed in each equipment and so the distribution of the irreversibility in the system. The Exergoeconomic analysis gives also practical indications for both managing and designing a new plant. The distribution of irreversibility shows that the material losses have a primary role in this kind of plant. The sequence of the equipment and the lack of efficiency that each one entails influence the final product unit costs; therefore, it has to be accurately considered in the design of the plant, which is a trade-off between the quality of SRF and recovered metals and the global exergy and economic cost. For the two analyzed chains, the pre-screening phase, the NIR separator and the third hammer mill strongly influence the energy consumption and material losses, leading to a lower Yield and exergy efficiency. Since these equipment are necessary for assuring the characteristics required for the SRF (especially if used in a cement kiln), their functioning has to be accurately monitored and optimized.

- Since the real working conditions of the plant can vary stochastically, a sensitivity analysis to external (waste composition) and internal (electric equipment energy consumption) uncertain variables is conducted. A Monte Carlo simulation is adopted for sampling from uniform and normal distribution of external and internal variables, respectively. The resulted mean values and standard deviations of efficiency, costs and energy consumption can be useful at the time of designing a new plant, e.g. considering the range of variation of selective collection in a certain area or the potential fluctuations in energy consumption. The analysis of the uncertainties confirms the primary importance of external variations over internal ones. In any case, the structure of the MBT plant tends to absorb and uniform the input fluctuations; this is consistent to the fact that those plants are aimed at manufacturing products with standard characteristics, or at least in certain ranges.

5.4 The paper stream exergy path

In this Section an analysis of a reduced SW treatment system (Figure 5.15) composed by a MBT plant for URW and a paper recycling plant is performed. The aim is to use the Embodied Exergy criteria to follow the path of the inlet paper stream and to evaluate the allocation of the material streams into the treatment system, testing its sensibility to uncertain working conditions.

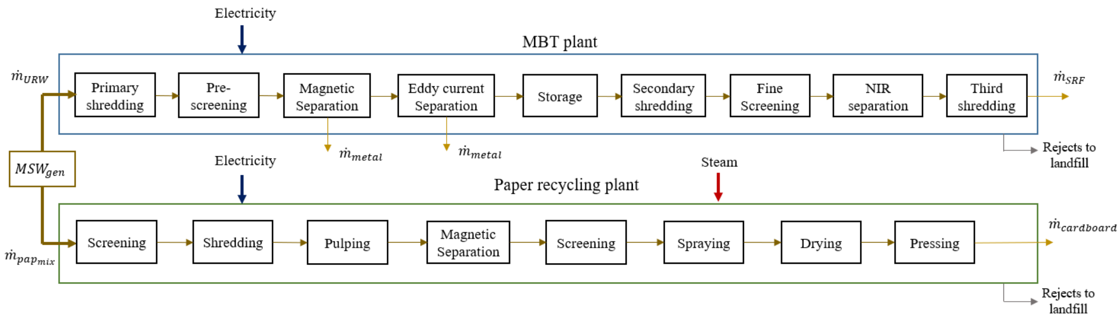


Figure 5.15: Reduced SW treatment under analysis in Section 5.4

5.4.1 Paper recycling

Among the recycling chains, paper recycling is one of the most well established with the highest index of recyclability (up to 80%) [154]. Besides, recycled paper substitutes materials which production cost from raw materials is about 50% higher in terms of energy consumption. In the present analysis, only cardboard production is considered, since it represents the first paper product from recycled pulp of the total European production [155].

The paper recycling plant is modelled considering only two macro parts: the stock preparation, which includes screening, shredding and pulping of the inlet paper material; the cardboard making process, composed by the pulp magnetic separation and the screening, spraying, drying and pressing.

In the paper recycling model, paper recovery factor and water consumption are given on inlet paper basis. In case of paper recycling, electricity is needed for the movement of the material and the pulping formation, depending on the type and quality of paper grade [156]. In this work, the deinking and dispersion phases are not considered, since cardboard is produced; this assumption reduces considerably the GEC of the recycling. Thermal needs for drying purposes are usually covered by superheated steam at 428 K and 1 bar [157]. Data on process are given in Table 5.12.

Table 5.12: Paper recycling data basing on [144, 156]

Water consumption for pulping formation (m^3/ton of paper)	1.5-35
Waste water (% on inlet paper flow)	5.4
Waste fibres (% on inlet paper flow)	1.62
Steam consumption (ton of steam/ton of paper)	5.54
Stock preparation (screening and cutting of inlet paper) (kWh/ton)	150-250
Paper making (conveyor for magnetic separation, vibrant screening, spraying and pressing) (kWh/ton)	150-300

5.4.2 Type of analysis

As can be seen in Figure 5.15, the boundary of the system analysed in this Section starts from the waste transport to the treatment plants (i.e. MBT and recycling) and ends with the manufacturing of the products, namely the SRF for cement kiln utilization and the recycled cardboard. Outside the system boundaries, the alternative chains for the production of substitute products are virgin paper manufacturing (i.e. from wood) and coal supply for cement kiln. Layout, assumptions and data on MBT plant are the same used for the Chain B in Section 5.3.

Global EE balance

The enlargement of the analysis outside the treatment system boundaries leads to a more accurate evaluation of all the contributions to the Embodied Exergy of the products (i.e. SRF fuel and cardboard); in fact, it is useful in order to account for the avoided or additional exergy and material consumption of the alternative scenarios. The exergy cost of extraction (or collection, in case of MSW), process and transport of raw materials are included in the global EE balance, in addition to the contribution of the single treatment process.

Assuming that the SRF is used in a cement kiln, the more common substitute fuel is the pulverized coal [158]. The exergy used to extract and process the coal is accounted for using the Thermo-Ecological Cost (TEC) indicator [36], with the hypothesis of barge transport. The correction factor of TEC, f_{TEC}=0.93, is introduced in order to account only the exergy cost associated to coal mining and extraction, ignoring the contribution of harmful substances abatement. The quantity of coal is calculated as the one for substituting the energy gap of SRF (ΔEn_{SRF}).

The alternative process to paper recycling for cardboard production is virgin production (*vp*) with mechanical pulping of wood as raw material. The exergy cost for processing wood $Ex_{wood_{pr}}$ includes the harvesting and transportation in a radius of 80 km according to [159], that can be a reasonable average for the European context.

The contribution of the input waste collection and transport $Ex_{tr_{UW}}$ and $Ex_{tr_{paper}}$ is calculated considering an average distance of 30 km between the generation point and the treatment plant [160]. All these factors are evaluated in terms of diesel consumption (Ex_{diesel}=45.6 MJ/kg). The exergy of products (Ex_{SRF} and $Ex_{cardboard}$) are calculated as their chemical exergy.

Table 5.13 resumes all the terms, internal and external to the process, used for calculating the EE balances expressed by Equations 5.25, 5.26, 5.27, 5.28 for SRF, cardboard from recycling, cardboard from wood and coal, respectively. The balances are expressed in kW, being $\dot{B}$ the product between the specific exergy and the mass flow.

Table 5.13: Specific exergy values used for EE balances, all expressed in MJ_{ex}/kg

URW transport	$Ex_{tr_{UW}}$	0.289
Inlet mixed paper	$Ex_{pap_{mix}}$	19.09
Waste fibres	Ex_{fib}	18.62
Mixed paper transport	$Ex_{tr_{paper}}$	0.235
Chemical exergy of wood	$Ex_{wood_{ch}}$	19.22
Processing exergy of wood	$Ex_{wood_{pr}}$	0.51
Thermo-ecological cost of coal	TEC_{coal}	1.12
Coal transport	$Ex_{tr_{coal}}$	3.1

$$EE_{SRF} = \dot{B}_{el_{MBT}} + \dot{B}_{URW} + \dot{B}_{tr_{URW}} - \dot{B}_{rejects} \tag{5.25}$$

$$EE_{card_{rec}} = \dot{B}_{el_{rec}} + \dot{B}_{paper_{mix}} + \dot{B}_{steam} + \dot{B}_{wat_{rec}} + \dot{B}_{tr_{paper}} - \dot{B}_{fib_{rec}} \tag{5.26}$$

$$EE_{card_{wood}} = \dot{B}_{el_{vp}} + \dot{B}_{wood_{pr}} + \dot{B}_{wood_{ch}} + \dot{B}_{wat_{vp}} - \dot{B}_{fib_{vp}} \tag{5.27}$$

$$EE_{coal} = \Delta En_{SRF} \cdot f_{TEC} \cdot TEC_{coal} + \dot{B}_{tr_{coal}} \tag{5.28}$$

For evaluating the additional or avoided resource consumption when different scenarios of selective collection occur, the difference in global EE balance (ΔEE_{gl}, Equation 5.29) is used. It is expressed by the algebraic sum of the difference of all the terms respect to the base case scenario (ΔEE_i); for example, an increase in SC_{paper} leads to an increase in $EE_{card_{rec}}$ and EE_{coal} (ΔEE>0) and a decrease in EE_{SRF} and virgin paper $EE_{card_{wood}}$ (ΔEE<0).

$$\Delta EE_{gl} = \Delta EE_{SRF} + \Delta EE_{card_{rec}} + \Delta EE_{card_{wood}} + \Delta EE_{coal} \tag{5.29}$$

The presented global embodied exergy balance can be considered as an opportunity cost, since it is an indicator of the savings or additional consumption encountered when a certain scenario is chosen respect to the base case (characterized by a certain value of SC_{paper}).

Sensitivity analysis

First, a sensitivity analysis is performed by varying the SC_{paper} in a range between -30/+30% respect to the base case, which is the same of Section 5.3 summarized in Table 5.7. The effect of the linear variation is investigated for two simulation scenarios: (A) fixed cardboard production $\dot{m}_{cardboard}$; (B) fixed MBT input mass flow $\dot{m}_{URW}$ and fixed $\dot{m}_{cardboard}$. The second case is the more realistic one, since the plants are always designed for working at a Nominal Capacity (NC), in case of MBT, or in order to reach a certain production, for recycling processes. In order to perform the simulation, the cardboard production $\dot{m}_{cardboard}$ is fixed to 2200 kg/h, while the input MBT flow to 5000 kg/h; these values are chosen according to the material flows of the base case scenario. The idea is to account the sensitivity of the system to the variation of the input conditions, evaluating the effects on the global exergy costs. In fact, if the generation of URW is different from the NC of the MBT plant, an additional cost of transport has to be accounting for importing ($\dot{m}_{URW}$ lower than NC) or exporting ($\dot{m}_{URW}$ higher than NC) the remaining URW from or to another waste transfer station (which is supposed to be in an area of 50 km). On the other side, a virgin paper production plant covers the fluctuations in cardboard production, due to variations in paper input to recycling plant.

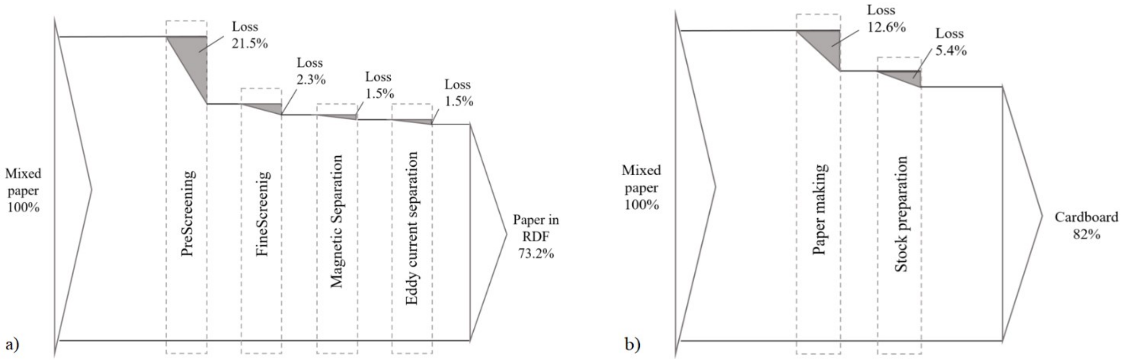
An uncertainty analysis is also conducted using the same methodology described in Section 5.3.

5.4.3 Results

Paper exergy path comparison

The allocation of the paper stream into a specific treatment path entails a different destiny for its internal exergy. The distribution of exergy losses is displayed in the Grassmann diagrams (Figure 5.16), which visualize the contribution of material losses for the MBT plant (a) and the paper recycling chain (b). The major losses of internal (chemical) exergy of paper are associated with the equipment with the higher degrees of material losses, namely the primary and secondary screening phase, followed by the eddy current and magnetic separators. The others components contribution is not significant. The portion of recovered internal exergy of paper is major in case of paper recycling (82% versus 73.2%), due to the small amount of rejected fibres.

Figure 5.16: Grassmann diagram representing the exergy destruction due to material losses



(a) MBT plant (b) Paper recycling

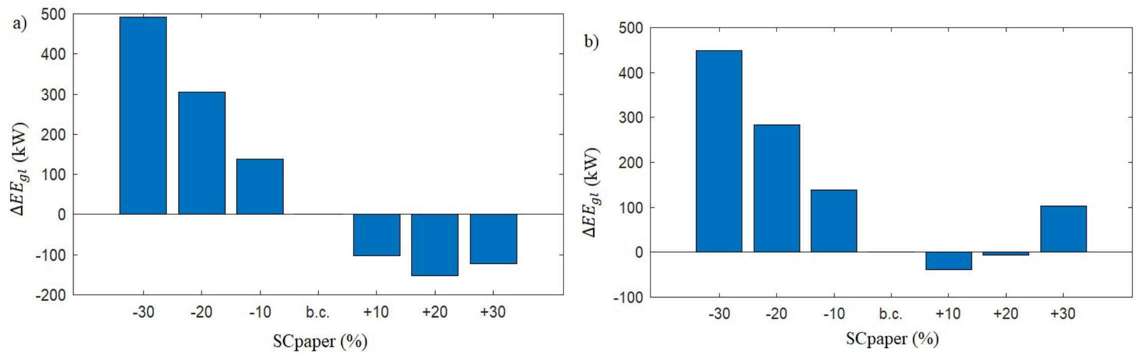
Global EE balance

The results of the linear variation of SC_{paper} are reported in Table 5.14 for the two simulation scenarios; the behaviour of each ΔEE_i in the reported ranges is linear. Global EE values for the base case of the two scenarios are 28,354 kW and 27,974 kW, for scenario A and B respectively. The $\Delta EE_{tr_{UW}}$ associated to URW transport is accounted separately. The resulting values of SRF exergy and Yield and MBT efficiency are also reported. In both cases the exergy efficiency of the MBT plant diminishes by about 13%, as a consequence of the less amount of paper in the final SRF; in fact, the Yield decrease (-28.8%) is not compensated by an equal increment in SRF specific exergy content (+13.5%). The exergy efficiency of the paper recycling plant is not influenced by the inlet composition, since the cardboard yield is fixed. Scenario A presents a quite symmetric distribution of values of ΔEE_i apart from ΔEE_{coal}, since it depends on the yield of SRF. This is the same cause of the asymmetry in ΔEE_{SRF} of scenario B; besides in this case ΔEE_{tr} is always positive, since it includes the transport cost for covering the capacity of the MBT plant. The trend of the resultant ΔEE_{gl} is shown in Figure 5.17. The greatest increments are associated to low degrees (-30%) of SC_{paper} for both scenarios (+1.73% for case A and +1.6% for case B); the major positive costs are associated to the production of cardboard from raw material, followed by the SRF production. The trend is generally decreasing, presenting a minimum of -0.53% for SC_{paper} = +20% (A) and of -0.13% for SC_{paper} = +10% (B). A new growth occurs for high percentage of SC_{paper}; this effect is more marked in scenario B, due to the higher additional costs of transport of the alternative fuel.

Table 5.14: Ranges of evaluation parameters and ΔEE_i resulting by a linear variation of SC_{paper}

	Scenario A	**Scenario B**
	Range (Min/Max value)	
Exergy efficiency MBT (%)	58.3/50.9	57.8/50.9
Yield SRF (%)	40.9/29.1	40.9/29.1
Exergy SRF (kJ/kg)	19214/21817	19214/21817
ΔEE_{SRF} (kW)	+2842.8/-2843.4	+875.2/-1213.3
$\Delta EE_{card_{rec}}$ (kW)	-5668/+5669	-5668/+5669
$\Delta EE_{card_{wood}}$ (kW)	+6385/-6387	+6385/-6387
ΔEE_{coal} (kW)	-3080/+3450	+1270/-1972
$\Delta EE_{UW_{tr}}$(kW)	+12.5/-12.5	+126.61/+61.63

Figure 5.17: Difference in Global Embodied Exergy respect to the base case for the two scenarios



(a) fixed $\dot{m}_{card}$ (b) fixed $\dot{m}_{URW}$ and $\dot{m}_{card}$

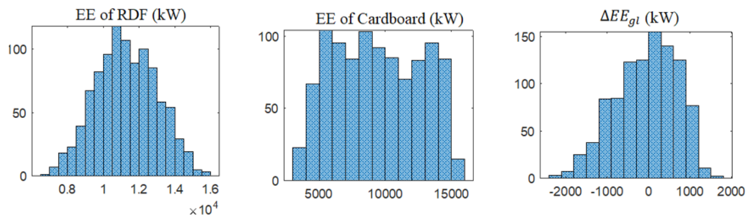
Uncertainty effect

Table 5.15 reports the μ values and RStD of the main output parameters resulted by the Monte Carlo sampling on external and internal uncertain variables. The trend of the evaluation parameters is graphically shown in Figure 5.18. The behaviour of the ΔEE_{SRF} follows the normal one, since it is influenced by the random variation of the different material streams; however, there is no direct correlation with one single parameter (SC_{gl}, SC_{paper}), but rather with a combination of SC_{paper}, $SC_{plastic}$ and $SC_{organic}$. Differently, the $\Delta EE_{cardboard}$ presents a more uniform distribution since only the paper random variation affects its behaviour; in fact, the value of the RStD is about 2.2 times higher than in the case of the ΔEE_{SRF}. The global EE balance, ΔEE_{gl}, is strongly influenced by the behaviour of the ΔEE_{SRF}, even if the resulting distribution is not normal centred. Results show that the random variation of waste composition has a moderate effect on the global balance of EE; the major differences respect to the base case are in the range of values between -500 and +750 kW (about +/- 2% of the total), which means that the opposing effects quite compensate each other. With regard to the internal uncertainties, the evaluation parameters affected by the random variation of energy consumption are the exergy efficiency, the unit exergy costs of products, the global energy consumption and, as a consequence, the embodied exergy. As it can be seen in Table 5.15,the RStD of the product costs and the efficiency is about two orders of magnitude lower than the one of the GEC. This result is a direct consequence of the less impact of energy consumption on system efficiency; besides, as in the case of external uncertainties, it shows that the effect of variation of energy consumption is reduced within the system. As expected, the discrete distribution of the values follows the behaviour of the normal distribution, as can be seen in Figure 5.18.

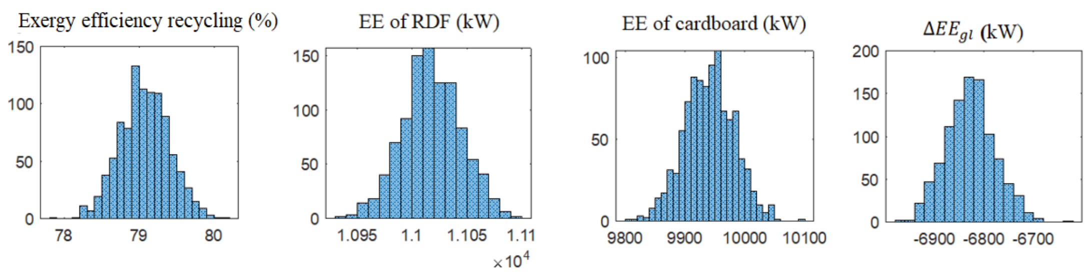
Table 5.15: Difference in Global Embodied Exergy respect to the base case for the two scenarios

	External uncertainties		**Internal uncertainties**	
	μ	RStD (%)	μ	RStD (%)
Exergy efficiency Paper recycling (%)	-	-	79.1	0.4
EE_{SRF} (kW)	11296	15.5	11017	0.24
$EE_{card_{rec}}$(kW)	9430.5	34.5	9940.2	0.42
Unit exergy cost Cardboard (kW/kW)	-	-	1.249	0.42
GEC Paper recycling (kWh/Mg)	-	-	424.6	7.2

Figure 5.18: Distribution of values due to uncertainties



(a) external



(b) internal

5.4.4 Conclusions and discussion

In this Section, a reduced SW treatment system composed by a MBT and a paper recycling plant is modeled and mass, energy and exergy balances are calculated in order to follow the path of the inlet paper material stream. The Embodied Exergy concept is used to evaluate the allocation of the waste paper stream into the treatment system, including the variety of operating conditions that can be faced in real working conditions. The major conclusions are discussed as follows.

- In general, a paper recycling plant requires, as expected, major energy consumption with respect to a MBT plant. However, the purpose is completely different, since recycled paper and cardboard have higher market values and substitute products whose production chains from virgin materials are particularly energy intensive. Therefore, paper recycling is not only a better alternative for recovering the waste paper internal exergy, but it is also cost-effective compared with cardboard production from wood. The SRF is a secondary product that would still be produced from URW. Waste paper has a consistent carbon fraction but also a considerable moisture content that reduces the SRF calorific value (this is why the SRF LHV increases for high values of SC_{paper}). The major disadvantage can be linked to the diminishing of the SRF Yield, but this can be compensated increasing the quantity of inlet URW to the MBT plant.

- The use of Embodied Exergy criteria together with the enlargement of the boundaries of the system lead to a more accurate evaluation of all the contributions to the EE of the products (i.e. the SRF fuel and the cardboard). This idea combined with the sensitivity analysis allowed the calculation of the avoided or additional resource consumption linked to the presence of the alternative scenarios (i.e. coal instead of SRF for cement kilns and wood-based cardboard production). It is interesting to notice the effect of the global EE variation of the entire system. In fact, a decrease in SC_{paper} leads to greater values of ΔEE_{gl}, but savings on EE diminish for high collection of paper, because of the influence of MSW transport and coal cost. Anyway, the variations are very moderate, in the order of $\pm 2\%$. This led to the conclusion that even if the SWM system has a good degree of self-regulation, high share of selective collection can still be hindered by economic burdens, most of them linked to transport issues. An optimized location of recycling plants will reduce the global exergy cost. Moreover, a comparison with alternative fuel (i.e. natural gas) for cement kilns would be recommended, in order to test a more flexible system for SRF energy recovery.

- A sensitivity analysis to external (waste composition) and internal (electric energy consumption of the equipment) uncertain variables was conducted in order to give indications for realistic working scenarios. The resulted mean values and RStD of efficiencies, costs and energy consumption can be useful at the time of designing a new plant. The analysis of the uncertainties confirms the influence of external variations is higher than the internal ones. In any case, the structure of the system (for both the MBT and the paper recycling plant) tends to absorb and uniform the input fluctuations, even if this effect is more evident in the MBT plant. This is consistent with the fact that these plants are aimed at manufacturing products with the standard characteristics required by the final users.

5.5 Exergy-based optimization

In this Section, the boundaries of the analyzed system are enlarged in order to include the paper, mixed plastic packaging and URW collection and treatment paths. It is still a reduced MSW system, but it includes the two main separated collected materials and the MBT plant that buffer the variations in *SC*. The aim of the analysis presented in this Section is to evaluate the effect on exergy-based resource consumption indicators of flow repartition between plants, including all the possible combinations from 0 to 100% of recycling of paper and plastic waste streams. Besides, a multi-objective optimization on cost and exergy efficiency is performed in order to find the trade-off points of system management within the system boundaries presented in the next Section.

5.5.1 System boundaries

The sub-systems included in the boundaries are shown in Figure 5.19: the Collection and Transport (C&T) of the separated material streams, $\dot{m}_i$; the transfer station; the MBT plant for URW stream, $\dot{m}_{URW}$; the paper recycling plant for paper stream $\dot{m}_{pap}$, aimed at cardboard production; the plastic sorting plant for mixed plastic stream $\dot{m}_{plas}$; the polymer recycling plants.

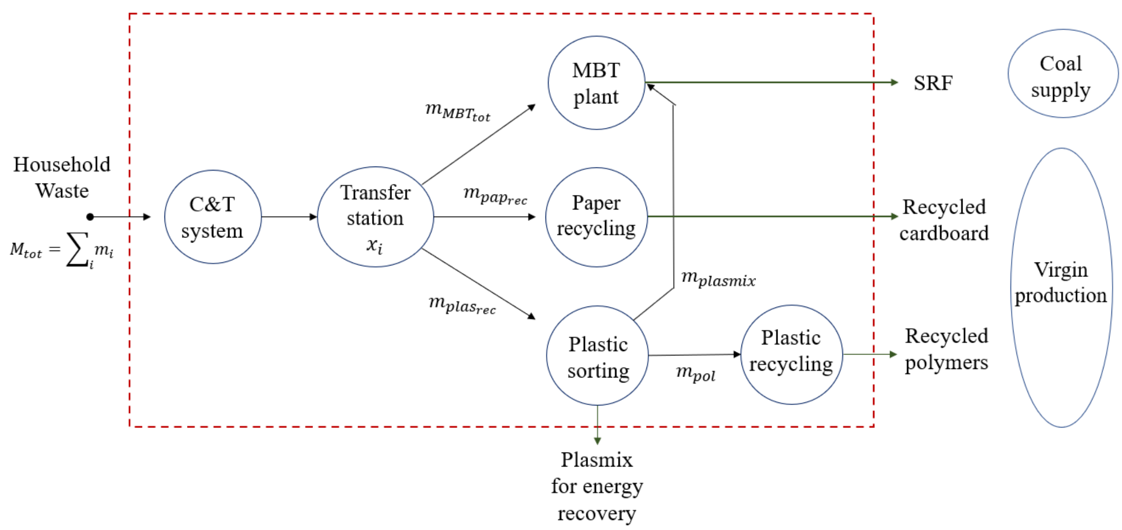


Figure 5.19: System boundaries and alternative processes

The inlet stream is the total household waste generation, which corresponds to the sum of the single material streams, $\dot{M}_{tot} = \sum_i \dot{m}_i$. Splitting of material streams can occur at transfer station, considering that part of paper and plastics can be added to URW and processed in MBT plant for SRF production. The split factors for the i-th stream and the resulting material flows to MBT and recycling plants are expressed by Equations 5.30, 5.31 and 5.32 respectively. All flow terms are calculated in kg/day.

$$x_i = \frac{\dot{m}_{MBT_i}}{\dot{m}_i} \tag{5.30}$$

$$\dot{m}_{MBT_{tot}} = \sum_i x_i \cdot \dot{m}_i \tag{5.31}$$

$$\dot{m}_{i_{rec}} = \dot{m}_i \cdot (1 - x_i) \tag{5.32}$$

Plastic packaging waste is a multi-polymeric stream. After an intermediate step of plastic sorting, only few polymers go to recycling in form of films, bottles or hard containers: Polyolefin (PO), such as Polyethylene (PE) and Polypropylene (PP), or polyesters like Polyethylene terephthalate (PET). Residual mixed plastic (also called plasmix) $m_{plasmix}$ from plastic sorting can be destined to energy recovery in cement kiln (71%) or cogeneration plants (29%) [161], as assumed here. The final destination of the products are cement kilns for SRF energy recovery and recycled products market for cardboard and recycled polymers. In the worst-case scenario of zero treatment, all waste would end up in landfill. Therefore, the alternative scenario in absence of these products includes the virgin materials production (for cardboard and polymers) and the pulverized coal supply for cement kiln. These alternative chains are modelled and used for evaluating the avoided/additional resource consumption in case of different recycling scenarios, simulated varying the splitting factor. For the MBT and the paper recycling plants, layout assumption and data are the same of Section 5.4. Data on plastic recycling and virgin production are the ones described in Chapter 4. For the C&T model, the analysis is done for a population of 500,000 inhabitants, considering a per-capita daily MSW generation of 1.3 kg/day. Since a typical Italian kerbside (or 'door-to-door') collection system is modelled, the degrees of selective collection for the i-th material stream (SC_i) are set to relatively high values (Table 5.16). In fact, it is demonstrated that kerbside collection allows reaching higher levels of household waste segregation [18]. The TUW gravimetric composition is the same reported in Table 5.7.

5.5.2 Exergy-based efficiency indicators

Equations 5.33- 5.45 summarize the EE balances of processes and products, with all terms expressed in kW, as follows: inlet URW (Equation 5.33), inlet paper (Equation 5.34), inlet mixed plastic (Equation 5.35), MBT process (Equation 5.36), paper recycling (Equation 5.37), plastic sorting (Equation 5.38), polymers recycling (Equation 5.39), SRF (Equation 5.40), recycled cardboard (Equation 5.41), plastic output (Equation 5.42), virgin polymers (Equation 5.43), virgin cardboard (Equation 5.44), coal (Equation 5.45).

Table 5.16: Degree of Selective Collection of each stream

Material Stream	**SC (%) w.b.**
Paper	80
Recyclable Plastics	65
Other Plastics	0
Organic Matter	85
Wood	85
Leather	0
Non-Ferrous Metal	65
Ferrous metal	65
Glass	85
Textile	35
Other Inorganics	0

$$EE_{URW_{in}} = Ex_{tr \to ts} \cdot \dot{m}_{URW} + (Ex_{tr \to MBT} + Ex_{URW_{ch}}) \cdot \dot{m}_{MBT_{tot}} \tag{5.33}$$

$$EE_{pap_{in}} = Ex_{tr \to ts} \cdot \dot{m}_{pap} + (Ex_{tr \to rec} + Ex_{pap_{ch}}) \cdot \dot{m}_{pap_{rec}} \tag{5.34}$$

$$EE_{pl_{in}} = Ex_{tr \to ts} \cdot \dot{m}_{plas} + (Ex_{tr \to rec} + Ex_{plas_{ch}}) \cdot \dot{m}_{plas_{rec}} \tag{5.35}$$

$$EE_{MBT} = Ex_{el_{MBT}} \cdot \dot{m}_{MBT_{tot}} \tag{5.36}$$

$$EE_{rec_{pap}} = (Ex_{wat} + Ex_{fuel} + Ex_{el} + Ex_{add})_{rec_{pap}} \cdot \dot{m}_{pap_{rec}} \tag{5.37}$$

$$EE_{pl_{sort}} = Ex_{el_{sort}} \cdot \dot{m}_{plas_{rec}} \tag{5.38}$$

$$EE_{rec_{pol}} = (Ex_{wat} + Ex_{fuel} + Ex_{el})_{rec_{pol}} \cdot \dot{m}_{pol} \tag{5.39}$$

$$EE_{SRF} = Ex_{URW_{ch}} \cdot RFTF \cdot \dot{m}_{MBT_{tot}} \tag{5.40}$$

$$EE_{card_{rec}} = Ex_{card} \cdot REC_{pap} \cdot \dot{m}_{pap_{rec}} \tag{5.41}$$

$$EE_{pl_{out}} = \dot{E}x_{PE} + \dot{E}x_{PP} + \dot{E}x_{PET} + \dot{E}x_{plx_{fuel}} + \dot{E}x_{plx_{el}} + \dot{E}x_{plx_{heat}} \tag{5.42}$$

$$EE_{pol_{vir}} = (Ex_{wat} + Ex_{fuel} + Ex_{el})_{prod_{pol}} \cdot \dot{m}_{pol} \quad (5.43)$$

$$EE_{card_{vir}} = (Ex_{wood} + Ex_{wood_{proc}} + Ex_{el} + Ex_{wat})_{prod_{card}} \cdot \dot{m}_{card} \quad (5.44)$$

$$EE_{coal} = \Delta EE_{en} \cdot f_{TEC} \cdot TEC_{coal} + Ex_{tr_{coal}} \quad (5.45)$$

For the inlet waste streams, in addition to the chemical exergy $Ex_{i_{ch}}$, the exergy cost of transport is included (to both transfer station $Ex_{tr\rightarrow ts}$ and MBT or recycling plant, $Ex_{tr\rightarrow MBT}$ or $Ex_{tr\rightarrow rec}$), in terms of diesel consumption (Ex_{diesel}=45.6 MJ/kg). The MBT and plastic sorting only use electricity (Ex_{el}), while the recycling processes require additives (Ex_{add}), water (Ex_{wat}) and fuel (Ex_{fuel}). In virgin cardboard production, wood chemical exergy ($Ex_{wood_{ch}}$), harvesting and transportation ($Ex_{wood_{proc}}$) are included. The exergy of products are calculated as their chemical exergy in case of SRF and cardboard. The plastic output is calculated as the sum of the chemical exergy of recycled PE, PP and PET, and the plasmix contribution in terms of the electrical ($\dot{E}x_{plx_{el}}$) and thermal energy ($\dot{E}x_{plx_{heat}}$) obtained by cogeneration, as well as the contribution as fuel for cement kiln ($\dot{E}x_{plx_{fuel}}$).

EE concept can be used for developing indicators accounting the resources invested in different scenarios management. In this work, three exergy-based indicators are developed and used. The first one is the Global Exergy Efficiency (GEE) (Equation 5.46). This represents a classical version of exergy efficiency, which compares the recovered exergy in products $EE_{products}$ (i.e. SRF, cardboard and plastic output) with the total invested exergy of inlet materials EE_{inlet} (i.e. URW, mixed paper and plastic), process $EE_{process}$ (i.e. MBT, paper and plastic recycling and sorting) and including the avoided or additional exergy consumption of alternative scenarios (EE_{vir} and EE_{coal}). This is due to the fact that the value of recycled products is not only linked to their chemical exergy, but mostly to the fact that they substitute virgin materials. The Additional Exergy Indicator (AEI) (Equation 5.47) expresses the additional exergy associated to treatment and transport to recycling plants as a percentage of the one that would be lost in case of landfill disposal after collection. Finally, the Exergy Scenario Comparison (ESC) (Equation 5.48) compares the actual scenario with the zero treatment case, including the alternative production chains. All the indicators are evaluated according to the variation of the split factor of paper and plastic (x_{pap} and x_{pl}) between 0 (corresponding to 100% of recycling) and 1 (no recycling case). If fractions of paper and plastics go to MBT ($\dot{m}_{MBT_{pap}}$ and $\dot{m}_{MBT_{plas}}$), the corresponding recycled products have to be produced in alternative ways, constituting an additional exergy burden ($+EE_{pol_{vir}}$ and $+EE_{card_{vir}}$); however, at the same time more SRF fuel is produced, leading to coal supply savings ($-EE_{coal}$).

$$GEE(\%) = \frac{\sum_j EE_{products_j}}{\sum_i EE_{inlet_i} + \sum_k EE_{process_k} + EE_{vir} - EE_{coal}} \tag{5.46}$$

$$AEI(\%) = \frac{\sum_k EE_{process_k} + Ex_{tr\rightarrow rec}}{\sum_i EE_{inlet_i} - Ex_{tr\rightarrow rec}} \tag{5.47}$$

$$ESC(\%) = \frac{\sum_i EE_{inlet_i} + \sum_k EE_{process_k} + EE_{vir} - EE_{coal}}{\sum_i EE_{inlet_i} - Ex_{tr\rightarrow rec} + EE_{vir_{tot}} + EE_{coal_{tot}}} \tag{5.48}$$

5.5.3 MOFs optimization

In general, it appears evident that the comparison between the various treatment options cannot be done only in an economic perspective. In fact, through recycling, MSW become a new source of materials, substituting energy and resource intensive virgin material production chains. As explained in Chapter 3, MOFs optimization is used when conflicting objectives are present, in order to find the best trade-off solutions. In this work, a MOFs optimization for total cost C_{TOT} minimization and GEE maximization is performed (Equation 5.49). The optimization is performed for a population P_{tot}=500,000 inhabitants, a population density W=0.4, a unit collection area U_b=2,000 and one weekly removal N_w.

$$min_{\mathbf{x}} \quad C_{TOT} \quad \& \quad max_{\mathbf{x}} \quad GEE \tag{5.49}$$

Two case studies are analysed with different optimization variables, as follows.

- In the first case, the optimization variables are the split factors (x_{pap} and x_{pl}), which can vary from 0 to 1. The variation of these parameters depends on the decisions that can occur at the transfer station, reflecting different waste management strategies. It means that part of material is intentionally sent to the MBT instead to the recycling plant after being collected. This could be done for different reasons, mainly linked to material surplus and lack of request or technical problems in the recycling plants.The possibility of splitting the paper and plastic streams implies savings in monetary costs linked to recycling options but, at the same time, an increasing exergy burden of the alternative production chains; thus, a minimization of monetary costs only is not sufficient to ensure a rational use of resources.
- In the second case, the optimization variable is the SC degree of paper (SC_{pap}), which can theoretically vary from 0 to 100%. The SC of plastic (SC_{pl}) and of the other materials are fixed; the SC_{pap} is chosen due to its great influence on the total SC, since paper weight share in total SW generation is consistent. The variation of the scenario occurs during the collection: assuming a constant MSW generation, the amount of paper that ends up in the URW decreases

with an increment in *SC*. Then, the variation is not intentional, but depends from the characteristics of the collection scheme, people's habits and training, waste policies and incentives. In this case, the denominator of the efficiency formula changes the signs of the alternative scenarios EE (Equation 5.50), since an increment in SC leads to savings in virgin production and additional energy burden for alternative fuel.

$$GEE'(\%) = \frac{\sum_j EE_{products_j}}{\sum_i EE_{inlet_i} + \sum_k EE_{process_k} - EE_{vir} + EE_{coal}} \tag{5.50}$$

In both cases, the aim is to find the existing optimal configurations and the corresponding range of cost and efficiency. The MOFs optimization is performed in MATLAB environment, using an elitist Genetic Algorithm (GA) technique [74]. The C_{TOT} (Equation 5.51) is the sum of: the fixed maintenance costs of the j-th plant C_{maint}, the process cost C_{proc}, the cost for residuals disposal C_{rej}, and the collection and transport cost C_{coll} and C_{tr} of the i-th material steams to the j-th treatment plants.

$$C_{TOT} = \sum_i \sum_j (C_{maint_j} + C_{proc_j} + C_{rej_j} + C_{tr_{ij}} + C_{coll_i}) \tag{5.51}$$

For the MBT plant, C_{maint} is calculated as the 10% of the total investment cost through the empiric correlation in Equation 5.52, obtained from equipment cost data referring to a range of capacity K between 60 and 300 tons/day. With regard to recycling plants, C_{maint} is about 5% of the global revenues based on products selling. The cost of MBT and plastic sorting processes is linked to electricity consumption only, while in the recycling process cost, the purchase of electricity, water, Natural Gas (NG) for auxiliary boiler, fuel and additives is included. For all plants, the rejects cost is the one of disposal in landfill. The C&T cost is calculated with the specific costs explained in Section 5.2. Total cost is expressed in €/day.

A summary of all the values of the parameters used for the exergy analysis and optimization are summarized in Table 5.17 .

$$C_{maint_{MBT}}(K) = 289.7 \cdot ln(K) - 2964.3 \tag{5.52}$$

5.5.4 Results

Scenario comparison based on EE

Figure 5.20 shows the trend of the exergy indicators with all the possible splitting configurations. The GEE (Figure 5.20a) is maximum (68.7%) when all the material streams go to recycling, while it drops down of 20% (55.17%) in case of

Table 5.17: Summary of parameters used for the analysis, based on [22, 36, 93, 100, 155, 159]

Waste transport		**Exergy**	
Truck capacity [m^3]	10	Exergy of diesel [kJ/l]	35,654
Route time [hours]	1.44	Exergy of additives [kJ/kg_{pap}]	551
Transfer station distance [km]	25	Exergy of NG [kJ/m^3]	42,182
Recycling plant distance [km]	50	Exergy of wood [kJ/kg]	19,223
MBT plant distance [km]	25	Exergy of sludge [kJ/kg]	18,624
Fuel consumption [l/km]	7	Exergy of wood transport [kJ/kg]	306
MBT plant		Exergy of wood harvesting [kJ/kg]	198
Electricity consumption [kJ/kg_{URW}]	432	TEC coal [kJ_{ex}/kJ_{en}]	1.12
URW density [kg/m^3]	80	Exergy transport coal [kJ/kg_{coal}]	2901
Paper recycling		Exergy of cardboard [kJ/kg]	20,972
Paper recovery factor	0.88	Exergy of PO [kJ/kg]	48,034
SW in paper (%)	9	Exergy of PET [kJ/kg]	25,242
Waste fibers (%)	1.62	EE PO recycling [kJ/kg]	3,014
NG consumption [m^3/kg_{pap}]	0.087	EE PET recycling [kJ/kg]	4,000
Water consumption [kg_{wat}/kg_{pap}]	14	EE PE virgin production [kJ/kg]	23,230
Electricity consumption [kJ/kg_{card}]	846	EE PP virgin production [kJ/kg]	39,006
Mixed paper density [kg/m^3]	75	EE PET virgin production [kJ/kg]	51,211
Polymer recycling		EE PE virgin production [kJ/kg]	23,230
Plastic sorting electricity [kJ/kg_{pl}]	129.6	**Costs**	
Mixed plastic density [kg/m^3]	23	Diesel cost [€/l]	1.55
PE fraction in plastic sorting	0.166	NG cost [€/m^3]	0.29
PP fraction in plastic sorting	0.144	Landfill disposal cost [€/kg]	0.105
PET fraction in plastic sorting	0.155	Waste paper cost [€/m^3]	0.035
Plasmix fraction in plastic sorting	0.326	Water cost [€/m^3]	4.192
PO recycling recovery factor	0.88	Cardboard cost [€/kg]	0.415
PET recycling recovery factor	0.76	Cellulose cost [€/kg]	0.47
Plasmix LHV [kJ/kg]	32,000	Electricity cost [€/kWh]	0.1
Virgin cardboard		Additive cost [% on cardboard production]	1
Electricity consumption [kJ/kg_{pulp}]	3600	PO cost recycling [€/kg]	1.33
Water consumption [kg_{wat}/kg_{pap}]	20	PET cost recycling [€/kg]	2.155
Waste fibers [%]	4.2	Salary for waste operator [€/year]	40,913

zero recycling. The paper split factor x_{pap} appears to have more influence, leading to a GEE variation of about 17% at constant x_{plas}; in the opposite case the difference is only 3-4%. As expected, the AEI (Figure 5.20b) follows the same behaviour; it ranges from 15.2% for x_{pap}=x_{plas}=0 to 2.2% for x_{pap}=x_{plas}=1. Even in this case, the variation is more marked with x_{pap}, with a decrement from 62% (x_{plas}=0) to 80% (x_{plas}=1); in the other case, the decrease is about 22% (x_{pap}=0) and 60% (x_{pap}=1). The ESC (Figure 5.20c) indicator has a different behaviour: it is maximum in case of total recycling of plastic and zero recycling of paper and minimum in the opposite situation. The increment with x_{pap} at equal x_{plas} is about 4%, while the decrement in the opposite direction is of 2%.

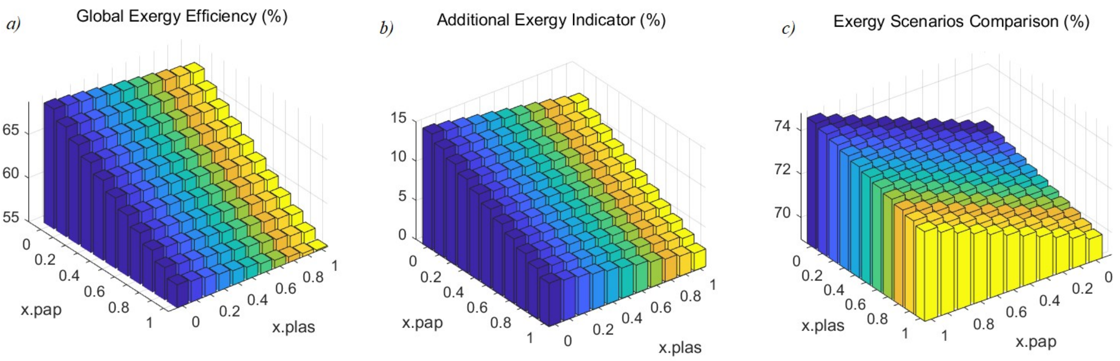


Figure 5.20: Variation of exergy indicators with splitting configurations

It is interesting to observe the process contribution to the Total Invested Exergy (kW), reported in Figure 5.21 for the case x_{pap}=x_{plas}= 0.5. The main considerations are the following.

- The highest share of the total invested exergy is associated to the chemical exergy of the inlet materials, in particular of the URW (57.47%), followed by the mixed waste plastic (15.26%) and paper (11.82%).
- In general, the exergy associated to waste transport is not so significant. Plastic transport has the major impact (1.66%) in terms of exergy with respect to paper (0.53%) and URW transport (0.98%).
- Among the treatment processes, paper recycling is the more resource intensive (4.17%), with respect to MBT plant (1.37%) and polymer recycling (0.68%).
- Plastic sorting represents the lowest contribution (0.05%) in terms of invested exergy.
- The comparison between the alternative scenarios shows that virgin paper production has higher impact than polymer production (16.3% versus 6.3%). The algebraic sum with the exergy savings in alternative fuel supply is always positive and it amounts to 4.73% in case of paper and 1.24% in case of plastic.

MOFs optimization: material split effect

Figure 5.22 shows the Pareto front resulting from a MOFs optimization for minimization of C_{TOT} and maximization of GEE, according to the split variables x_{pap}

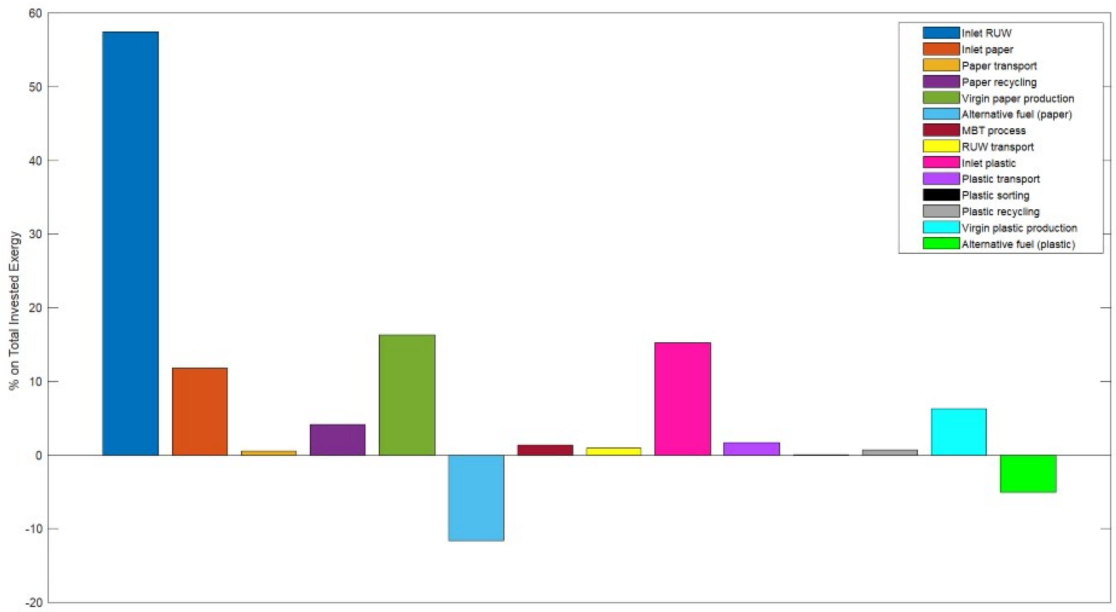


Figure 5.21: Process contributions to Total Invested Exergy

and x_{plas}. The curve is continuous, with *GEE* values ranging from 55.8% to 71.2% and cost values between 43.1 and 61.5 k€/day. The extreme points of the curve corresponds to the opposite scenarios of no recycling (low efficiency and costs) and total recycling (high efficiency and costs). The solutions circled in red in Figure 5.22, represent a sort of turning point, accompanied by a slight change in gradient. These points corresponds to total recycling of plastic (x_{plas} ≈0) and no recycling of paper (x_{pap} ≈1). Continuing on the front, the split of paper is constantly increasing (green circled solutions). For example, an increment of 40% in x_{pap} (from 25% to 65% of paper recycling) involves an increment of about 14% in costs (from 49 to 56 k€/day) and of 9% in GEE (from 61.2 to 66.5%). It is interesting to notice that the majority of solutions (85%) implies near or total recycling of plastics, while only 9% of solutions are associated with high levels of paper recycling.

MOFs optimization: selective collection effect

The Pareto front resulting from the second MOFs optimization is shown in Figure 5.23. The SC_{plas} is fixed to 65% (i.e. a likely value in case of kerbside collection), while SC_{pap} is the optimization variable. The cost and efficiency range is higher since it is the area corresponding to high recycling rates (since it is supposed that x_{pap}=x_{plas}=0, so all the collected material is recycled). The *GEE'* values rang from 61.9% to 75.3%, whit corresponding costs from 61.4 to 73.6 k€/day. The fact that the Pareto front is not continuous is a consequence of the presence of integer variables (i.e. number of purchased vehicles) into the cost objective function. The

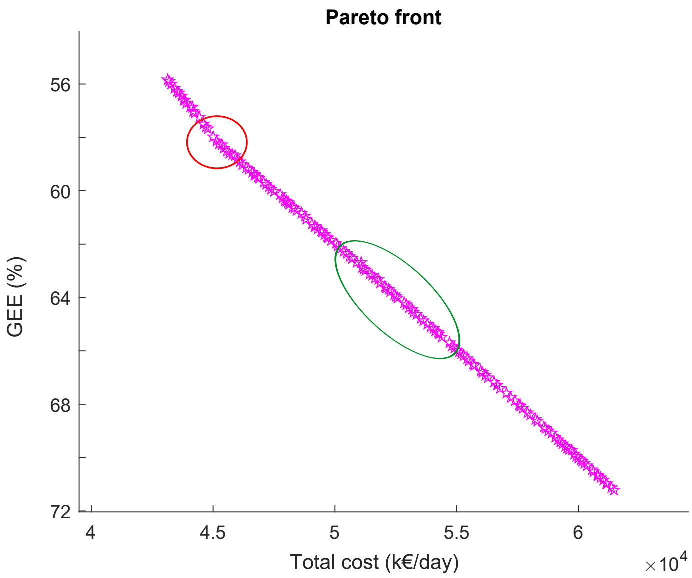


Figure 5.22: Pareto front from MOFs optimization of material split factor

first segment corresponds to SC_{pap} values from 25% to 52%. Then, a step of 7% in efficiency occurs, while SC_{pap} grows up to 76%. The second segment of the front corresponds to SC_{pap} values from 76% to 93%. A second step of 7% occurs in cost when SC_{pap} passes from 93% to 96.8%. The last segment ends for SC_{pap}=98.6.

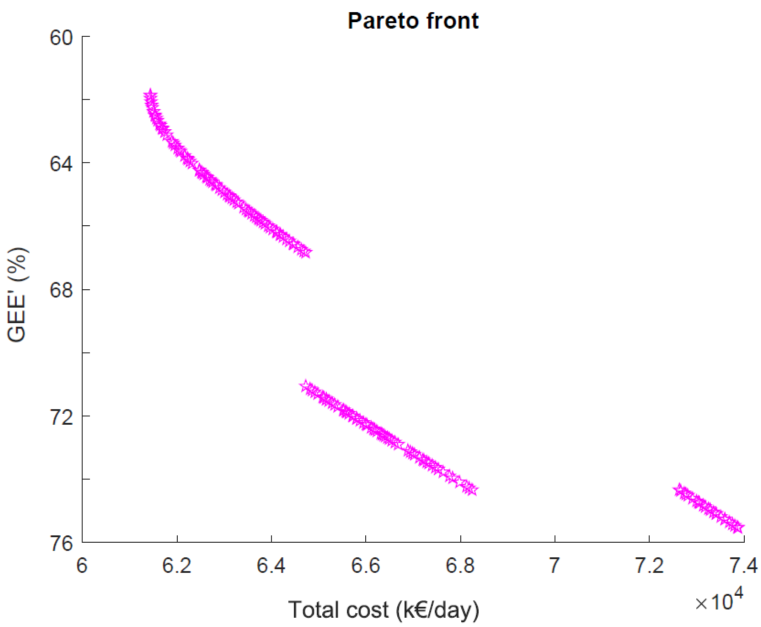


Figure 5.23: Pareto front from MOFs optimization of selective collection degree

5.5.5 Conclusions and discussion

A reduced MSW treatment system including MBT and recycling plants for paper and plastic streams is modelled. Three exergy-based indicators are calculated according to different recycling scenarios, obtained by the split of paper and plastic waste that can occur at the transfer station. Since the output of the system are the SRF and the recycled materials, the exergy of alternative scenarios for substituting products supply is included. Besides, a MOFs optimization is performed for finding trade-off solutions between monetary costs and exergy efficiency. The main conclusions are discussed below.

- The behaviour of the exergy-based indicators confirms the fact that, in any case, recycling options result in a better use of resources. The two main factors that influence the improvements in exergy efficiency for this type of systems are the weight percentage of material streams in URW and the exergy consumption of the alternative chains. In this case, paper stream has the highest share in waste composition and the virgin production of cardboard counts for three times the resources of paper recycling. The comparison based on the AEI shows that the additional exergy is a relatively small percentage of the exergy that would be lost in case of absence of treatment, which includes the chemical exergy of waste and the EE of collection and transport. The ESC expresses the comparison between the exergy invested in the actual and the no-treatment scenario. ESC shows higher values than AEI (difference percentage of about 60%) but, in any case, lower than 100%. This fact is mostly due to the impact of the virgin production chains and confirms the advantage of having a waste treatment system.

- The distribution of the Total Invested Exergy underlines that waste material streams are still important in terms of exergy content (84.55% of the total); the possibility of recovering part of this exergy requires an additional investment for transport (3.2% of the total) and recycling processes (6.22% of the total). Virgin plastic production results less exergy-intensive than paper production; however, it has to be considered that the polymer production chain is assumed to start with the heavy hydrocarbons, so the fossil fuel extraction and pre-treatment is excluded from the calculation of EE. The scenario of the alternative chains shows that, in case of half splitting of material streams, the additional and avoided exergy burden quite compensate each other, even if the balance is still positive.

- The output solutions from MOFs optimization show that a certain number of trade-off configurations exist, even higher monetary costs are associated to total recycling options. In particular it appears that the paper recycling is associated to higher costs than plastic one. It implies that the split paper variable is the most influencing of the cost range of the optimal solutions.

For this reason, in the second optimization, only the degree of collection of paper is varied. It is important to remind that the calculated cost is not really sustained from a single entity since, in real conditions, the management of the various parts of the ISWM system occurs separately. It implies that the economic factor is crucial and it is almost the only objective for decision-making. However, the exergy perspective gives the measure of the resource utilization in the big picture, which should be considered since the aim is to dispose the waste in the most rational way, i.e. minimizing the global resource consumption.

Chapter 6

Conclusions and future developments

In this work Exergy Analysis criteria and tools are used to assess the resource utilization into the Solid Waste (SW) treatment systems, including multiple stochastic scenarios and conflicting objectives. The development of an Integrated Solid Waste Management (ISWM) system is still a crucial challenge for local communities. One of the main issues is linked to the correct management of the waste streams in terms of rational use of resources, complying with the economic and bureaucratic constraints. Besides, these systems are strongly influenced by heterogeneous and aleatory factors (i.e. social, political, technological, economic) that entail a certain degree of uncertainty on short and long time. Many times, the recycling operations are hindered by the End-of-Life products design.

Two main novelties are introduced in this work for the analysis of the SWM systems with respect to the previous literature. First of all, the application of exergy-based tools for exergy cost calculation and resource assessment to SWM and the coupling of exergy-based efficiency indicators with the economic ones in the optimization. The main advantages resulting from the application of this methodology are listed below:

- in case of Exergoeconomics applied to a specific plant (e.g. MBT plant), the analysis pointed out the distribution of irreversibility and their influence on the cost of the products;
- the possibility to broader the vision including alternative scenarios and evaluate all the streams of different nature with a single common basis makes it a powerful tool for resource assessment;
- the possibility to create indicators for assigning a value to recycled products which is not only link to their monetary cost or savings.

It is important to remind that both the calculated costs (i.e. economic and exergetic) are not really sustained from a single entity since, in real conditions, the management of the various parts of the ISWM system occurs separately. However, their definition and calculation give the the idea of the order of magnitude of the economic and natural resources invested for the management of the system. The economic factor is usually the only objective for decision-making, but the exergy perspective gives the measure of the resource utilization in the big picture, which should be considered since the aim is to dispose the waste in the most rational way, i.e. minimizing the global resource consumption.

The second relevant novelty regards the application of uncertainty analysis for evaluating the effect of waste composition variability and plants energy consumption on the output and evaluation parameters of SW treatment chain. The analysis was justified by the aleatory conditions that influence the entire system and it was worth to be done for quantifying the effects. Once the methodology is assessed, it can be useful at the time of designing a new plant for obtaining information.

An extended discussion of the results has been already reported at the end of each Chapter. A summary of the main conclusions is reported below.

- **Chapters 1-2-3**. These introductory Chapters present the technical and theoretical background of the further analysis. In Chapater 1 an overview of SWM is offered, introducing the legislative framework and providing data on MSW generation, composition, collection, treatment alternatives and management issues. In Chapter 2 the theory of Exergy Analysis is summarized, both for Exergoeconomic principles and resource assessment. Chapter 3 is dedicated to the description of the mathematical methods used in the analysis, namely the stochastic methods for uncertainty evaluation and the Multi-Objective Optimization solution techniques.
- **Chapter 4**. In this Chapter, an example of an exergy-based resource assessment is applied to polymeric materials. The methodology is based on the grave-to-cradle identification of polymers life cycle and the developing of four exergy-based recycling indexes. The material and energy flows linked to the production and recycling routes of nine commercial polymers (i.e. PE, PP, PVC, ABS, PU, PA6.6, PET, SBR, EPDM) are identified. The polymers are compared and ranked according to the global EE (i.e. resources invested in their production) and the values of the thermodynamic indexes. The range of values of EE for the analyzed polymers ranges from 0.036 toe/kg of PVC to 0.479 toe/kg of SBR, being PET in the second position. The major exergy investment (60% of the global EE) occurs in the first steps where the primary natural resources are concentrated in form of fossil fuel. The quantification of this 'natural bonus' gives the measure of the rarity of fossil fuels and the cost that would be paid in case they will disappear from the Earth's crust. The recycling indexes comparison confirms the convenience of some already used practices (e.g. mechanical recycling is a better option for PE, PP, PVC and

PET than chemical one). This last option has to be accurately evaluated depending on the context, comparing it with the energy recovery path. The fact that all the recycling indexes are lower than 100% (some of them even significantly) confirms the benefit of recycling in terms of global resource utilization. Thus, the real challenge is the optimization of the connection between all the stakeholders. Finally, a specific application for a thermodynamic assessment of EoL vehicle plastic components is presented. Calculating the total EE of the vehicle plastic components gives an idea of the order of magnitude of the resources (expressed in MJ of exergy) that are definitively dispersed in case that the materials are not reused or recycled (i.e. landfill disposal or incineration). For the four analysed part (i.e. instrumental cluster, dashboard, rear bumper and floor covering) values of total EE of polymers ranges from 0.1 to 0.8 toe of exergy. The exergy-based methodology applied to the single component can be useful to reveal which polymer can be critical with respects to the others at the time of recycling.

- **Chapter 5**. In this Chapter, in a system-based view, an exergy-based assessment of Solid Waste treatment alternatives is proposed. It starts from focusing on the collection system, then including the MBT plant, until including paper and plastic recycling. First of all, a typical kerbside (or 'door-to-door') collection scheme is modelled and the effect of influencing parameters on collection cost is evaluated. The sensitivity analysis shows that the combination of external parameters (i.e. population density, total population and degree of SC) and design variables (i.e. weekly removals and unit collection area) has a strong influence on the unsorted waste specific collection cost. The range of optimal unit collection area is between 1000 and 5000 inhabitants, with preference for solutions between 1000 and 3000. The advantage of having smaller collection areas is the reduction of the collection downtimes in the collection and the possibility to cover the entire collection using the same number of trucks in different days of the week, leading to reduced operating and fixed costs. The Exergoeconomic analysis applied to the MBT plant is aimed at calculating the unit exergy-based cost of the products (i.e. SRF and recovered metals) and evaluating the irreversibility distribution trough the equipment. Two structures of treatment chains are compared. Results show that material losses are the primary source of irreversibility and are mainly concentrated in the pre-screening phase (70% of the global input exergy is lost in this equipment). An uncertainty analysis is conducted by sampling from uniform distribution of SC values and normal distributions of equipment electric consumption using a Monte Carlo simulation. The unit exergy cost of products is the most influenced by the uncertainties, showing an RStD of about 16%, while the exergy efficiency is the less affected (about 3%). As a general consideration, the RStD of the output parameters (i.e. Yield, LHV of SRF, exergy efficiency and cost of products) are considerably lower than the fluctuations of the input random variable. In the case of internal uncertainties, the RStD values are about 90% lower with respect to the external ones. This result confirms the small impact of energy consumption of the equipment on the global performance of the system. The inclusion of the paper recycling plant in the model gives the possibility to perform a broader resource assessment. The EE balances are calculated for each process including the additional/avoided exergy burdens of the alternative scenarios of production (i.e. coal supply instead of SRF for cement kilns and virgin paper from cellulose). The global EE variation of the entire system with respect to a base case is evaluated for different SC values and two scenarios. In general a decrease in SC_{paper} leads to greater values of ΔEE_{gl}, but savings on EE diminish for high collection of paper, because of the influence of SW transport and coal supply cost. Anyway, the variations are very moderate, in the order of ±2%, which means that the system has a good degree of self-regulation. Finally the analysis is extended to include also the polymers recycling and virgin production routes, using the data found in Chapter 4. Three exergy-based indicators are developed and evaluated according to the paper and plastic split that can occur at transfer station (i.e. part of material is sent to MBT for SRF production for pursuing different recycling strategies). Then, the Global Exergy Efficiency is coupled with the global cost for a MOFs optimization with different optimization variables (i.e. split factors and degree of SC). In general,the values of exergy-based indicators confirm the advantage of having recycling options for a better use of resources with respect with the no-treatment case (landfill disposal). The additional exergy investment for recovering the input waste internal chemical exergy amounts to about 3.21% for transport and 6.22% for recycling, expressed as a percentage of the total invested exergy. The output solutions from MOFs optimization show a series of trade-off solutions, even higher monetary costs are associated to total recycling options. The split paper variable is the most influencing of the cost range of the optimal solutions.

Future developments

The present work is a first step that leaves space to further improvements and developments. The main ideas are summarized below.

- An extension of the 'grave-to-cradle' methodology to other commercial diffused polymers (e.g. PS, PPS, PC, PMMA) may enlarge the data set available for comparison. Moreover, for the already analysed polymers, an integration with information from industries would be recommended. The presented values of EE for polymers can be useful for a first comparison of different options. However, the analysis of specific case studies, with defined boundaries, plants and transport layout, would give more precise and reliable information for ranking the different options.

- Further investigation should concern the quantification of polymeric material degradation on an exergy basis, since it is one of the main factors hindering the market of recycled products. The integration with the exergy methodology could start from an extension of the exergy definition: not only the capacity of producing work, but also the possibility to be transformed into something valuable computing the downcycling with respect to a initial condition.
- The thermodynamic assessment of vehicle components should be extended integrating the obtained information with eco-design principles. The author has already been started to work on the topic, developing a quantitative scale of eco-design points for polymers in vehicle components, combining qualitative information on recyclability limitations and numerical data on EE of polymers and recycling indexes.
- An improvement of the analysis of SW treatment system could include other separated material streams (e.g. organic, glass, metals) and options (e.g. energy recovery, anaerobic digestion). Even in this case, the analysis of a specific case study would imply the more precise definition of plant distance, layout and context characteristics (e.g. presence of recycling plants, virgin material supply). A comparison with other alternative scenarios (e.g. natural gas instead of coal for cement kiln) would be recommended.
- The analysis of the uncertainties can be extended, for example including the short-term variations in available waste flows and evaluating the effect on decision making criteria. A coupling of MOFs between exergy efficiency and monetary cost and uncertainty optimization would give interesting and useful insight for the management of the SW treatment system.

Nomenclature

Roman Symbols

ΔG_0 Gibbs energy of formation [kJ/kmol]

$\dot{B}$ Exergy rate [kW]

$\dot{C}$ Cost rate [kW]

$\dot{I}$ Irreversibility rate [kW]

$\dot{m}$ mass flow [kg/sec]

$\dot{Q}$ Heat rate [kW]

$\dot{S}$ Entropy rate [kW]

$\overline{b}$ Molar exergy [kJ/kmol]

b Specific exergy [kJ/kg]

c Exergy-based average unitary cost [euro/kJ]

C_a vehicle annual depreciation

C_{eq} equipment cost

C_{fix} vehicle purchase cost

c_v specific collection cost per unit volume of waste

$cons_{fuel}$ fuel consumption

d_{ts} distance between last drop point and transfer station

f_a actualization factor

f_{OM} operation and maintenance factor

h Specific enthalpy [kJ/kg]

i interest rate

Ins Insurance

K equivalent kilometres

$Maint$ Maintenance

N capital recovery period

N_{bt} number of big trucks

N_d number of collection rounds in a working day

N_{st} number of small trucks

N_w number of waste weekly removal

p Pressure [atm]

P_h hourly productivity

P_{tot} total population

q Specific heat transfer [kJ/kg]

REC_{ch} chemical recycling index

REC_{gl} global recycling index

REC_{mec} mechanical recycling index

REC_{ter} tertiary recycling index

s Specific entropy [kJ/kgK]

Sal Salary

T Temperature [K]

t_{coll} collection time

t_{drop} dropping off time into the big truck

t_p picking time

t_{st} route time of small trucks

Tax Taxation

U_b unit collection area

V_{bt} big truck capacity

V_{pc} per-capita waste generation

V_p waste volume at the collection point

V_{st} small truck capacity

W recovery time factor

w Specific work flow [kJ/kg]

x Molar fraction

y specific irreversibility

Y_{rec} annual recovery period

Greek Symbols

δ Lack of efficiency

η_{ex} Exergy efficiency

μ Mean value

ϕ Szargut factor

ψ_I Irreversibility

σ Variance

Subscripts

add additive

bt big trucks

ch chemical

$depol$ depolymerization

el electricity

fib fibre

fix fixed

gl global

kin kinetic

lab labour

met metal

nap.prod naphtha production

oil.prod oil derivatives production

pap paper

ph physical

plas plastic

plx plasmix

pol polymerization

pot potential

pr products

rec recycling

rej rejects

sort sorting

st small trucks

tot total

tr transport

ts transfer station

vp virgin production

wat water

Acronyms / Abbreviations

AEI Additional Exergy Indicator

C&T Collection and Transport

CDF Cumulative Distribution Function

CEENE Cumulative Exergy Extraction from the Natural Environment

CExC Cumulative Exergy Consumption

EE Embodied Exergy

EEA Extended Exergy Analysis

EO Evolutionary Optimization

EoL End of Life

ERC Exergy Replacement Cost

ESC Exergy Scenario Comparison

GEC Global Energy Consumption

GEE Global Embodied Exergy

HHV Higher Heating Value

$ISWM$ Integrated Solid Waste Management

LCA Life Cycle Analysis

LHV Lower Heating Value

MBT Mechanical Biological Treatment

MC Moisture Content

$MOFs$ Multiple Optimization Functions

$MOLP$ Multiobjective Optimization Linear Problem

MSW Municipal Solid Waste

NF Non-ferrous

$NSGA-II$ Non-dominated Sorting Genetic Algorithm

OF Objective Functions

OI Other Inorganic

OM Organic Matter

OP Other Plastics

PDF Probability Distribution Function

RE Reference Environment

$RFTF$ Recovery Factor Transfer Function

$RSTD$ Relative Standard Deviation

SC Selective Collection

SRF Solid Recovered Fuel

SW Solid Waste

SWM Solid Waste Management

TEC Thermoecological Cost

TUW Total Unsorted Waste

URW Unsorted Residual Waste

$WEEE$ Waste Electrical and Electronic Equipment

WFD Waste Frame Directory

WtE Waste to Energy

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