Technologies for the recycling of plastic waste

Mass, energy and climate change balances



Loan Terrien

Olivier Talon

Julien Cayuela

September 2023

Table of contents

Abbreviations 3
Summary 4
General introduction 6
1 Mechanical recycling 10
1.1 Mechanical recycling of PET 11
1.1.1 Technical aspects 11
1.1.2 Balances aspects 13
1.2 Mechanical recycling of PLA 15
1.2.1 Technical aspects 15
1.2.2 Balances aspects 16
1.3 Mechanical recycling of PS 19
1.3.1 Technical aspects 19
1.3.2 Balances aspects 20
1.4 Mechanical recycling of PP/PE 22
1.4.1 Technical aspects 22
1.4.2 Balances aspects 23
1.5 Compared balances of mechanical recycling of sorted plastics 25
1.6 Climate change impacts of mechanically recycled and virgin plastics 27
Conclusion about mechanical recycling 29
2 Chemical recycling 30
2.1 Chemical recycling of PET 32
2.1.1 Technical aspects 32
2.1.2 Balances aspects 36
2.2 Chemical recycling of PLA 38
2.2.1 Technical aspects 38
2.2.2 Balances aspects 41
2.3 Chemical recycling of PS 44
2.3.1 Technical aspects 44
2.3.2 Balances aspects 46
2.4 Chemical recycling of PE/PP 47
2.4.1 Technical aspects 47
2.4.2 Balances aspects 52
2.5 Compared balances of chemical recycling processes 55

3 Comparison between recycling processes for plastics 56
3.1 The impossibility of a comparison 56
3.2 The possibility of a comparison? 57
3.3 Comparison between the recycling processes 58
Conclusion 61
Disclaimer 64
References 65

Abbreviations

BHET	Bis(2-Hydroxyethyl) terephthalate
CHAR	Carbon-rich solid residue
DMT	Dimethyl terephthalate
EG	Ethylene glycol
EoL	End-of-life
LA	Lactic acid
LCA	Life cycle assessment
MMA	Methyl methacrylate
MRF	Material recovery facility
NIR	Near infrared
PCW	Post-consumer waste
PE	Polyethylene
PEF	Product environmental footprint
PET	Polyethylene terephthalate
PG	Propylene glycol
PIW	Post-industrial waste
PLA	Polylactic acid
PMMA	Polymethyl methacrylate
PO	Polyolefin
PP	Polypropylene
PS	Polystyrene
rPE	Recycled polyethylene
rPET	Recycled polyethylene terephthalate
rPLA	Recycled polylactic acid
rPO	Recycled polyolefin
rPP	Recycled polypropylene
rPS	Recycled polystyrene
SSP	Solid state polymerisation
TPA	Terephthalic acid
TRL	Technology Readiness Level

Summary

The aim of this report is to scrutinize the state-of-the art of mechanical and chemical recycling processes for plastic waste (with a focus on PET, PLA, PS, PE and PP) and use available environmental assessment information about these processes in an attempt to compare their environmental relevance. The report is based on desk research performed between May and September 2023 by Materia Nova team.

Different types of recycling processes for plastics exist, that differ in the level at which the structure of the material to be recycled is dismantled. The first type is thermomechanical (or mechanical) recycling, in which the discarded plastic waste is processed over melting temperature to obtain new plastics pellets. The macromolecular nature of the plastic remains unchanged in such processes. Chemical recycling processes can be divided into two main categories. Some plastics can be treated by chemical depolymerization processes. In that case, the macromolecules are converted into monomers that can further be repolymerized to obtain virgin plastics. Almost all plastics can also be recycled by thermochemical degradation processes such as pyrolysis or gasification. In these processes, the macromolecular structure is also lost, and the obtained molecules are not monomers but a mixture of small molecules, a fraction of which can be further transformed into monomers and thus new polymers. However, in these thermochemical processes, a fraction of the output can only be valorised as energy.

The different recycling processes are hardly comparable, since they are not all suited to the same type of waste (in terms of nature of the main component, but also in terms of purity) and do not produce the same type of outputs. Generally speaking, processes that less harm the structure of the material will have lower impacts[1], but are more fit for high quality waste streams (e.g. single stream post-industrial waste or very well sorted and cleaned post-consumer waste are good candidates for thermomechanical recycling). On the other side of the process range, pyrolysis can be used for mixed and/or contaminated streams but will have higher impacts.

Also, regenerated plastics from chemical recycling can reach exactly the same properties than virgin plastics, whereas regenerated plastics from thermomechanical processes in most cases have slightly degraded properties.

Almost all studies underline that all recycling processes for thermoplastics make sense from the environmental balance point of view when compared to incineration with energy recovery. However, occasions where different processes

[1] The term “impacts” in this report refers in general to the potential environmental impacts that are or can be determined by LCA tools and methodologies, and particularly to climate change impacts which is, with energy and mass balance, the focus point of the report.

would really be in competition should be scarce, and a ranking of plastic recycling processes in terms of environmental impacts would hence be hardly relevant. Such a ranking, relevant or not, is anyway difficult to provide due to the poor availability, transparency and comparability of environmental data.

General introduction

The aim of this report is to scrutinize the state-of-the art of mechanical and chemical recycling processes for plastic waste and use available environmental assessment information about these processes in an attempt to compare their environmental relevance. The report is based on desk research performed between May and September 2023 by Materia Nova team.

Two types of recycling processes for plastics waste are dealt with in this report. The first type is thermomechanical recycling, also referred to as mechanical recycling, where sorted and pre-treated waste is melt processed into plastic pellets that can be used by plastic transforming industry. In mechanical recycling, the macromolecular nature of the polymers that constitute the main part of the plastic material is conserved, even if some degradation is likely to occur. The second type is chemical recycling, where the macromolecules are broken down into small molecules, that can be used by the chemical industry to synthesize polymers again, directly or after a series of chemical conversions.

Chemical recycling of plastics is a generic term that encompasses thermal degradation processes and chemical degradation processes (sometimes referred to as thermal and chemical depolymerization[2], respectively).

The report only examines the recycling of thermoplastic material, with a focus on PET, PLA, PE, PP and PS. Specific processes for thermosets are not studied here.

The report focuses on the recycling of pre-sorted post-consumer waste (PCW), for two main reasons:

- Most of the information available in the literature is about PCW, because post-industrial waste (PIW) recycling mostly relies on business-to-business relationships, thus increasing the confidentiality of data and their scarcity.
- In general, recycling processes adapted to PCW can easily handle post-industrial waste, but the opposite is not true. This is mainly due to the purity of the waste, which is far higher with PIW, drastically lowering the needs for sorting, separation and purifications steps. The core of the recycling process

[2] It can be considered that the term “depolymerization” is abusively used in many instances, since it should be reserved for cases where the thermal or chemical process directly results into the monomer that can be used for polymerization (that may be the case, for examples, for controlled thermal degradation of PMMA that produces MMA or for hydrolysis of PLA that results in LA), but not when the degradation processes yields other chemical species than the monomers (for example, the pyrolysis of PE results in a mixture that can further be partially converted into ethylene, but does not by itself produce the ethylene monomer). We tried therefore to avoid inappropriate use of this word in this report.

however remains the same between the two types of waste once PCW attains a certain purity level.

To give a better insight about the upstream processes occurring before the generation of sorted polymer bales or flakes that are considered in the report, a general overview of the whole waste recovery chain is given in figure 1.

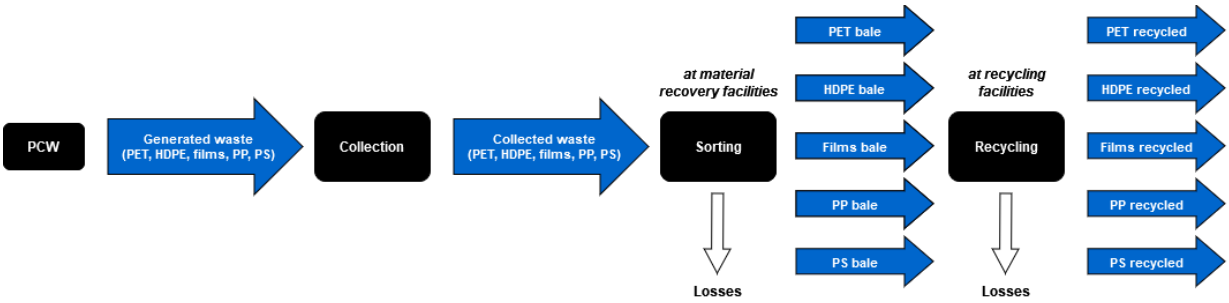
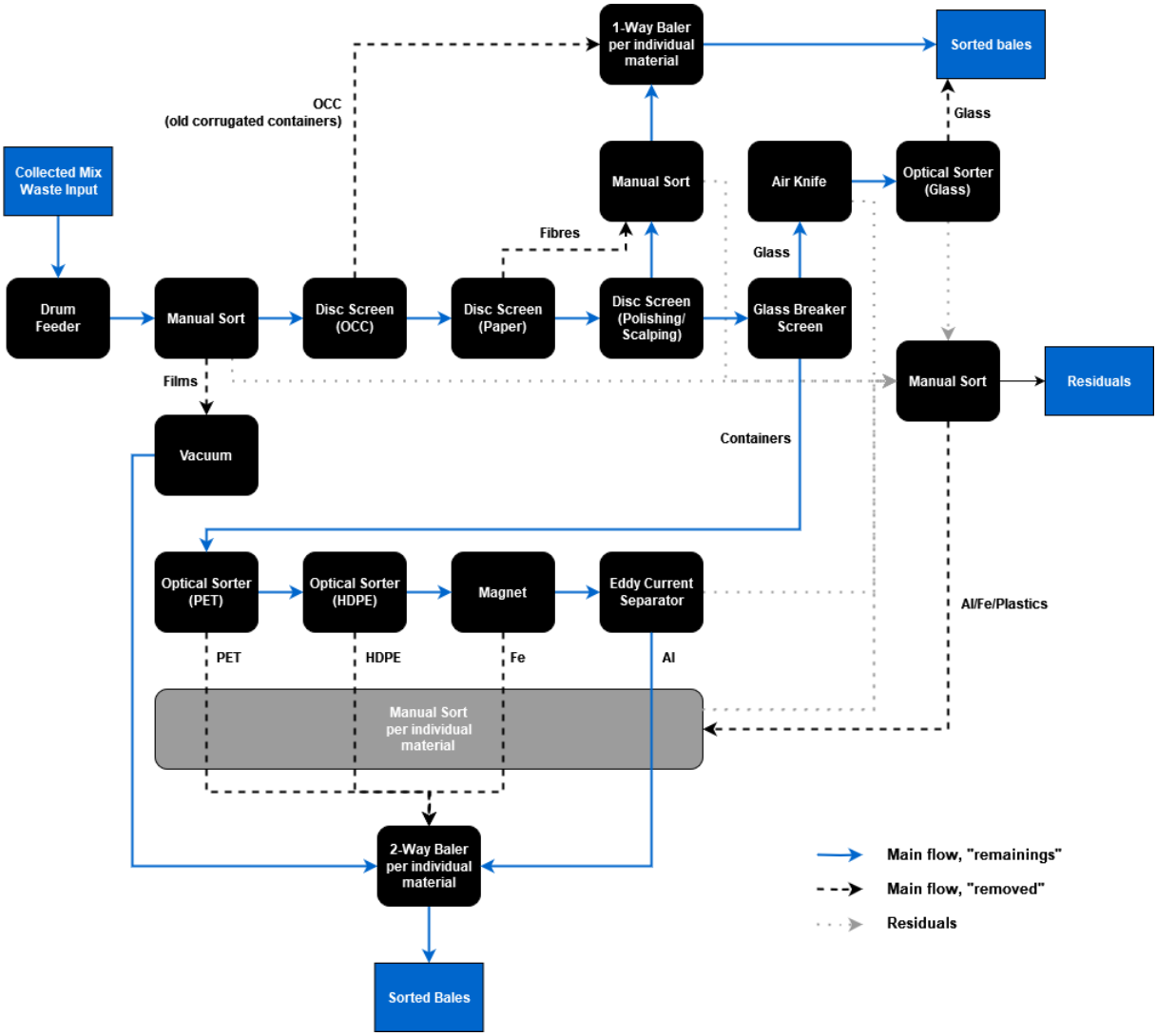


Figure 1 – Value chain of plastic waste recovery, based on ***Pressley 2015***

In the following parts of this report, pre-sorted polymers are considered as the main input of the recycling processes, i.e., bales of single polymers or flakes generated after the receiving of the bale. However, this does not imply the absence of additional sorting steps during the recycling process itself. A very common example concerns recycling of PET from bottles. Material recovery facilities (MRFs) are equipped to segregate bottles from other types of plastics packaging, however, residual materials are still present in the PET bales, such as PP from caps or labels. Thus, additional sorting steps must be carried out at recycling facilities and are totally indivisible from the recycling step in itself (e.g., extrusion for mechanical recycling of PET). These steps are thus considered to be inherent to the recycling process and further included in it, which has an effect on the calculation of yields and mass balances.

It should be reminded that the presence or absence of these sorting steps inside the recycling process are mostly dependent on the purity (i.e., absence of contaminants) of the incoming pre-sorted flow. State-of-art MRFs can currently attain very high rates of purity, between 90 and 98 % for the usual polymers (**Antonopoulos 2021**). Representative sorting processes at MRFs include several separation steps targeting one type of material, depending on the composition of the incoming waste flow. To give an example, the process diagram of an MRF designed to recover fibre, glass, metals and plastics from a commingled recyclables stream is presented in figure 2. The process represents the sorting of a single stream of recyclable materials, which is of common practice in Europe. However, other MRF types can exist, such as dual-stream MRFs or pre-sorted (source-separated) material streams. These cases are not discussed, but it is important to remember that sorting can be handled in various ways, having an impact on the purity of recovered materials, in addition to the energy demand of the process.



Remainings: materials that are not targeted by the sorting step.
Removed: materials that are targeted and segregated by the sorting step.

Figure 2 – Process diagram of a MRF plant for single-stream waste sorting, based on ***Pressley 2015***

One goal of the report is to synthesize the efficiency of the recycling processes in terms of mass balance, energy use and climate change impact.

One representative process was selected for each recycling path (mechanical and chemical) for each polymer (PE/PP, PS, PET and PLA). For each case, the choice for the representative process is explained and a process diagram is given, and balances are provided. Climate change impacts were either directly taken from the literature sources or, when possible, calculated with a LCA software based on the information provided in theses sources.

The energetic and environmental balances of recycling were not compared here to other end-of-life (EoL) options of the polymer waste, i.e., incineration and landfilling. In general, landfilling of plastic waste is often found to be less impacting than

incineration, mainly because the degradation rate of these materials does not traditionally exceed 1 % over a 100 years horizon. Since landfilling is prohibited in many European countries, incineration with energy recovery is often considered as the baseline EoL scenario for plastic waste. Typically, energy recovery enables to partially compensate the impacts of incineration but can never achieve the potential savings attained by recycling through virgin material displacement. Besides, the importance of environmental credits offered by energy recovery depends on the type of energy mix that is substituted. In a world where the share of renewable (and less impacting) energies is expected to grow, the benefit of energy recovery from incineration treatment of waste is obviously expected to decrease, and hence the benefits of recycling processes compared to incineration scenarios will increase.

Reuse of long-life polymers is also a possible EoL option, however, polymers investigated in this document are mainly used for short-life products, e.g., for packaging, for which reuse is not a viable option. Moreover, the opportunity to reuse is mainly influenced by the product properties and is hardly determined by the material itself.

1 Mechanical recycling

Mechanical recycling consists in converting polymer waste (either industrial or post-consumer waste) in a second life material. This regeneration step is usually performed by extrusion, which allows to produce a granulated material.

During this thermomechanical treatment, the polymer undergoes a degradation of its chains (modification of their lengths), either during regeneration step or during the in-use phase of the material. This change of the length of the chains leads to a modification of the properties of the material. Usually, properties of the reprocessed material are inferior to those of the virgin polymer.

To counter the degradation processes which occur during the extrusion, it is common that a percentage of the virgin polymer is fed in during the reprocessing. It is also useful to choose process conditions where temperature, shear and residence time of the material in the extruder are moderate. The type of degradation mechanism can differ depending on the type of plastic, the reactions that lead to chain scissions in polyolefins or in polyesters are not the same. Therefore, obviously, the strategies that can be used to prevent or minimize the effects of are also different depending on the plastic type.

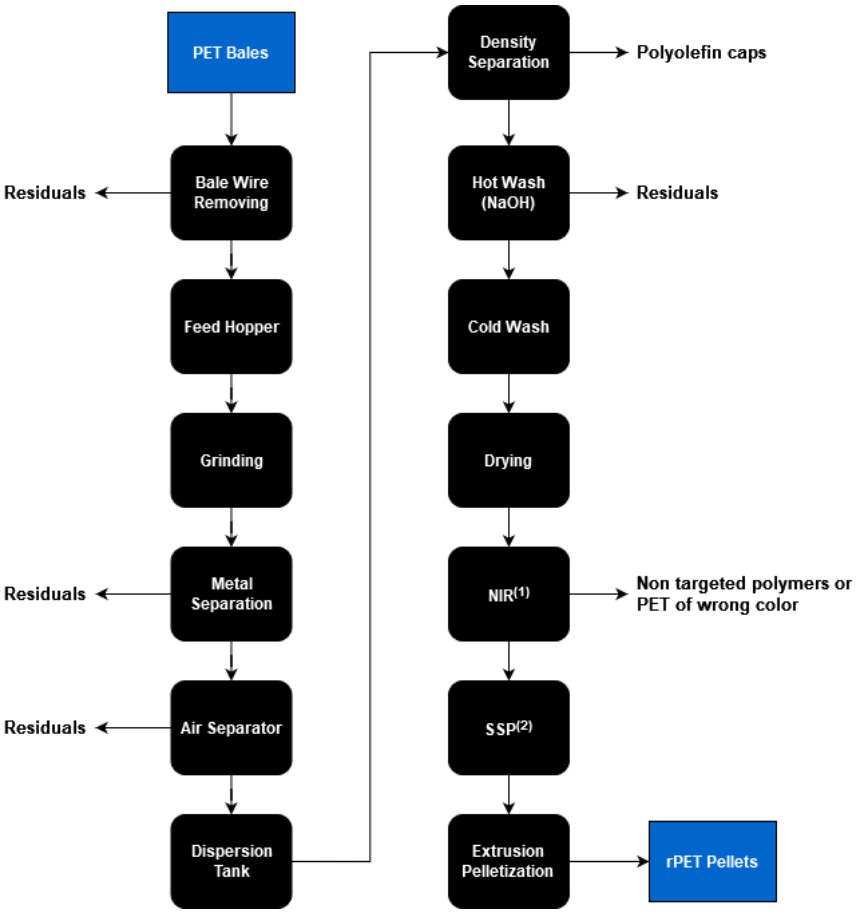
This chapter describes for each polymer concerned by the study (PET, PLA, PS, PE, PP) the mechanical recycling process, and also the degradation process encountered during the extrusion step. Methods to counter this degradation process are presented. Besides, information about the mass, energy and climate change balances are given for representative processes, and these balances are summarized in an infographic.

In a final paragraph, the balances for the mechanical recycling of all types of plastics considered are compared.

1.1 Mechanical recycling of PET

1.1.1 Technical aspects

A typical process for the mechanical recycling of PET waste is described in figure 3.



(1) Common step added for information purposes, but not included in the considered representative process. Near Infrared sorting might be necessary depending on the purity of the incoming pre-sorted PET, and on the targeted application of the rPET.

(2) Solid State Polymerization (SSP) is only carried out to achieve bottle-grade rPET pellets.

Figure 3 – Process diagram of PET mechanical recycling, based on ***Kägi 2017***

The process, considered to be representative of state-of-art industrial practices, uses PET bales as input material. First, the wire around the PET bales is cut away and the bottles are separated again. PET is then shredded with knives to 12 mm size and passes through a metal separator, notably to separate common aluminium-containing labels. This shredded material then arrives into an air separator that separates the label residues from the PET flakes. The label residues end up in an incinerator. Purified from the labels, the flakes land in a pool of water where the bottle caps, made of PE or PP, float on top whereas the PET flakes which are heavier than water sink to the bottom. The PET flakes are then treated with a 50 % solution of sodium hydroxide and heated up to 200 °C, enabling the liquor to dissolve the

PET surface layer. With this procedure, even the SiOx coating of the bottle-inside is removed. The purified PET flakes are washed with water and then dried. rPET pellets are then either produced by SSP followed by extrusion to give bottle-grade pellets, or by simple extrusion to give amorphous pellets.

An additional sorting step with near-infrared separator is also of common practice. This step is not included in the considered process but has been added to the flowchart of the process because it is of common practices within rPET producers. This step mainly depends on the purity of the incoming PET bales and if the colour of the polymers is of importance or not.

During such a thermo-mechanical reprocessing of PET, different degradation processes are observed (**Samperi 2016, Romao 2009, Montaudo 1993, Colin 2006, La Mantia 1994, Botelho 2001, Lecomte 2006, Silva Spinacé 2001**). Scission of chains can occur by hydrolysis, β-CH-transfer, intramolecular transesterification, reaction from weak structures such as diethylene oxide groups, radical oxidation... Intermolecular transesterification is also observed, which tends to modify dispersity of chains lengths. Polycondensation can take place if residual concentration in water or in ethylene glycol is below their equilibrium concentrations (that allows to restore high molar masses). Finally, some studies mention the occurrence of cross-linking by radical oxidation.

To show the extent of thermo-mechanical degradation of PET during processing, **Silva Spinacé 2001** mentions that MFI values varies from 23 to 80 g/10 min for a virgin PET and for the same polymer after five extrusion cycles performed from a dried polymer in a single extruder at 295 °C.

The SSP strategy is used in the process chain described above to compensate for the degradation when high performance is expected from the recycled PET. In the SSP process, the PET is heated at 180-230 °C (6-20 h) under vacuum (**Welle 2011, Ma 2003**), which enables the removal of moisture and ethylene glycol traces from the core of the material. The equilibrium of condensation reactions (1) and (2) is therefore shifted towards higher molecular weight compounds (figure 4).

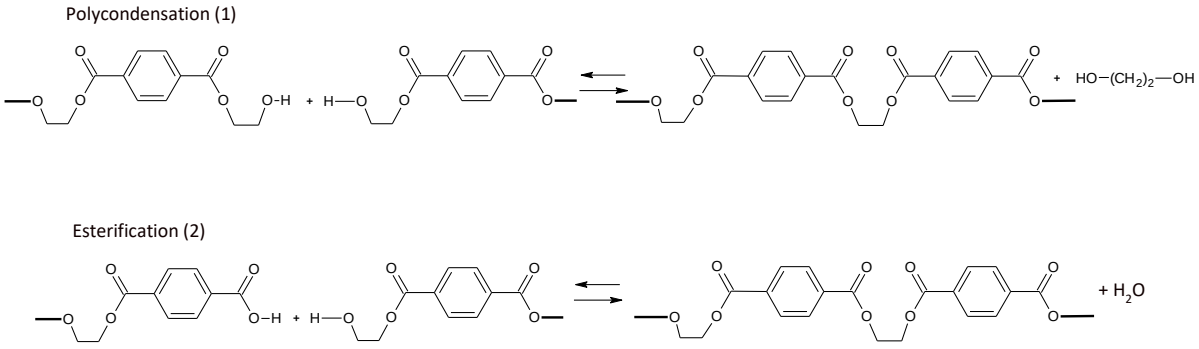


Figure 4 – condensation reactions for PET

Other strategies can be used to limit the degradation of PET during reprocessing, mainly the use of chain extenders (**Jang 2022**). A low molar mass compound with a functional group is added to react with the hydroxyl and/or carboxyl PET end-groups and link the affected polymer chains, resulting in chain extension and/or branching and an increase of M_w. Typical functional groups are epoxy, isocyanate, oxazoline and anhydride. The use of additives such as antioxidants, metal deactivators and anti-hydrolysis agents is also employed to stabilize the PET during the reprocessing, and some studies show the interest of reprocessing the PET under vacuum (**Awaja 2005**).

The majority of collected end-of-use PET is currently being subjected to mechanical recycling. Today, PET bottles with up to 50% post-consumer PET recyclates are on the market in some regions of the world (**Welle 2011**).

1.1.2 Balances aspects

Environmental data regarding the mechanical recycling of PET are well represented in the literature. Notably, the ecoinvent database includes several datasets concentrated on this material, including primary information directly recovered from several industrial recyclers within Europe and the United States of America. The selected representative data are thus taken from ecoinvent database and represent the industrial process carried out by Müller Recycling in Switzerland, recycling more than 20 000 tons of PET each year, representing more than half of Switzerland's plastic bottle waste. Switzerland is recognized as one of the most advanced countries in terms of plastic management and recycling (**Federal Department of Foreign Affairs, Switzerland, 2022**). These data are representative of the process depicted in the above figure 3.

1.215 kg of pre-sorted PET bales are needed to produce 1 kg of rPET, however, the segregation of 0.122 kg PE from caps is reported for this stream, leading the recovery rate on PET alone to be about 91 %. An average value of 1.91 kWh/kg rPET energy demand is reported, representing both grades of rPET polymer pellets (i.e., amorphous and bottle-grade). These values refer to the weighted average of amorphous and bottle grade rPET production in Switzerland, i.e., 60 and 40 % respectively, since both products are representative of PET recycling practices.

In addition, to comfort the reader about the representativeness of the chosen process, this dataset has been selected to be representative of the European average recycling scenario for PET in two major reports from the Joint Research Centre of the European Commission published in the context of the EU Product Environmental Footprint (PEF) method (*Environmental effects of plastic waste recycling* - **Tonini 2021** - and *Life Cycle Assessment of alternative feedstocks for plastics production part 2* - **Nessi 2022**).

The climate change impact of the mechanical recycling of PET has been assessed by using the ecoinvent 3 dataset as available in database in SimaPro, using the impact assessment calculation method from the Intergovernmental Panel on Climate Change (IPCC) updated in 2021[3]. A value of 0.6 kg CO_2 eq/kg rPET was found.

Figure 5 summarizes the mass, energy and climate change balances of the mechanical recycling of PET.

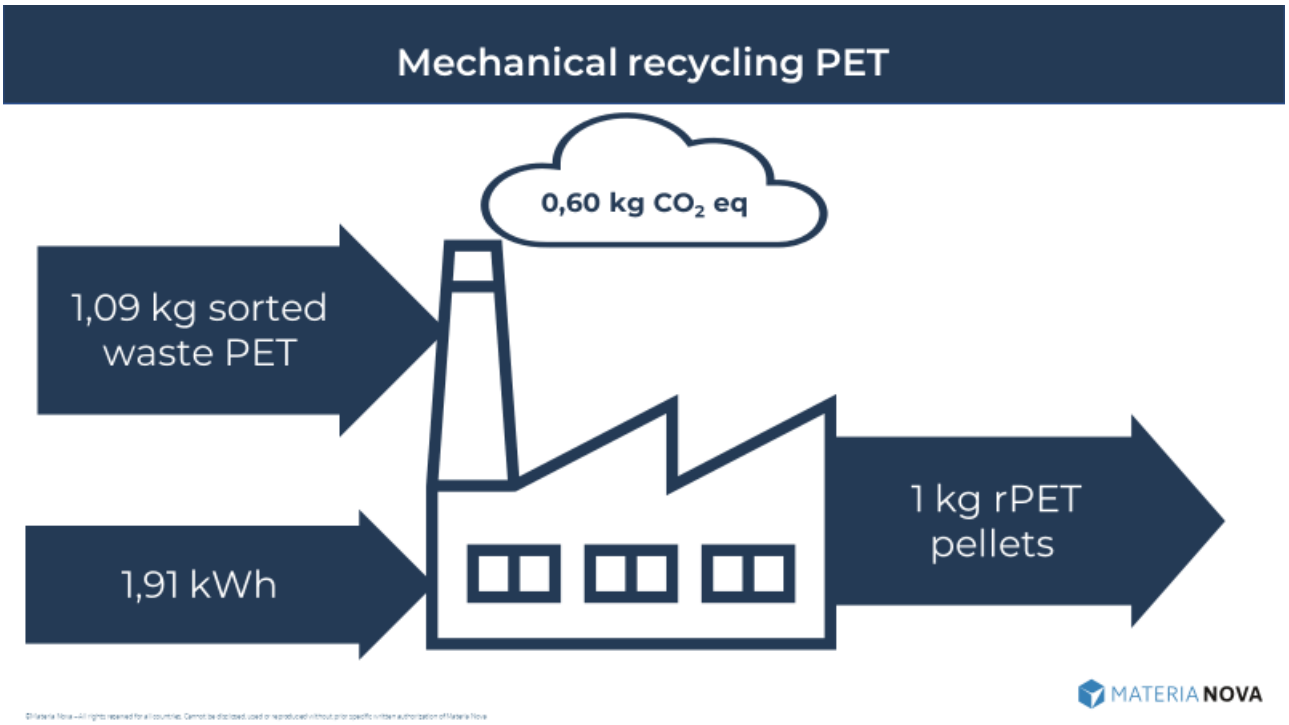


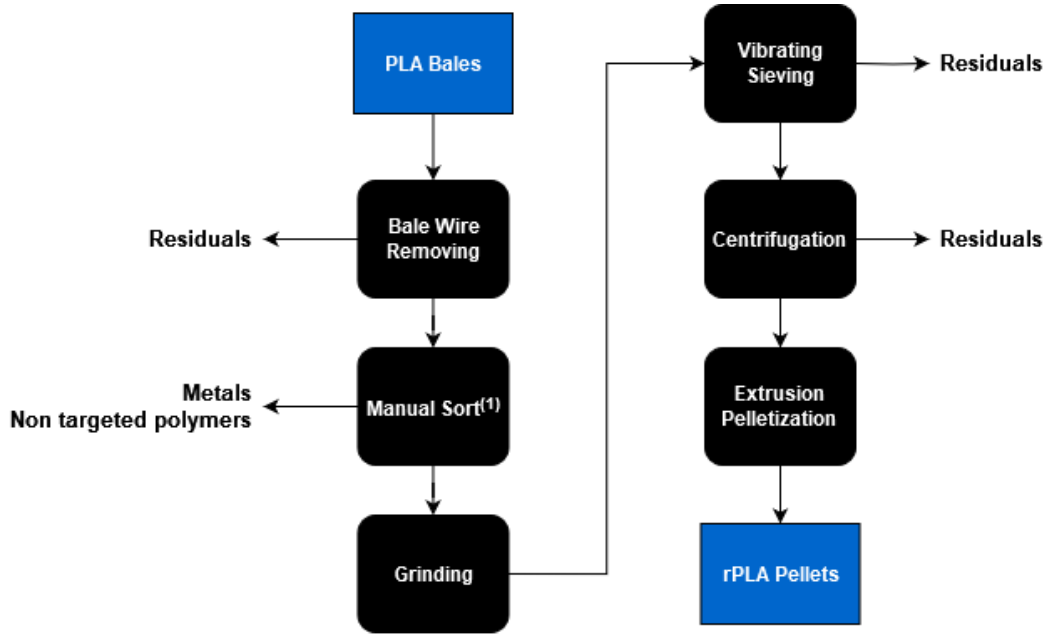
*Figure 5 – Balances for mechanical recycling of PET (based on **Kägi 2017**)*

[3] https://www.ipcc.ch/report/sixth-assessment-report-working-group-i/

1.2 Mechanical recycling of PLA

1.2.1 Technical aspects

A typical process for mechanical recycling of PLA is shown in figure 6. This process diagram is based on the study from **Maga 2019**, that is one of the very few available studies to propose data concerning the mechanical recycling of PLA waste at an industrial scale. This process has been considered as the reference for this report because waste PLA bales are received by the recycling facility just as if PLA was sorted from post-consumer waste. Industrial data come from the company Bösel Plastic Management GmbH based in Germany.



(1) Manual sort is used for the same purposes than metal separator and NIR in mechanical recycling of PET. (see Figure 3).

Figure 6 – Process diagram of PLA mechanical recycling, based on ***Maga 2019***

The PIW is delivered to the recycling facility in the form of pressed bales. The bales are manually sorted (automated sorting using NIR technology, for example, is also possible for PLA) for the separation of impurities such as other plastics or metals. Afterwards, the bales are transported to a cutting mill, where PLA flakes are produced under dust separation. Finally, the flakes are extruded using a melt filter in order to remove impurities. As a final step, the recovered PLA undergoes strand pelletizing to form granulates.

As for PET, thermomechanical processing of PLA is likely to lead to a series of degradation reactions. The reactions of PLA degradation generally follow routes

which tend to decrease the chain length of the polymer: hydrolysis, intramolecular transesterification, cis-elimination, unzipping depolymerization, radical scission in presence or not of oxygen. Intermolecular transesterification is also observed (**Gonçalves 2020, McNeill 1985, Kopinke 1996, Badia 2011, Castro-Aguirre 2016, Badia 2016, Al-Itry 2012, Amorin 2014**).

To illustrate the degradation of PLA during extrusion cycles, **Amorin 2014** mentions that the MFI values (2,16 kg, 190 °C) gradually increases between cycles, ranging from 10,9 for the neat PLA to 15,2 g/10 min for the same polymer after the fifth cycle of extrusion in a single screw extruder (polymer previously dried before each extrusion). **Gonçalves 2020** shows that the average molecular weight M_n of a recovered PLA, dried before each extrusion cycle in a twin-screw extruder, decreases by 22% after 5 cycles of extrusion at 180 °C.

To limit degradation during reprocessing, firstly, it is important that the material is as dry as possible before reprocessing in order to prevent hydrolysis of the PLA. However, PLA is hygroscopic, which makes efficient drying difficult. Morever, PLA is sticky above T_g (60 °C) when it is amorphous and is slow to crystallize, which also complicates the drying process (**Niaounakis 2019**). Few compagnies have patented PLA drying methods as in **Wendelin 2008** (method with mixing, grinding, crystallizing, drying steps, at 90–110 °C) and **Xiao 2008** (method with drying and recrystallization with ascending temperature gradients, 30–110 °C).
As for PET, the use of chain extenders with the functionnal groups epoxy, isocyanate, oxazoline and anhydride shows an interesting stabilizing effect (**Al-Itry 2012**). The use of antioxidant agents is useful as well because they can limit the chains scission caused by radical degradation reactions (**Amorin 2014**).

To our knowledge, industrial implementation of mechanical recycling of PLA is rather low at this time and mostly concerns just few grades for 3D printing.

1.2.2 Balances aspects

Environmental literature about mechanical recycling of PLA is scarce because, as stated above, the collection and sorting of this polymer is not yet implemented at large scale. Only two documents assessing the potential environmental impacts of PLA mechanical recycling have been reported, with only one including data based on an existing factory in Europe.

The data retrieved from the study of **Maga 2019** can enable to evaluate the balances of the mechanical recycling process of PLA.

1.21 kg of pre-sorted PLA bales are needed to produce 1 kg of rPLA pellets. Most of the residues (90 %) reported consist of paper, labels and metals, the rest being polymer dust generated during the process. Excluding the impurities from the flow,

the recovery rate on PLA alone is about 97 % (losses during grinding and extrusion). An average value of 0.22 kWh/kg rPLA is reported for the whole recycling process.

Even though the process is based on PIW, the authors have also estimated the inventory for a scenario for bales of PLA recovered at MRFs from PCW, based on pilot-scale installations. The main differences thus appeared during the sorting stage, and not for the recycling process in itself. Inventories for recycling are very close with the data provided for the considered representative process. Climate change impacts of the process have been assessed by reproducing the inventory of the authors in SimaPro with the impact assessment calculation method from IPCC 2021. A value of 0.09 kg CO_2 eq/kg rPLA was found. Though it is expected that the impact of recycling PLA should be lower than that of recycling PET, since processing temperatures are significantly lower due to lower glass transition and melting temperatures, the difference between the two values seems very high, and it is likely that the process steps considered in both studies for PET and PLA may differ, or that different assumptions were made for the models.

The other relevant literature reference about mechanical recycling of PLA (**Cosate de Andrade 2016**) reports very close recycling rates (96 %), but with higher energy demand (0.74 kWh/kg rPLA) and climate change impacts (0.4 kg CO_2 eq./kg rPLA). However, this difference is likely to be partly due to the fact that the purity of incoming material is lower and that the scope of the study includes pre-treatment steps leading to the bales, that are excluded from the scope of **Maga 2019** and from ours. The respective shares of pre-treatments and recycling itself cannot be retrieved from this study due to a lack of transparency, however it confirms anyway that the energy and climate balances of mechanical recycling of PLA would be lower than those of PET.

Figure 7 summarizes the mass, energy and climate change balances of the mechanical recycling of PLA. Since it is difficult to evaluate, based on their respective transparencies, which of the two studies is the most reliable and representative, it seems appropriate to use here the average of the values retrieved form these two studies for energy and climate balances.

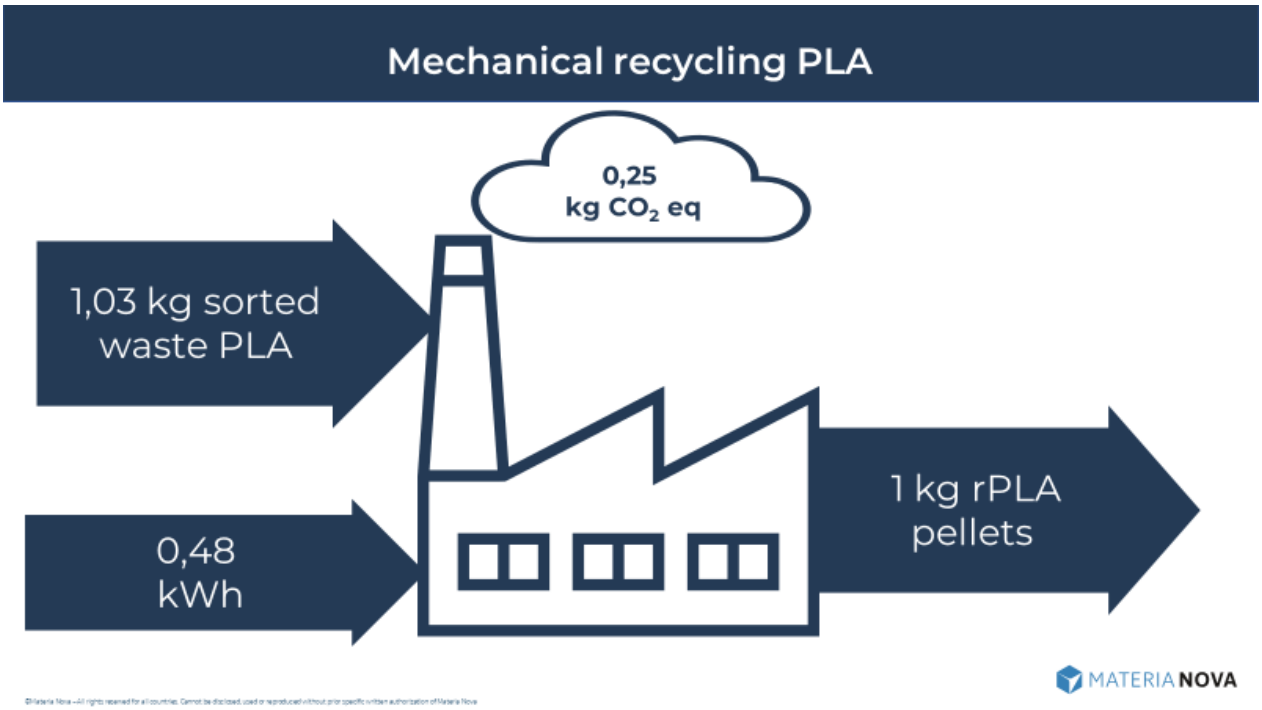
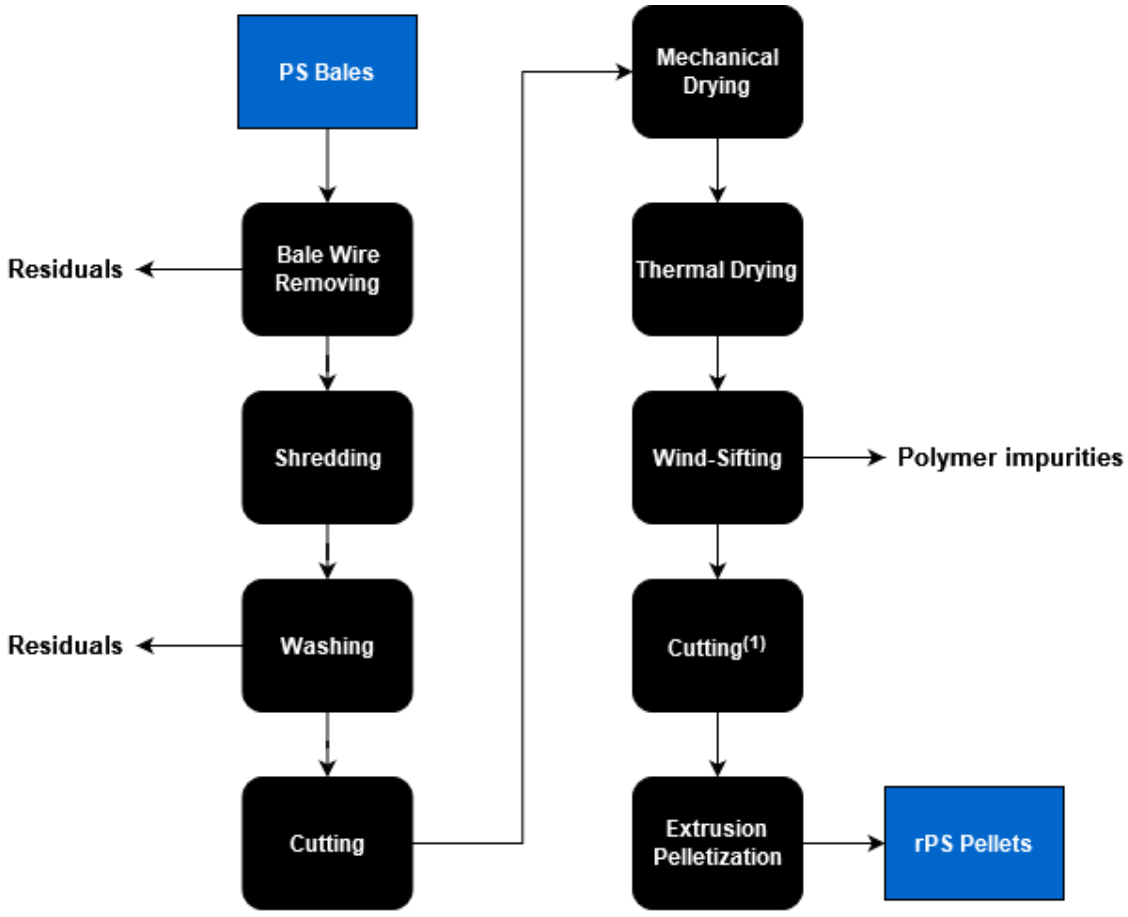


*Figure 7 – Balances for mechanical recycling of PLA (based on **Maga 2019** and **Cosate de Andrade 2016**)*

1.3 Mechanical recycling of PS

1.3.1 Technical aspects

The process for thermomechanical recycling of PS is described in the flow-chart of figure 8, based on **Civancik-Uslu 2021**. This study proposes a LCA for the PS recycling process operated by ECO-oh! with an annual recycling capacity of 22 000 tons (including the recycling of other polymers than PS). Literature about PS mechanical recycling is scarce, and this reference has been considered to be representative of large-scale practices.



(1) A second step of cutting is necessary to reduce the size of rigid polystyrene which has not reach the requirements in the previous processing steps.

Figure 8 – Process diagram of PS mechanical recycling, based on ***Civancik-Uslu 2021***

After pre-treatment and sorting, PS from bales is shredded, washed and cut in smaller pieces for the removal of contaminants. After drying, wind-sifting enables to remove small particles from the fraction before the extrusion and regranulation of PS into pellets.

During the extrusion step, PS can degrade according to a radical chain process which mainly leads finally to chain scission obtained by β-scission reactions (**Guyot 1986**). Final products are a little modified if oxygen is present in extruder (**McNeill 1994**). The literature shows that these degradations reactions are accelerated by shear stress generated in the extruder (**Capone 2007, Goshayeshi 2023**). **Remili 2011** reports that after 8 reprocessing cycles at 180 °C in a twin-screw extruder, the molecular weight (M_w) of PS decreases by about 33%.

To counter radical degradation mechanism occuring during processing, the use of antioxidants is recommended, and the use of metal stearates is also mentioned (**Goshayeshi 2023**). As PS seems to be more sensitive to thermo-mechanical stress than other polymers, it is better to use the extruder with a short residence time and a low shear stress (**Capone 2007**).
It should be noted that PS is used in solid and expanded forms. Recycling of the latter requires a de-foaming step, in order to reduce its volume, before reprocessing. De-foaming can be performed either by pre-melting or using a solvent based method for which weak solvents of PS such as natural vegetable oils are used (**Goshayeshi 2023**).

1.3.2 Balances aspects

The data retrieved from **Civancik-Uslu 2021** can enable to evaluate the balances of the mechanical recycling process of PS. 1.12 kg of pre-sorted PS bales are needed to produce 1 kg of rPS pellets. The majority of the residues present in the PS fraction at the beginning of the process (reported to be about 7 % of the incoming fraction, mostly dirt and missorted polymers) is segregated during the process, leading the recycling rate of PS alone to be 96 %. An average value of 0.60 kWh/kg rPS pellets is reported for the whole recycling process. Climate change impacts of the process have been assessed by reproducing the inventory of the authors in SimaPro, using the impact assessment calculation method from IPCC 2021, a value of 0.51 kg CO_2 eq/kg rPS was found. **Civancik-Uslu 2021** was the only study found in the literature with specific balance data about the mechanical recycling of PS, no comparison with other sources was therefore possible. Figure 9 summarizes the mass, energy and climate change balances of the mechanical recycling of PS.

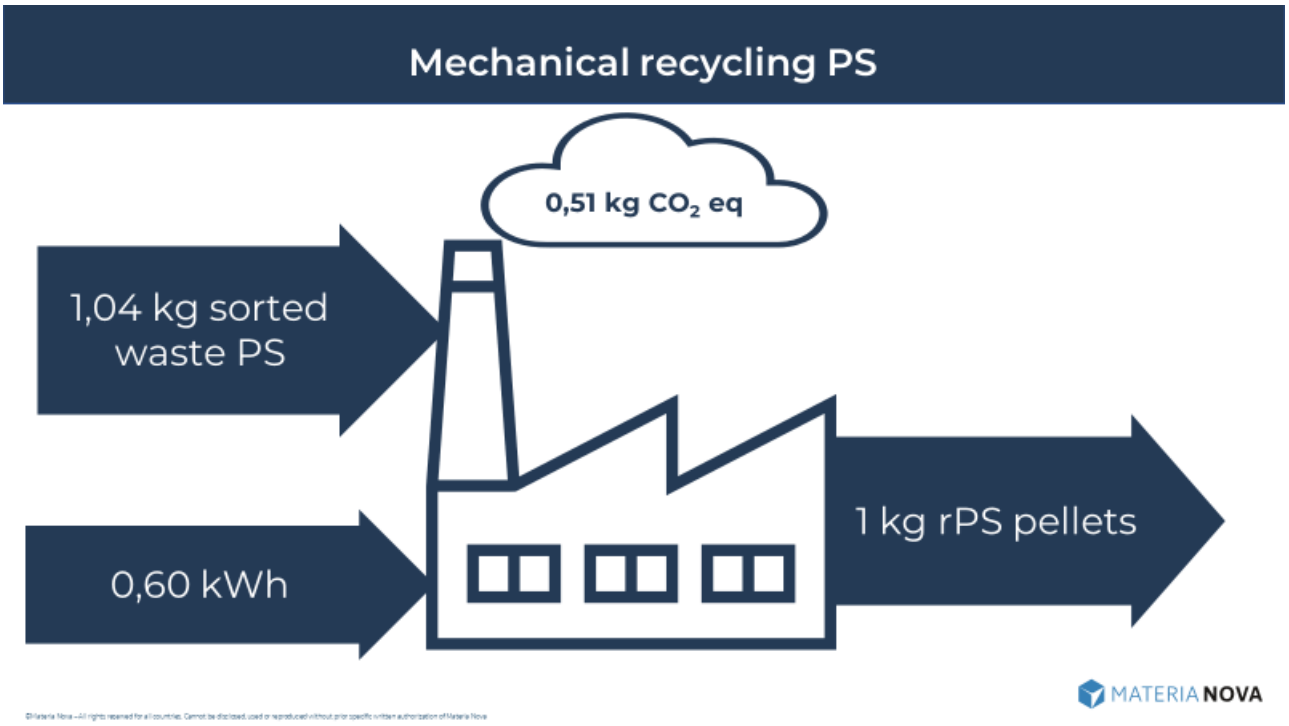


*Figure 9 – Balances for mechanical recycling of PS (based on **Civancik-Uslu 2021**)*

1.4 Mechanical recycling of PP/PE

1.4.1 Technical aspects

The processes for mechanical recycling of PE and PP are both handled in the same manner. The delivered sorted waste are firstly ground and washed to remove any unwanted debris. NIR separation techniques are often used in order to separate PP and PE from the incoming feed because PP and PE have similar specific density, making their separation in previous sorting steps at MRFs complicated. This additional sorting step depends on the incoming pre-sorted waste flow, i.e., PE/PP alone, PP/PE mix or purity of the single stream. At the end, polyolefins (PO) are extruded and pelletized to produce rPP or rPE. Figure 10 shows the process flow chart for the mechanical recycling of PO.

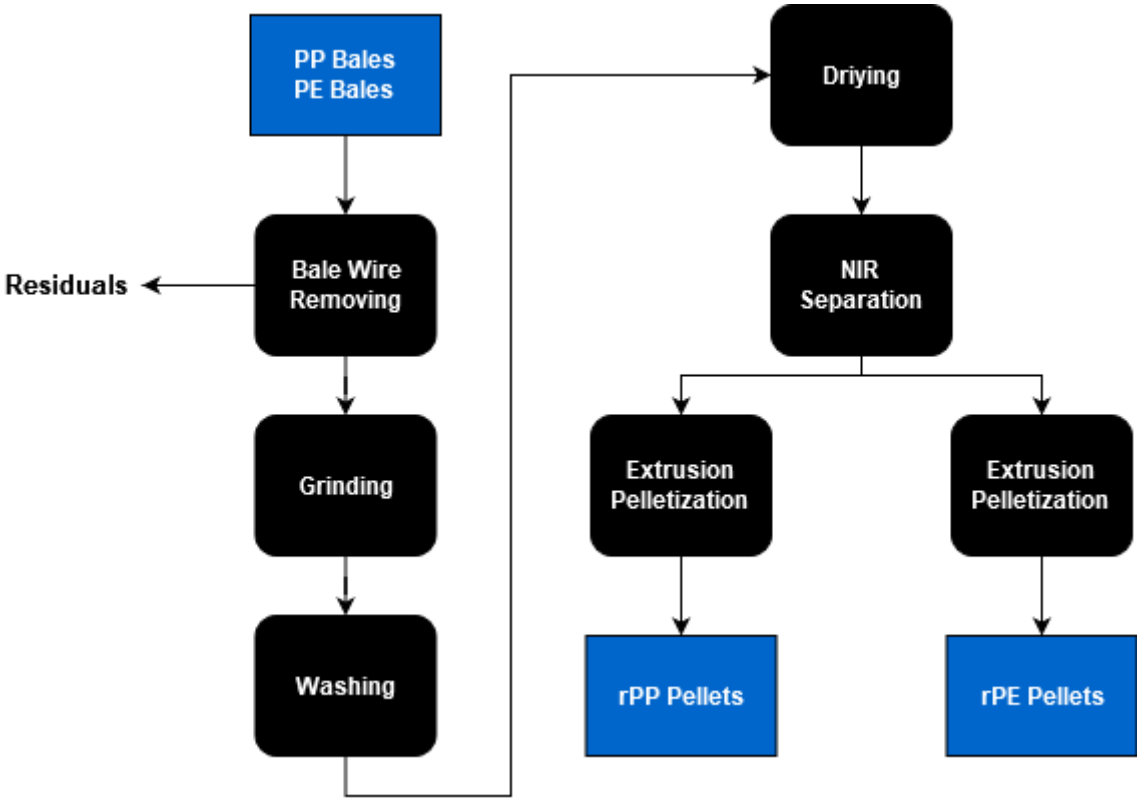


Figure 10 – Process diagram of PE/PP mechanical recycling, based on ***Kägi 2017***

As for other types of plastics, the extrusion step of the process of polyolefins (LDPE, HDPE and PP) recycling leads to degradation reactions, mostly by radical processes, but differences are observed according to the nature of the extruded polymer.

In the case of PP, chain scission of the macromolecules is caused by β-scission, the breakdown of peroxide radicals and shear, leading to a decrease in the molecular weight of the polymer. **Hinsken 1991** shows that the M_w of a PP (without stabilizer)

gradually decreases during extrusion cycles, varying of 418 400 g/mol for the neat polymer to 125 300 g/mol for the same polymer after the seventh cycle of extrusion.

In the case of HDPE, some studies show that chain branching and crosslinking, leading to an increase of the molecular weight of the polymer, is favored compared to thermo-oxidative and thermo-mechanical induced chain scission which take place simultaneously (**Hinsken 1991**). The chain branching and crosslinking reactions can be assigned to the addition of alkyl radicals to vinyl groups. As for example, the MFI (190 °C, 2,16 kg) of a HDPE (without stabilizer) gradually decreases after each cycle of extrusion, varying of 5,03 for the neat polymer to 1,0 g/10 min for the same polymer after the fifth cycle of extrusion (**Hinsken 1991**).

For LLDPE, **Dordinejad 2018** shows that the degradation during a multiple extrusion process in a single-screw extruder proceeds by branching and chain scission. M_w gradually decreases and viscosity $|\eta^*|$ gradually increases during extrusion steps.

The route usually used to limit these radical degradation processes encountered for polyolefins is addition of antioxidants during reprocessing.
In an interesting way, in case of PP, the introduction of long chain branching during PP extrusion is a useful method to counter the scission chains. It is a well-known industrial process which can be promoted particularly by reactive extrusion (**Kamleitner 2017, Klimke 2014**).

1.4.2 Balances aspects

The process as described in figure 10 above was used as a reference process for establishing the ecoinvent inventory for PO recycling. 1.06 kg of input PE/PP bale are necessary to produce 1 kg of recycled pellets. An average value of 0.63 kWh/kg rPO energy demand is reported. Climate change impacts of the process have been assessed by using the inventory available in the ecoinvent 3 database in SimaPro, using the impact assessment calculation method from IPCC 2021, a value of 0.25 kg CO_2 eq/kg rPO was found. Figure 11 summarizes the mass, energy and climate change balances of the mechanical recycling of PO.

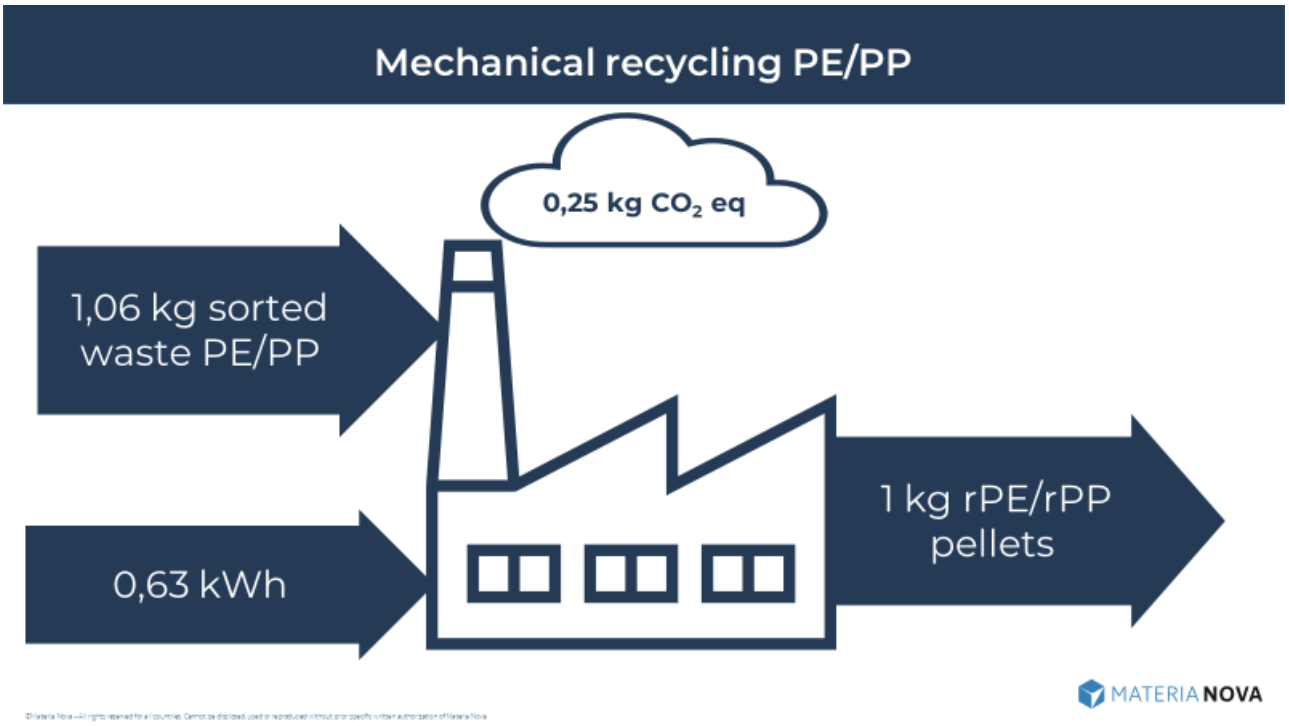


*Figure 11 – Balances for mechanical recycling of PS (based on **Kägi 2017**)*

Some other data in the literature indicated additional sorting and washing steps of the pre-sorted waste in order to attain the requested purity to produce recycled pellets. However, energy demand of the global processes stays in the same order of magnitude, e.g., **Franklin Associates 2018** reported values of 0.53 kWh/kg rPP and 0.52 kWh/kg rPE for municipal waste recycling after the receiving of pre-sorted bales, and **Martin-Lara 2022** reported a value of 1.07 kWh/kg rPE pellets for the recycling of waste films. Energy demand announced by **Martin-Lara 2022** are higher notably because more processing steps are reported in comparison with the other systems. In particular, two distinct crushing steps are reported. Even though the study is based on the real case of municipal recycling facilities of the city of Granada in Spain, the representative process has been chosen because it represents an average of state-of-the-art recycling installations for polyolefins mechanical recycling.

1.5 Compared balances of mechanical recycling of sorted plastics

Table 1 summarizes all the results of the previous paragraphs for the mechanical recycling of PET, PLA, PS and PO. The results are given for 1 kg of recycled pellets.

Comparisons should be considered by the reader with caution, of course because the outputs differ, but also given the fact that the source, reliability and transparency of the data used to provide this table is variable depending on the type of plastic, even if a selection was made among available data to determine the most appropriate and representative ones. The corpus of available data was very limited, and it is difficult to estimate which of the data is more representative.

Besides, it may have attracted the attention of the reader in the description of the recycling processes that many common operations can be used in the sort-refining steps for all the polymers. This is mainly because the key for mechanical recycling is the maximum separation of impurities of the target polymer in the waste flow, and separation methods used for one plastic can usually be used for another one. For example, vibrating-sieving associated with centrifugation reported for the mechanical recycling of PLA has the same objective than wind-sifting reported for the mechanical recycling of PS, which is to increase the purity of the target polymer before final extrusion-pelletization. It is thus important to note that several different sub-processes might achieve the same goal and be interchangeable, so that multiple “representative” processes exist on the market. By exchanging some of the sorting steps between plastics, it may occur that the differences observed in the balances would be slightly modified. However, since the extrusion-pelletization step is high energy consuming, this step is the main contributor to the global impacts of the mechanical recycling process, and fine-tuning of the sorting steps should only have a minor influence. Hence it seems rather logical that the global impacts would be ranked according to the extrusion temperature range of the different plastics, since the impact of the extrusion step is expected to be higher for PET (extruded at 230-250 °C) than for PLA (extruded at 170-200 °C).

Polymer	Mass balance (w/o impurities) (input → output)		Energy demand	Climate change impacts	Type of data
PET	***PET waste***	***rPET pellets***	1.91 kWh /kg rPET	0.60 kg CO_2 eq. /kg rPET	**Industrial**
	1.09 kg	1 kg			
PLA	***PLA waste***	***rPLA pellets***	0.48 kWh /kg rPLA	0.25 kg CO_2 eq. /kg rPLA	**Industrial**
	1.03 kg	1 kg			
PS	***PS waste***	***rPS pellets***	0.60 kWh /kg rPS	0.51 kg CO_2 eq. /kg rPS	**Industrial**
	1.04 kg	1 kg			
PE/PP	***PO waste***	***rPO pellets***	0.63 kWh /kg rPO	0.25 kg CO_2 eq. /kg rPO	**Industrial**
	1.06 kg	1 kg			

Table 1: compilation of balances for mechanical recycling of plastics at industrial scale

1.6 Climate change impacts of mechanically recycled and virgin plastics

The climate change impacts of the mechanical recycling processes considered as representatives have been calculated by using the calculation methodology recommended by the Intergovernmental Panel on Climate Change (Bern model, global warming potentials over a 100 year time horizon). The obtained values have already been reported in previous paragraphs. It is reminded that representative datasets were already available in ecoinvent for PET and polyolefins, whereas recycling processes for PS and PLA were modelled based on literature references. The figure 12 below represents the compared climate change impacts related to the production of 1 kg plastic pellets, virgin or recycled by thermomechanical process. However, the straight comparison of virgin and recycled pellets would not be fair in terms of functionality since the recyclate is generally of a lower quality than virgin-grade plastics mainly due to the changes in the polymer structure during the melting process.

To reflect the potential degradation of the recycled materials, the comparison with their virgin equivalent is therefore not carried out on a 1:1 mass basis, but a substitution factor of 0.9 is applied, i.e., 1 kg of virgin material is not compared to 1 kg of recyclate, but to 1/0.9 = 1.11 kg. This value is commonly used by LCA practitioners to account for polymer degradation during mechanical recycling, but might be challenged depending on the polymer and the recycling process considered (e.g., rPET produced through SSP can almost reach the quality of virgin PET, so the substitution factor may be closer to 1, while rPO recycled from films might be of low quality in comparison to virgin materials, so a more appropriate substitution factor could be lower than 0.9). The climate change impacts of the production of virgin materials were assessed by using the corresponding ecoinvent 3 datasets as available in SimaPro, which are based on data provided by Plastics Europe. Due to the substitution factor, the values for recycled pellets in the graph below are different from the values shown in the global balance figures of previous paragraphs for each type of plastic.

For information purposes, the climate change impacts of the production of virgin PLA are also displayed in this graph by considering carbon uptake. In that case, environmental credits are given to the product because carbon dioxide is removed from the atmosphere during the growth of plants used as raw materials, leading its carbon footprint to be lower.

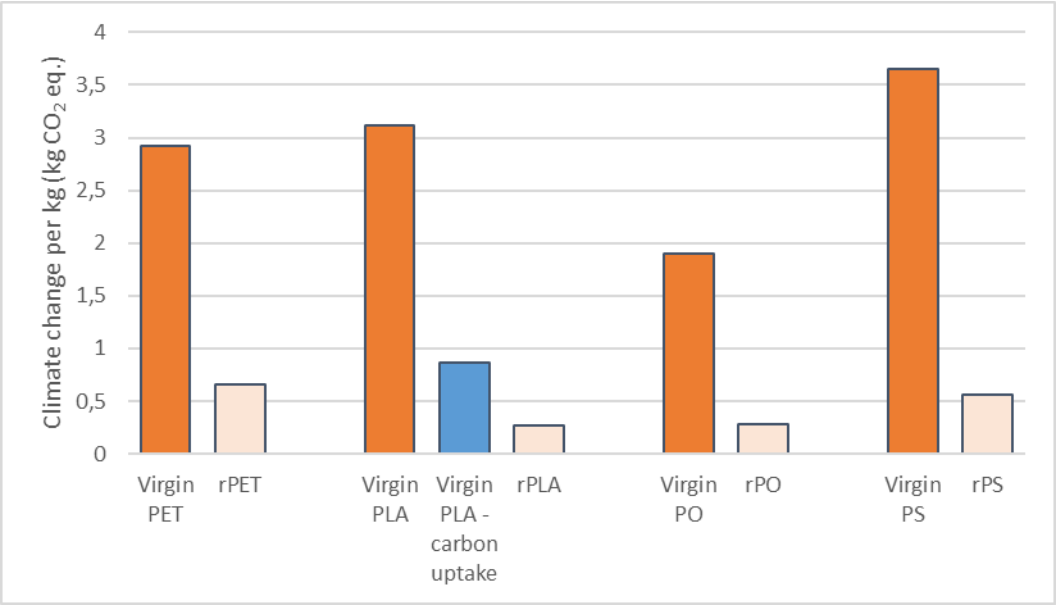


Figure 12 – Comparison of the climate change impacts between the production of secondary polymers from mechanical recycling and their virgin equivalents.

These results tend to show that plastics pellets obtained by mechanical recycling of sorted plastic waste would have a lower climate change impact than the virgin plastic pellets, whatever the type of plastic considered, by a 5 to 10 factor, roughly. It can be observed that the most significant impact reduction could be obtained in the case of PLA. However, a real comparative LCA study of all processes, having access to transparent primary data for all of them, would be needed to draw such fine conclusions.

Based on these results, it seems obvious that the thermomechanical recycling of thermoplastic waste, when it is possible, would always make sense from a climate perspective, provided that the quality of the regenerated material can be good enough for meeting applications' requirements. Initiatives to enhance waste (and therefore output) quality by developing better collection and sorting schemes should therefore be encouraged for all these plastics, and there seems to be no reason to discredit one of these plastics over the others in recycling strategy policies.

Conclusion about mechanical recycling

Thermomechanical recycling of plastic waste produces recycled plastic pellets that can be used as a substitution material to virgin pellets by the plastic transformation industry. The process for this type of recycling includes sorting steps prior to an extrusion-pelletization step, and the process flow-charts for the mechanical recycling of all types of thermoplastics are very similar. In all cases, due to high temperature processing and shear rate, degradation reactions may occur during the process that lead to a deterioration of the properties of the final material. Strategies for limiting these degradation phenomena can be used in all cases.

The mass balance of thermomechanical recycling is rather high (>90%) and similar whatever the type of plastic. Available information to determine energy and climate change balances of those processes are rather scarce and of variable reliability and transparency, thus making the comparison between all processes difficult. Due to similar processes, the relative energy balances of plastic mechanical recycling is more or less linked to the processing temperatures of the concerned polymers, thus explaining a better energy balance for PLA, PS or polyolefins than for PET. When climate change balance is concerned, it appears that for all types of plastics recycling should be considered favorable, since the climate change impact of recycled pellets are in all cases lower than those of virgin pellets, even when a substitution factor is applied to account for the degradation of the properties.

However, it should be reminded that not all recycled plastics can substitute all virgin plastics in all applications, and that comparison of balances should preferably be made for specific cases with defined applications rather than at a global level.

2 Chemical recycling

Two main types of chemical recycling processes for plastic waste can be distinguished. First is thermal decomposition (sometimes abusively called thermal depolymerization even if such a wording should be preferred exclusively for a decomposition process that converts the waste into polymerizable monomers), second is chemical depolymerization.

Whereas thermomechanical recycling globally preserves the macromolecular structure of the polymers that constitute the plastic, both types of chemical recycling processes consist in breaking, by the action of temperature and/or chemical agents, the covalent bonds within the macromolecules in a controlled way that returns smaller molecules that can be monomers usable for polymer synthesis or other chemical intermediates, that can also further be converted into monomers.

Both should be considered as controlled degradation processes. Solvent-based purification processes are sometimes referred to as chemical recycling processes, but those are only separation processes that selectively sort the targeted macromolecules from the additives and other contaminants of waste plastics. Since no breaking of covalent bonds of the skeleton of the macromolecules occur here, such processes should rather not be called chemical, and will not be specifically examined here.

Two main types of thermal processes can be described, pyrolysis and gasification. Pyrolysis is conducted at high temperatures (300-900 °C) in an oxygen free environment and results in breaking down the macromolecules into a mixture of hydrocarbon molecules called pyrolysis oil and non-condensable gases. Pyrolysis oil can be further converted into monomers or other chemicals thanks to cracking or refinery processes.

An advantage of pyrolysis is that the process can be used to treat waste streams that may be more mixed and more contaminated than what mechanical recycling can treat. However, the quality of input feedstock needs to be steady to enable economically viable purification and separation processes, and by-products and process waste issues have to be addressed. Several purification and process steps are indeed necessary to obtain polymer grade monomers from pyrolysis oil.

In gasification processes, the plastic waste is heated at higher temperature (500-1300 °C) with controlled oxygen supply to result in a mix of H_2 and CO called syngas, that can further be used as feedstock in chemical processes for production of light hydrocarbons or methanol. The level of quality of input waste can be lower than for pyrolysis because of the higher processing temperatures. The use of gasification remains however mostly applied to the production of fuels rather than to the

production of chemicals that would be used for new polymer synthesis, and plastic-to-fuels scenarios can hardly be considered as plastic recycling.

Chemical depolymerization consists in controlled breakage of chemical links within the skeleton of macromolecules to obtain monomers or oligomers that can further be used as building blocks for next generation polymer synthesis. Chemical depolymerization mainly concerns polymers that are (or could be) produced by polycondensation reactions, such as polyesters or polyamides (PET, PLA, nylons...). The ester or amide links of those result indeed from equilibrium chemical reactions (alcohol + acid → ester) and can therefore easily be broken (ester → alcohol + acid). Such chemically reversible links do not exist in polymers resulting from polyaddition reaction such as polyolefins, that are therefore more difficult to be treated by comparable processes and are better candidates for thermal decomposition processes. Chemical depolymerization for some polyaddition polymers is however possible in certain conditions, e.g. for PS.

Depending on the type of plastic and the type of recycling, chemical recycling processes can be operated in a wide range of conditions of temperature, with or without specific catalysts, with addition of specific reactants and with or without solvents. Such different processes will obviously lead to different impacts. In this chapter, the main chemical recycling processes for PET, PLA, PS, PE and PP will be explored.

2.1 Chemical recycling of PET

2.1.1 Technical aspects

At industrial scale, PET can be chemically recycled according to six routes as described in table 2 below. Five of this six routes basically consist in chemically targeting the ester linkages of the polyester backbone to produce reverse reactions of the condensation leading to monomers or simple derivatives thereof. This sixth route is a pyrolysis process that does not specifically targets the ester linkages but can break other covalent bonds of the polyester backbone, thus leading to a mixture of small molecules.

Among these routes, the most used is glycolysis of PET with ethylene glycol (EG). It is also one of the oldest and simplest methods in commercial PET recycling processes. It results in the formation of BHET monomers and oligomers. Viability of PET glycolysis depends on the feed specification (PET waste input type and quality). Among industrial processes for glycolysis of PET, Bring Technology™ from JEPLAN is applied for bottle-to-bottle recycling and for textile-to-textile recycling. BHET is produced in two major steps, starting with a pre-decomposition step (220 °C, 1 h) to form oligomers followed by the addition of EG and a sodium methylate catalyst (200 °C, 2 h). JEPLAN uses separately activated carbon to remove dyes and impurities from the depolymerization mixture. A few additional purification steps yield 98% monomer in pure form. The new process Rewind™ PET process developed together by JEPLAN, AXENS and IFPEN aims to recycle all types of waste PET-based materials via an optimized glycolysis process (**Barnard 2021**). In Ioniqa Technologies' process, an ionic capture complex is used to degrade a wide range of PET materials (ie re-PET bottles, PET carpets, and multi-layered PET trays containing other polymers). The capture complex comprises three distinguishable entities: a magnetic nanoparticle, an ionic liquid catalyst and a bridging moiety connecting these two entities. The catalyst complex can depolymerize PET waste at a temperature of 200 °C, with an EG:PET ratio of 8:1, and catalyst loading of 2 wt%. Further advantages of Ioniqa's capture complex include its ability to absorb pigment contaminants, the ease of its recovery from the process line via magnetic attraction, and its subsequent reusability up to 50 times (**Barnard 2021**).

Methods	Chemical reactions	Industrial processes and companies
Glycolysis	PET + EG → BHET + oligoPET (few repeat units)	Bring Technology™ (JEPLAN - JP) Rewind™ PET process (JEPLAN - JP/AXENS - FR/IFPEN - FR) Ioniqa Technologies (NL) - pilot ChemPET (Garbo s.r.l. - IT) – pilot Poseidon process (Poseidon Plastics (GB) – pilot Polyester Renewall Technology (Eastman-US) Volcat Technology (IBM) – lab scale Meltem Kimya (TR)
Partial glycolysis	isocyanate PET + EG → oligoPET → polyurethane (route 1) PET + EG → oligoPET → PET -EG (route 2)	Sopraloop process (Soprema - FR) (route 1) PerPETual Global Technologies (GB) (route 2) EverPET® (Aquafil - DE) (route 2)
Methanolysis	PET + MeOH → DMT + EG	Polyester Renewall Technology (Eastman-US) Infinite Loop™ (Loop Industries - CA) - pilot
Saponification	PET + NaOH → DT + EG ↓ acid TA	DEMETO (Gr3n - CH) – pilot Tyton Biosciences (US)
Enzymatic hydrolysis	enzymes PET + water → TA + EG low T	Carbios (FR)
Pyrolysis	high T, without O_2, + catalyst PET → hydrocarbons	Mitsui Chemicals (JP)

Table 2: industrial routes for chemical recycling of PET

A process flow for glycolysis was retrieved from **Shen 2009**. The considered process diagram is presented in figure 13. The glycolysis of PET yields the oligomer bis-hydroxyl ethylene terephthalate (BHET). After the glycolysis process, the oligomer passes through a fine filtration step before it can be repolymerised into PET.

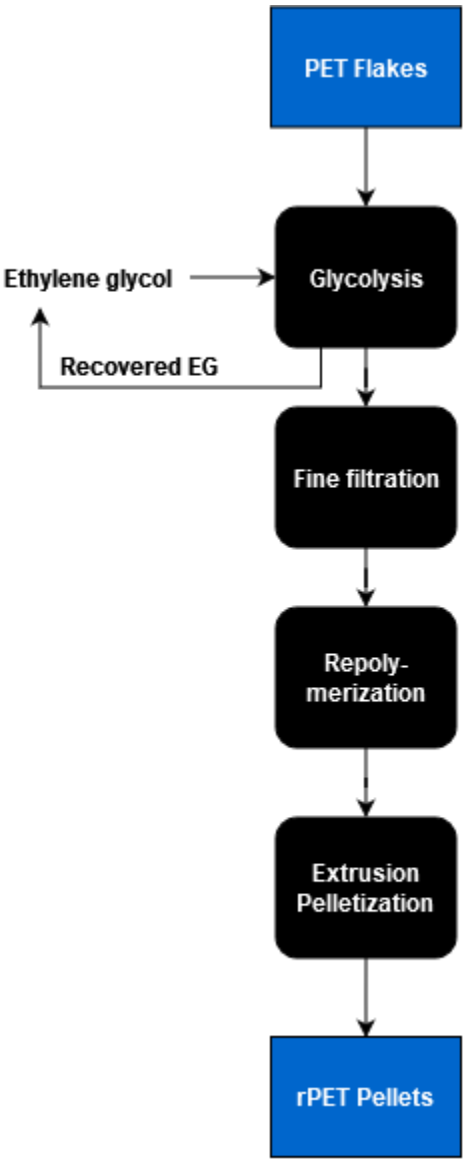


Figure 13 – Process diagram of PET chemical recycling through glycolysis, based on ***Shen 2009***

In recent years, there has been increased interest in performing partial PET glycolysis. Partial PET glycolysis can be carried out under suitable preselected reaction conditions (EG/PET molar ratio, amount of catalyst, reaction time). This route does not lead to monomers of PET but to low molecular weight PET oligomers with hydroxyl end groups. Those oligomers can be used as polyols in polyurethane production, for example to make PU insulating foams as in the Sopraloop Process. Another further use of these oligomers is to produce new PET grades as In PerPETual Global Technologies's and EverPET® processes.

The DEMETO (DEpolymerisation by MicrowavE TechnolOgy) uses a saponification route. The waste of PET is ground up and mixed with a solvent composed typically of ethylene glycol and an alkali base, such as NaOH, KOH or LiOH. This

heterogeneous mixture is then transferred to a reaction chamber where microwaves are used to heat the chamber to a temperature of 150–350 °C with a pressure between 1 and 20 atm. The salt formed is finally treated with an acid such as HCl to obtain terephthalic acid (**Barnard 2021, Thiounn 2020, Parravacini 2013**).

Carbios's enzymatic hydrolysis allows to depolymerize PET waste (bottles and polyester textiles) to produce terephthalic acid (**Barnard 2021**). In a recent paper published in Nature (**Tournier 2020**), the enzyme-catalyzed approach achieves, over 10 hours, a minimum of 90% PET depolymerization into recycled purified TA, with a productivity of 16,7 grams of terephthalate per litre per hour (200 grams per kilogram of PET suspension, with 0.3 wt% enzyme). The recycled TA has successfully been used to remake PET products (e.g. clear PET bottles) of a quality equivalent to virgin PET.

Among those chemical recycling processes, the most challenging for PET may be the pyrolysis process. For PET, pyrolysis yields a rather low amount of oil and the fuels obtained have a low calorific value due to the presence of benzoic acid (**Gebre 2021**). Only Mitsui Chemicals seems to work on this strategy at a pilot scale.

Other chemical recycling routes for PET can be found in the scientific literature but are not yet developed at industrial level. Those are listed for information in table 3.

Method	Chemical reactions
Alcoholysis	PET + ROH → DAT + EG
Glycolysis	PET + $R(OH)_2$ → BHAT + EG
Neutral hydrolysis	PET + water → TA + EG
Acid hydrolysis	PET + water → TA + EG acid
Aminolysis	PET + RNH_2 → DATA + EG PET + $(RNH_2)_2$ → BAATA + EG
Ammonolysis	PET + NH_3 → T + EG
Electrolysis	PET → TA + EG

Table 3: complementary routes for chemical recycling of PET.

2.1.2 Balances aspects

Precise balance data in the literature about chemical recycling of PET at large scale is scarce. No life cycle inventory data have been reported for the glycolysis that would have enabled to assess the energy demand of the process, nor its climate change impacts. Other types of chemical recycling of PET, notably hydrolysis, are also very badly represented in the environmental literature.

Data available in literature are gathered in table 4. The information relates either to PET to PET systems or only to the chemical degradation process, and reflect different scales of implementation; sources can therefore not be soundly compared. Data regarding enzymatic recycling of PET were also found in **Uekert 2022** but are not included in the table since this lab-scale technology is still at very low TRL, and the values (energy demand of 12.25 kWh/kg PET in. and climate change of 3.16 kg CO_2 eq/kg PET in.) might be far from the ones that would be obtained from upscaled process.

It is not possible, based on available data to attempt to provide a general infographic as those given for the mechanical recycling processes in the previous section.

Balances - Chemical recycling PET							
Recycling	**Mass balance (input → output)**		**Energy demand**	**Climate change impacts**	**Type of data**	**Source of data**	**Authors of study**
Glycolysis	***PET flakes***	***rPET pellets***	N.D.	N.D.	**Industrial**	Far Eastern New Century Co., Taiwan	**Shen 2009**
	1 kg	0.98 kg					
	Yield : 98 %						
	PET flakes	***Oligomer***	0.62 kWh /kg PET in.	N.D.	**Pre-industrial**	N.D.	**Barboza 2009**
	1 kg	1.25 kg					
Hydrolysis	***PET waste***	***rPET pellets***	N.D.	N.D.	**Pilot-scale**	Gr3n process	**Cornago 2021**
	1 kg	0.88 kg					
	Yield : 88 %						
Methanolysis	***PET flakes***	***DMT***	3.32 kWh /kg PET in.	0.98 kg CO_2 eq. /kg PET in.	**Industrial + Literature**	Teijin; Patagonia (2005)	**Shen 2009**
	1 kg	1.01 kg					

Table 4: Mass, energy and climate change balances for PET chemical recycling

2.2 Chemical recycling of PLA

2.2.1 Technical aspects

The chemical recycling of PLA is not very well developed on an industrial scale. Only the hydrolysis process, which produces lactic acid, has been exploited to some extent (table 5).

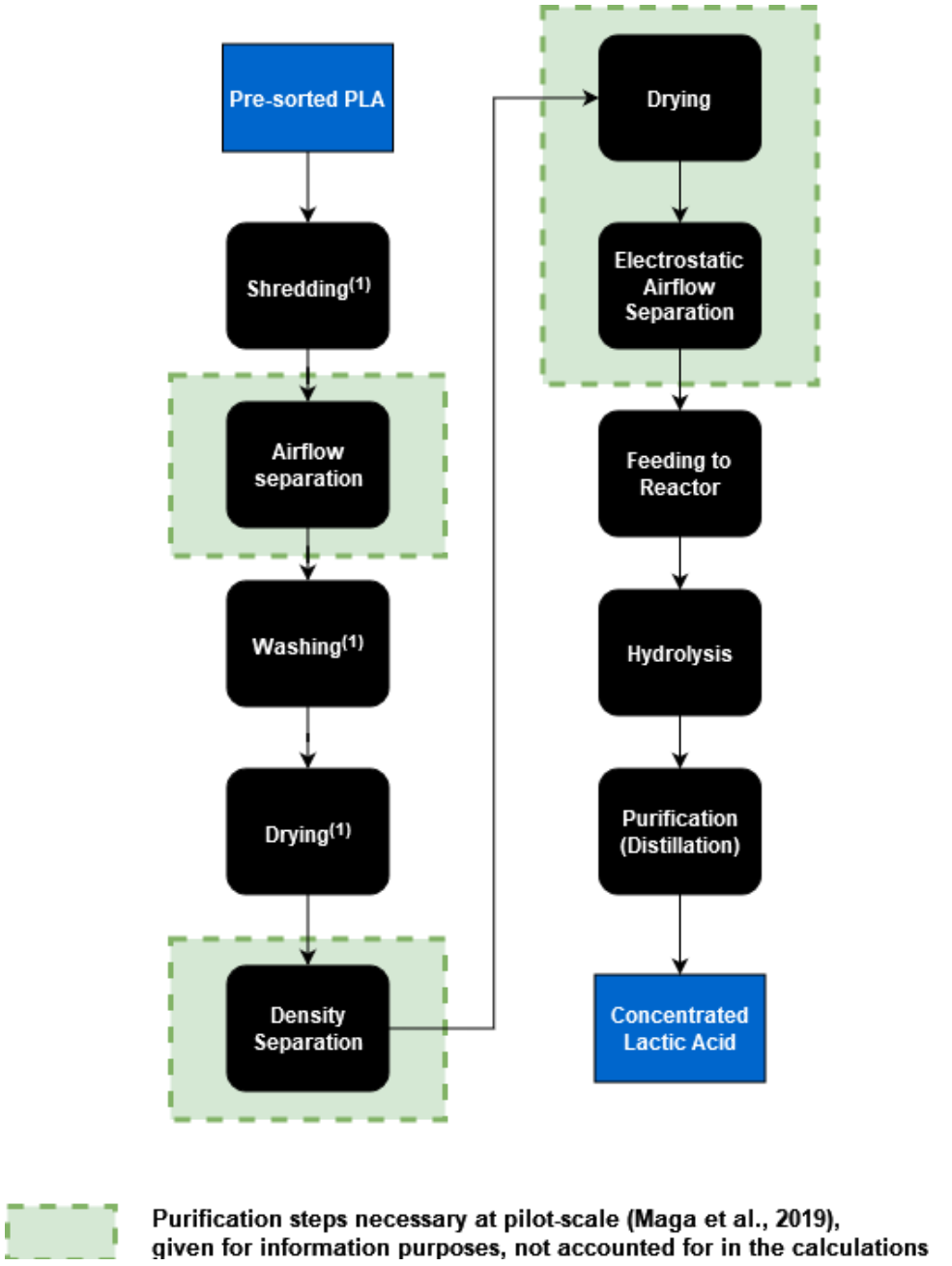
TotalEnergies Corbion commercializes a Luminy PLA grade containing 20% of chemical recycled PLA. The latest is obtained by hydrolysis (**De Bie 2023**). NatureWorks announces have recycled by hydrolysis about 7700 tons of grade Ingeo PLA since 2004 by hydrolysis. Noosa has developed a pilot to recycle by hydrolysis all types of textiles containing PLA. Recovered lactic acid is converted back into a virgin PLA polymer so that it can be made into textile fibre again (**Gomez Urgoiti 2021**).

For complete hydrolysis, when there are only PLA and water in the system, the system needs high temperature and pressure to promote the hydrolysis of PLA. To improve the hydrolysis rate, a catalyst can be used. Strong acid (like sulfuric acid) and alkali (like sodium hydroxide) are the main employed catalysts. It can be also used a solvent as in the case of the patent of Galactic/Futerro in which a first step is the dissolution of PLA in a lactic acid ester.

Methods	**Chemical reactions**	**Industrial processes and companies**
Hydrolysis	PLA + water → lactic acid acid or basic catalyst (eventually)	TotalEnergies Corbion NatureWorks Noosa – pilot

Table 5: industrial route for chemical recycling of PET.

A process flow for the hydrolysis recycling process was retrieved from **Aryan 2021** and is presented in figure 14. This refers to the hydrolysis of PLA waste to lactic acid at 180 °C and 1.5 MPa for a period of 50 minutes. The reaction is autocatalytic and therefore, sustains itself on its own. However, the insolubility of PLA in water requires the use of large quantities of water, high temperature and elevated pressure (**Grewell 2014**).



*(1) Process steps added for uniformity purposes, based on **Maga 2019***

*Figure 14 – Process diagram of PLA chemical recycling through hydrolysis, based on **Aryan 2021** and **Maga 2019***

Other methods than hydrolysis exist to chemically recycle PLA. Table 6 presents the routes for which patents have already been applicated (**Niaounakis 2019**).

Methods	Chemical reactions	Applicants for a patent
Complete hydrolysis	PLA + water → lactic acid acid or basic catalyst (optional)	MITSUI CHEM INC EP0573042A1 (1993) US5264626A (1994) SHIMADZU JPH1036553A (1998) INST NAGOYA IND SCIENCE RES JP2003300927A (2003) UNIV TOYOHASHI, TEIJIN FIBERS LTD JP2007210889 (2007) NAKAMURA WO2007102488A1 (2007) JP2007238691A (2007) JP4118313B1 (2008) REAL PLASTIC JP2008179713A (2008) GALACTIC/FUTERRO WO2010118954 (2010) NOOSA (2021) WO2021148549A1 (2021)
	PLA + water → lactic acid + oligoPLA acid or basic catalyst (optional)	DU PONT US5229528A (1993) US5264626A (1993) EP0628533A1 (1994)
Partial hydrolysis	PLA + water → LA	JAPAN STEEL WORKS LTD JPH07309863A (1995)
	PLA + water → oligoPLA → LA	KYUSHU INST TECHNOLOGY / MUSASHINO KAGAKU KENKYUSHO JP2009249508A (2009) UHDE INVENTA FISCHER GMBH EP2559725A1
Alcoholysis	PLA + ROH → alkyl lactate	DU PONT US5264614A (1993) US5264617A (1993) TEIJIN FIBERS LTD JP2009029757A (2009) GALACTIC/FUTERRO – 2011 WO2010118955A1 (2010) UNIV QINGDAO SCIENCE & TECH CN102659590A (2012) CN105017013A (2015) CN107382718A (2017) WROCLAWSKIE CT BADAN EIT & ZOO WO2016111635A1 (2016) ZEUS IND PRODUCTS US2018051156 (2018)
	PLA + ROH → LA (or $R(OH)_2$)	DAINIPPON INK & CHEM INC JPH09241417A (1997)
	PLA + ROH → oligoPLA	UNIV KEIO WO2005105908A1 (2005) ZEUS IND PRODUCTS US2018051156 (2018
Dry heat depolymerization	T > Tm PLA → LA catalyst	SHIMADZU CORP / TOYOTA MOTOR CO LTD DE19637404A1 (1997) KITAKYUSHU FOUNDATION JP2010168415A (2010)

		XIAOGAN ESUN NEW MATERIAL CO LTD WO2014000277A1 (2014) PTT PUBLIC COMPANY LTD WO2015112098A1 (2015) TOYO SEIKAN KAISHA LTD WO2017130551A1 (2017) NARAYAN M., WU W.M.., CRIDDLE CRAIG S. US2013023674A1 (2013)
Enzymatic depolymerization	enzymes, µ-organisms, low T PLA + water → lactic acid	CARBIOS / CNRS / UNIV POITIERS WO2016146540A1 (2016) CARBIOS WO2014079844A1 (2014)
	enzymes, µ-organisms, low T PLA + water → lactic acid (+ dimer)	CARBIOS / AINR / CNRS / INSA WO2016062695A1 (2016)
	enzymes, µ-organisms PLA + water → cyclic oligoPLA low T	UNIV KEIO WO2004013217A1 (2004)
	enzymes, µ-organisms, low T PLA + water → lactic acid or/and oligoPLA	TOYO SEIKAN KAISHA WO2010050482A1 (2010)

Table 6: patented routes for chemical recycling of PLA.

Additional routes that apparently did not go further academic lab-scale experiments, are reported in table 7 (**Sun 2022**).

Method	Chemical reactions
Alcoholysis	PLA + $R(OH)_{2 \text{ or } 3}$ → (mono or polylactate) hydroxyl → (mono or polylactate) →(mono or polylactate) dihydroxyl reactions usually catalysed PLA + $R(OH)_{2 \text{ or } 3}$ → (mono or polylactate) dihydroxyl → polyurethane catalyst
Ammonolysis	PLA + NH_3aq → analine

Table 7: academic complementary routes for chemical recycling of PLA.

2.2.2 Balances aspects

As previously stated, current industrial practices are heading for the implementation of hydrolysis regarding the chemical recycling of PLA, which has thus been considered for balance studies. **Aryan 2021** (cf. process flow figure 14) provides mass and energy balances for the chemical recycling of PLA by hydrolysis, methanolysis and ethanolysis, all generated by process simulation.

The inventories were reproduced in SimaPro and the potential climate change impacts of each process were assessed, using the impact assessment calculation method from IPCC 2021. Yields refer to the conversion rate of PLA into the product of interest reported by the authors.

In order to get a point of comparison, data from **Maga 2019** and **Cosate de Andrade 2016** regarding hydrolysis are also displayed in table 8. **Maga 2019** includes many steps used to increase the purity of the PLA and remove high amounts of impurities such as cardboard, paper and other plastics. These considerations were specific to the case of the authors and the pilot-plant under study, which has been judged not to be representative of potential upscaling of the technology in a context of global recovery of PLA waste. These steps have been indicated in the process diagram but not considered in the calculations for this report because the chosen representative process considers, on the contrary, PLA flakes without any impurities, which is also unrepresentative of plastic flows entering recycling processes. In addition, important differences in climate change can be observed, due to differences in the process parameters between the studies. On the other hand, data from **Cosate de Andrade 2016** are mostly based on laboratory experiments, limiting their representativeness at higher TRL. Finally, data from a study made by Materia Nova based on primary data from NOOSA at pilot scale are also included.

The summary of balances data found about the chemical recycling processes of PLA is presented in table 8. Due to the variability of results and of data transparency, we chose to use for figure 15 the results from Materia Nova study for NOOSA.

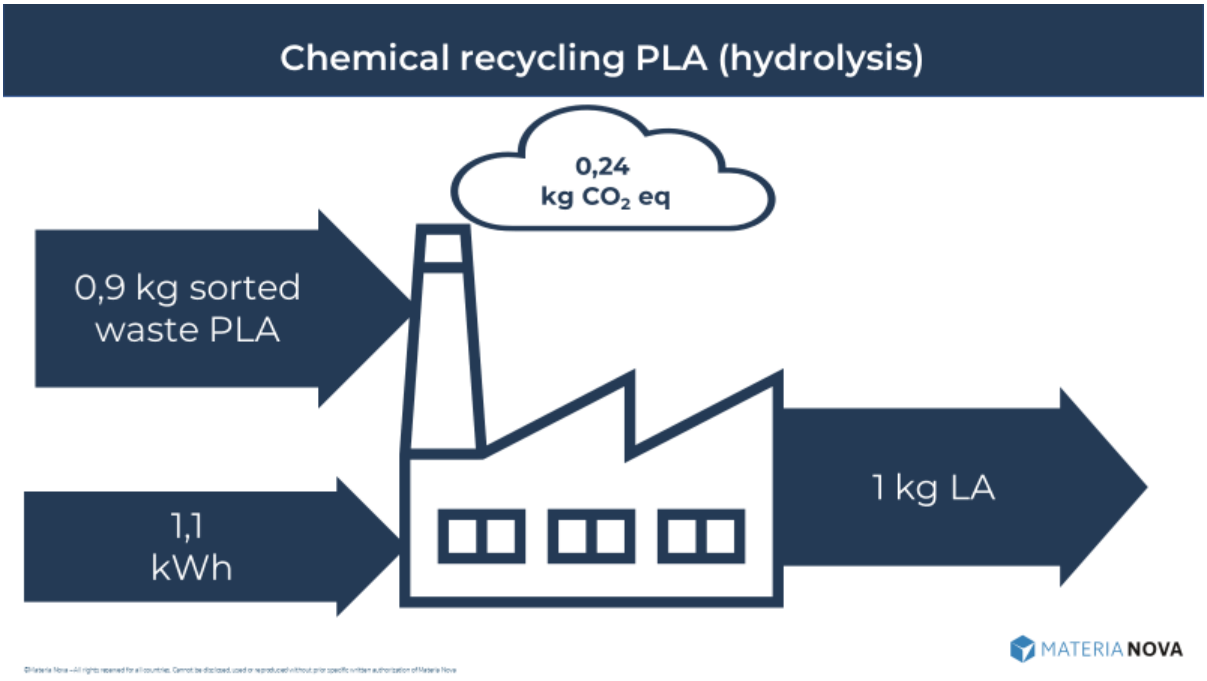


*Figure 15 – Balances for hydrolysis recycling of PLA (based on **Materia Nova study for Noosa**)*

Balances - Chemical recycling PLA						
Recycling	**Mass balance (input → output)**	**Energy demand**	**Climate change impacts**	**Type of data**	**Source of data**	**Authors of study**
Hydrolysis	***PLA flakes*** → ***Lactic acid*** 1 kg → 1.22 kg Yield : 98 %	6 kWh/kg PLA in.	≈ 1.5 kg CO_2 eq. /kg PLA in.	**Process simulation**	University of Rome	**Aryan 2021**
	PLA flakes → ***Lactic acid*** 1 kg → 1.25 kg Yield : 97 %	N.D.	0.55 kg CO_2 eq. /kg PLA in.	**Pilot-scale**	N.D.	**Maga 2019**
	PLA flakes → ***Lactic acid*** N.D. → N.D.	3.6 kWh/kg LA out.	N.D.	**Process simulation**	N.D.	**Piemonte 2013**
	PLA flakes → ***rPLA pellets*** 1 kg → 0.97 kg Yield : 97 %	3.1 kWh/kg PLA in.	≈ 0.9 kg CO_2 eq. /kg PLA in.	**Lab scale + Literature**	Martinez *et al.* (2011)	**Cosate de Andrade 2016**
	PLA flakes → ***Lactic acid*** 1 kg → 1.08 kg 92.6 %	1.1 kWh/kg LA out.	≈ 0.27 kg CO_2 eq. /kg PLA in.	**Pilot-scale**	NOOSA®	**Int. data Materia Nova**
Methanolysis	***PLA flakes*** → ***Methyl lactate*** 1 kg → 1.44 kg Yield : 100%	2.9 kWh/kg PLA in.	≈ 1.7 kg CO_2 eq. /kg PLA in.	**Process simulation**	Zeus Ind. Products Inc.	**Aryan 2021**
Ethanolysis	***PLA flakes*** → ***Ethyl lactate*** 1 kg → 1.33 kg Yield : 81 %	1.7 kWh/kg PLA in.	≈ 1.6 kg CO_2 eq. /kg PLA in.	**Process simulation**	Fraunhofer ICT	**Aryan 2021**

Table 8: mass, energy and climate change balances for PLA chemical recycling processes

2.3 Chemical recycling of PS

2.3.1 Technical aspects

As it is not a condensation polymer, PS is not suitable for chemolytic depolymerization. The chemical processes for PS recycling are therefore only based on controlled thermal degradation strategies.

PS degrades at a lower temperature (< 400 °C) than PE and PP (cf. next chapter). The behaviour of PS in pyrolysis is different than that of polyolefins, since depolymerization is possible and styrene can be obtained, whereas pyrolysis of PE or PP only yields a mixture of small molecules, called pyrolysis oil, that are not PE or PP monomers.

The mechanism of PS pyrolysis indeed mainly involves radical β-scission reactions at the chain ends, that leads to depolymerization and the obtention of styrene and dimers or trimers of styrene (**Guyot 1986, Goshayeshi 2023**). Consequently, by choosing appropriated conditions for the pyrolysis of PS (presence or not of a catalyst, nature of the catalyst, residence time…), it is possible to develop pyrolysis processes resulting in high yields of styrene.

Currently available industrial processes for PS depolymerization are presented in table 9 (**Maisels 2022, Ormonde 2022**).

Method	**Chemical reactions**	**Industrial processes** **Compagnies**
Thermal pyrolysis **or** **Catalytic pyrolysis**	high T, without O_2, (+ catalyst) PS → styrene	TruStyrenix™ Solution (Agilyx – US, Technip Energies – US) Plastics to chemical (P2C) (Indaver – BE) (Toshiba Plant System - JP) (Toyo Styrene - JP) (uses technology licenced by Agilyx)
Microwave induced pyrolysis	high T, without O_2, microwave PS → styrene	Pyrowave process (Pyrowave – CA)

Table 9: industrial routes for PS chemical recycling by depolymerization.

TruStyrenix™ Solution combines Agilyx's proprietary technology of pyrolysis, which produces Agilyx Styrene Oil (ASO), with Technip Energies's purification process (T.EN) which produces styrene monomer (99,8% purity) from ASO (**Faulkner 2023, Cavinaw 2019**).

Indaver's process is a pyrolysis occurring in two steps. PS waste is cracked in a first pyrolysis reactor. The gaseous product produced is separated in a first lighter fraction which contains styrene monomer and in a first heavier fraction which contains styrene oligomers. The heavier fraction is fed to a second pyrolysis reactor wherein the styrene oligomers are further cracked at a second temperature, at a second gas pressure which is higher than the first gas pressure in the first pyrolysis reactor. Such a two-step pyrolysis process enables to recover a higher amount of the low molecular weight liquid polystyrene pyrolysis products including styrene monomer and other low molecular weight liquid products such as alpha-methyl-styrene, cumene, ethyl benzene and toluene (**Alderweireldt 2021**).

Pyrowave employs industrial microwave reactors to depolymerize PS to form monomers. Their process uses a pyrolysis reactor and a proprietary catalyst loaded 0.5–50% w/w. Using the catalyst allows them to affect transformation of the PS to monomers at a lower temperature (350–500 °C) than in the Agilyx process. The Pyrowave process then employs two sequential condensers, facilitating efficient separation of target styrene monomer from other impurities. Yields for styrene monomer recovery can be up to 95% in purity needed for synthesis of virgin PS (**Thiounn 2020, Doucet 2018**).

PS can be also included in pyrolysis industrial processes resulting in hydrocarbon products other than styrene. In this case, styrene may not be the only polymer feeding in the process. It can be mixed with other types of plastics, such as PE and PP. Examples of companies concerned by this type of pyrolysis are: Plastic Energy (GB), Sapporo Plastics (JP)/ Klean Industries (US), Nippon Steel (JP), New Hope Energy (US), Resinergy (US), Showa Denko (JP), Adherent Technologies (US).

Though it was chosen to exclude such processes from the scope of this study, it seems worth mentioning that solvent-based purification processes for polymer recovery from PS waste, especially PS foam from construction waste, are rather developed (**Thiounn 2020, Côté 2016**).

2.3.2 Balances aspects

Industrial data about PS pyrolysis are very scarce and most of the literature is based on laboratory experiments. The process is however really close to the one of polyolefins pyrolysis (see next part) and the process diagram is supposed to be very similar to the one for polyolefins. Without a better choice, no representative process is selected for this case. The summary of balance data found about the chemical recycling process of PS is presented in the table 10. It was not possible to reproduce inventories for the processes and evaluate, even roughly, climate change impacts for PS depolymerization. The available information is therefore not sufficient to provide a global infographic for chemical recycling of PS.

Balances - Chemical recycling PS							
Recycling	**Mass balance (input → output)**		**Energy demand**	**Climate change impacts**	**Type of data**	**Source of data**	**Authors of study**
Pyrolysis back-to-monomer	***PS flakes***	***Styrene***	0.52 kWh /kg PS in.	N.D.	**Lab scale**	N.A.	Monteiro 2022
	1 kg	0.456 kg					
	PS flakes	***Styrene***	N.D.	N.D.	**Pilot-scale**	N.A.	Perez-Bravo 2022
	1 kg	0.76-0.86 kg					
	PS flakes	***Styrene***	N.D.	N.D.	**Pilot-scale**	N.A.	Zayoud 2022
	1 kg	0.36-0.56 kg					

Table 10: Balances for chemical recycling of PS

Even though very few information about environmental and energetic balances are available in the literature at large scale, pyrolysis of PS is promised to be a growing subject, with many publications at lab scale reporting growing conversion yields to styrene, reported to range from 65 to 95 % (**Perez-Bravo 2022**).

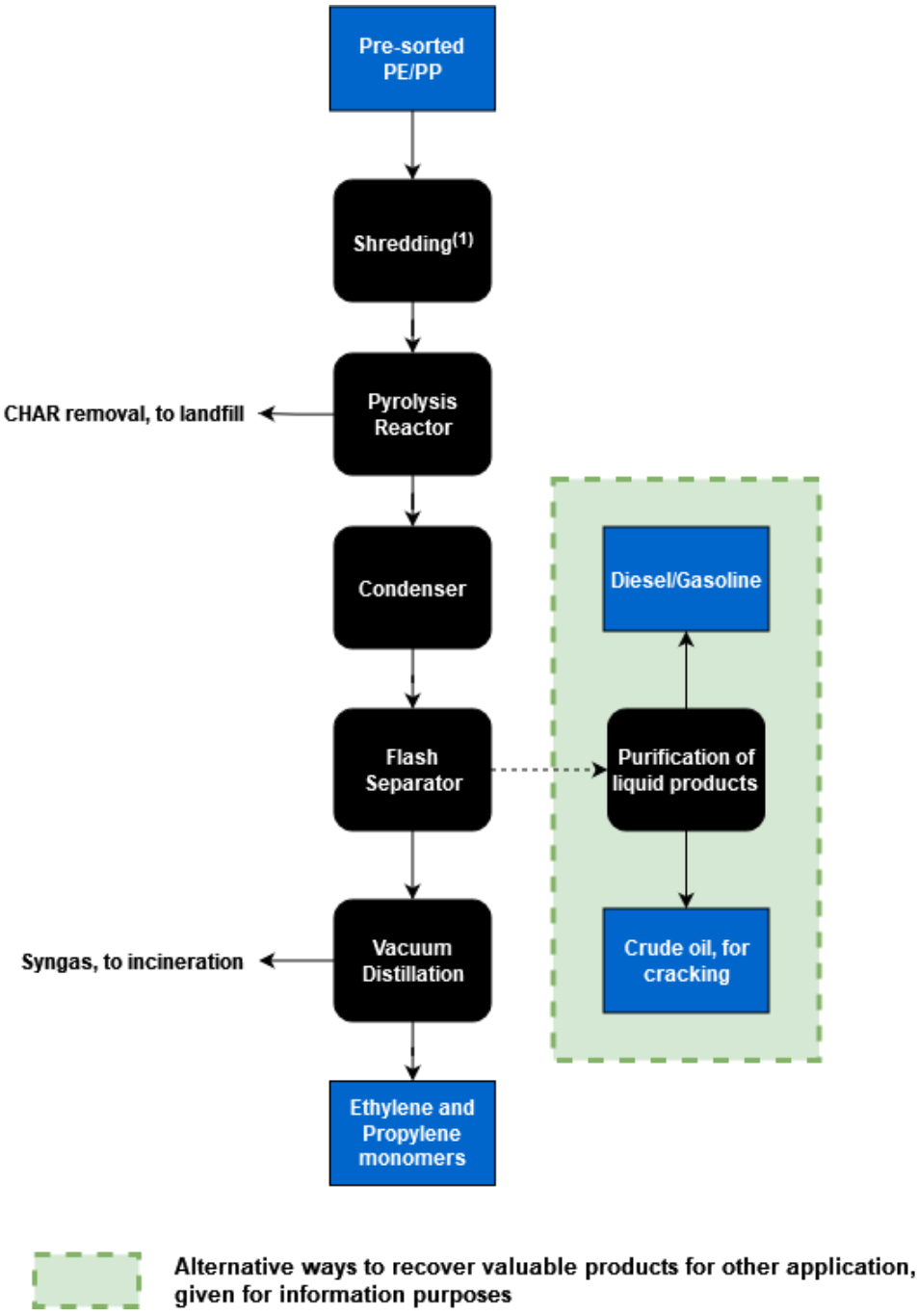
2.4 Chemical recycling of PE/PP

2.4.1 Technical aspects

At industrial scale, the major process to recycle polyolefins (PE, PP) is pyrolysis which can be noncatalytic or catalytic. Table 11 shows the different industrial processes dealing with pyrolysis of PE and PP. In addition to traditional pyrolysis, there are unconventional approaches such as pyrolysis under microwave and plasma assisted pyrolysis. There is also a process combining pyrolysis and gasification. Globally, pyrolysis treatment of polyolefin results in a mixture of small molecules, the so-called “pyrolysis oil”, that can be used as a basis through refining and cracking processes to produce chemicals (among which possibly monomers for polymerization) or fuels, and a gas fraction that can be converted into energy.

A typical flow chart for pyrolysis of polyolefins is proposed in figure 16 based on **Xayachak 2023**. This flow chart represents a case where monomers (ethylene / propylene) are the target products, and it illustrates the fact that this whole pyrolysis scenario is a multistep and multioutput process, with some fractions that can be valorised as chemicals, but also fractions that will only be used as energy carriers. Thermochemical recycling of plastics will indeed always include a part of “plastic-to-fuel” and cannot be 100% “plastic-to-plastic” scenarios.

Wastes recycled with pyrolysis processes presented in table 11 do not include only PE or PP or a mixture PE/PP. These processes can also be applied to a mixture PE/PP/PS and even to other types of plastic. This is indeed a characteristic of thermochemical plastic recycling processes, in comparison to chemical depolymerization or mechanical recycling processes, that they can be applied to waste streams with lower levels of purity - though the quality of the stream matters anyway for achieving good yields (**Hann 2020, Rizos 2023**). Specific characteristics of all these processes are given in the paragraphs after table 11.



(1) This step has been added to the flowchart for uniformity reasons

Figure 16 – Process diagram of PP/PE chemical recycling, based on ***Xayachak 2023***

Method	Chemical reactions	Industrial processes Compagnies
Pyrolysis or Catalytic pyrolysis	high T, without O_2, (catalyst) PE or/and PP → hydrocarbons	Plastics2Chemicals Indaver - BE TAC™ process Plastic Energy - GB Plastic2Oil® Technology Plastic2Oil, Inc – US ReOil® OMV – AT Sapporo Plastic Recycling Sapporo Plastics-JP/Klean Industries-US Hitachi Zosen Corporation – JP Chiyoda Corporation - JP Nissan / Mitsui Chemicals – JP Nippon Steel - JP Lummus New Hope New Hope Energy – US Adherent Technologies – US Encina Technologies – US GreenMantra Technologies - CA
Microwave induced catalytic pyrolysis	high T, without O_2, microwave PE or/and PP → hydrocarbons	CMAP™ system Resinergy - US
Plasma assisted Pyrolysis	high T, without O_2, plasma PE or/and PP → hydrocarbons	Ecogy® Fuenix Ecogy – NL
Pyrolysis + gasification	Very high T, without O_2 PE or/and PP → syngas	Ebara Ube Process Showa Denko – JP

Table 11: industrial routes for chemical recycling of PE and PP wastes by pyrolysis.

Pyrolysis oil produced from PE or PP is a complex mixture of hydrocarbons such as alkanes, alkenes, and aromatics. PE and PP-based plastic required higher temperatures for their complete degradation as compared to PS plastic due to their complex structures (**Gebre 2021**).

The TAC™ process (Thermal Anaerobic Conversion) patented by Plastic Energy is performed in two steps. Firstly, pellets or flakes of waste plastic are extruded at about 300 °C. Then, the molten waste is transferred into a pyrolysis chamber operating at 390-410 °C without catalyst. The products are diesel, kerosene and light oils which can be sold as fuels (**Thiounn 2020, McNamara 2011**).

The Plastic2Oil® Technology comprises a premelt of the waste at a temperature of 250-340 °C, a temperature at which some of the lower molecular weight impurities are burned off or volatilized as well. The premelted waste is then fed into a pyrolysis reactor held at 340–445 °C, with residence times as short as 10 min. The pyrolysis gases are then taken to catalyst towers. These catalyst towers feature different temperature/catalyst zones to facilitate sequential reaction of target gases at each stage. The overall process yields approximately 87% liquid fuel products with the balance consisting of unspecified residue and syngas. The entire process is typically performed at atmospheric pressure (**Thiounn 2020, Bordynuik 2015**).

Sapporo Plastic Recycling (SPR) claims recovering light oil that is used as a chemical feedstock for the production of new plastics, a medium fuel oil equivalent to diesel, and heavy oil that is used to generate electricity for export to the grid.

Encina Technologies's process is a catalytic pyrolysis. The firm intends to sign an agreement with Braskem to supply it its feedstock for the manufacture of PP.

GreenMantra Technologies's process utilizes catalysts to transform PE, PP, and PS into either liquid fuels or polymer additives for PE and PP (Ceranovus®). The plastic waste is pretreated by extrusion and then preheated and finally placed in the pyrolysis reactor in which it undergoes decomposition. This latest step can include catalysts such as zeolites or alumina-based catalysts (**Gil 2017**).

Resynergi's process uses microwave energy to induce a fast pyrolysis in which the plastic waste is heated to temperatures between 650 and 700 °C and broken down into liquid fuel. The pyrolysis chamber is under inert atmosphere of nitrogen or argon, with low pressures (0,07 – 0,13 bars). The chamber contains silicon carbides spheres and a screw-type reactor to ensure uniform heating during the pyrolysis process. The pyrolysis gases are then sent through a catalyst-filled cracking chamber to further decompose the plastic waste. The gases are then sent through subsequent condensers, which first condense heavy gases and waxes, then diesel gases and then lighter gases such as gasoline fuels (**Thiounn 2020, Bauer 2020**).

Unlike pyrolysis processes that are conducted under inert atmosphere, some treatment in the presence of oxygen are also developed at industrial scale. Those are listed in table 12; some of them are detailed hereafter.

Method	Chemical reactions	Industrial processes Compagnies
Heat decomposition	PE or/and PP → DKV fuel (diesel)	KDV process Alphakat – DE
Thermal decomposition under supercritical water	PE or/and PP → monomers	Kobe Steel, Ltd – JP
	PE or/and PP → hydrocarbons	HydroPRS™ Mura Technology – GB
Oxidation	PE → organic acids	ATOD BioCellection - US

Table 12: other industrial thermal treatments for PE or PP chemical recycling.

KDV process is a thermal treatment which occurs in two steps. Firstly waste, a catalyst of natural origin, and lime (for pH control) are mixed to a carrier oil. The mixture is heated to 180 °C. Then the oil mixture is subsequently sent to a turbine reactor which the temperature is raised to 250–320 °C. This process leads to a product corresponding to diesel fuel. Both the initial mixer and turbine reactor operate at pressures slightly beneath atmospheric pressure (**Ragaert 2017**).

The use of supercritical water makes efficient heating and fast dissolution of plastic. Moreover, it enhances decomposition due to a catalytic effect of the supercritical fluid. HydroPRS™ method, initially developed by Licella, involves initial grinding of waste feedstock to produce slurry with water and oil (paraffinic, crude, bio oil...), in some cases with catalysts. This slurry is then fed into a reactor at 250–350 °C under 7-24 bars for 10–25 min prior to cooling to 50–180 °C at atmospheric pressure. A liquid oil is obtained that can be used for various fuel applications. One of the main reasons for the addition of oil to the process is that the use of sub/super-critical water generally restricts the concentration of organic matter that can be put into the slurry. Additionally, water requires more energy per unit volume to heat and can lead to charring of the feedstock waste. The addition of oil mitigates these issues (**Thiounn 2020**).

To accomplish the oxidation, ATOD process (Accelerated Thermal Oxidative Decomposition) utilizes an oxidizing acid, such as HNO_3, to treat mixed PE waste at 60-200°C for 30 min – 30 hr. The resulting mixture is purified to yield the various organic acid compounds such as succinic, glutaric, adipic, pimelic, suberic, and azelaic acids (**Thiounn 2020, Yao 2019**).

As already explained for the case of PS, solvent-based purification processes were also developed at industrial scale but were not considered as chemical recycling scenarios for this report.

2.4.2 Balances aspects

The representative process of chemical recycling of polyolefins back to monomer has been chosen based on the data from **Xayachak 2023** (cf. process flow chart in figure 16) where coupled industrial and literature data about the pyrolysis process are provided. Chemical recycling of PE/PP is handled by pyrolysis, to produce various products depending on the downstream treatments of the outputs of the process. Pyrolysis to produce monomers, oil for further cracking, or fuels are all implemented at industrial scale, however, precise data about balances are relatively scarce at these scales, at a few notable exceptions.

Interesting data were also obtained from **Jeswani 2021** that presents the results of an LCA study commissioned by BASF about the recycling of mixed waste plastics by pyrolysis, with very detailed balance data (**BASF 2020**). However, this process was not chosen as the most "representative" one for this report because no information is given about the composition of the waste processed. Anyway, the balance data represent state-of-art installations operated by BASF, which can be considered as very representative of pyrolysis recycling of polyolefins. A detailed flowchart for this specific scenario is shown in figure 17.

The most relevant data about balances for the pyrolysis recycling of polyolefins are gathered in table 13.

Regarding climate change impacts of polyolefins pyrolysis, reported values are relatively close in most studies. For example, in addition to the values of table 13, **Dong 2019** reported an average value of 0.15 kg CO_2 eq./kg input PE, **Benavides 2017** a value of 0.31 kg CO_2 eq./kg input PE, **Faraca 2019** a value of 0.5 kg CO_2 eq./kg input PE, and **Bora 2020** a value of 0.61 kg CO_2 eq./kg input PP. However, due to the intrinsic capacity of pyrolysis to produce several recoverable by-products, important differences are reported between all studies, whether it concerns energy demand or climate change impacts, due to individual specific considerations of substitution and energy recovery, conducting the reliability of results to be questionable for comparison with the recycling of the other polymers.

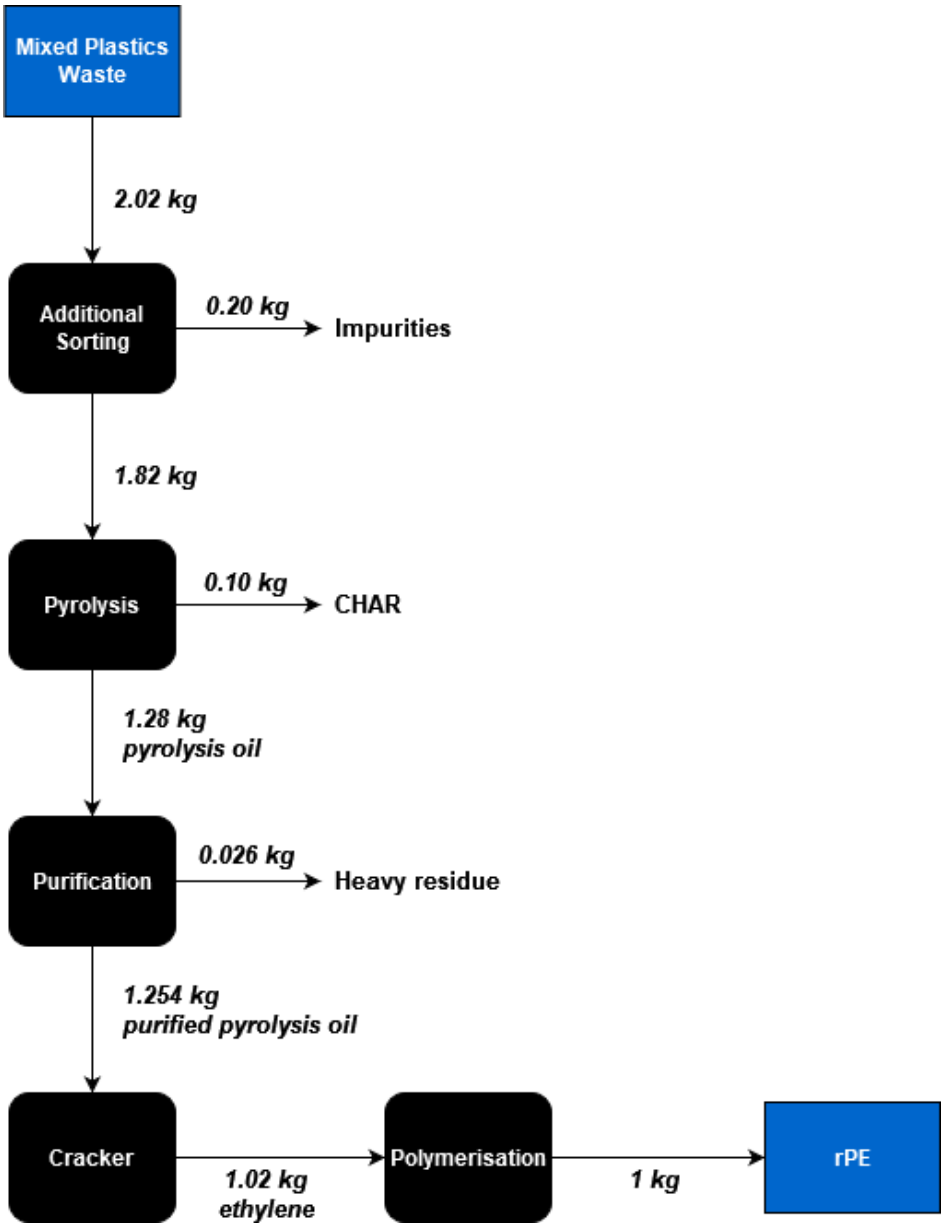


Figure 17 – Flowchart of mixed plastics chemical recycling, based on ***Jeswani 2021***

Balances - Chemical recycling PE-PP							
Recycling	**Mass balance (input → output)**		**Energy demand**	**Climate change impacts**	**Type of data**	**Source of data**	**Authors of study**
Pyrolysis back-to-monomer	***PE/PP mix*** 1 kg	***Ethylene*** 0.40 kg ***Propylene*** 0.43 kg Yield : 83 %	0.63 kWh/kg PO in.	N.D.	**Industrial + Literature**	Multiple	**Xayachak 2023**
	PE flakes 1 kg	***Ethylene*** 0.46 kg ***Propylene*** 0.17 kg	2.91 kWh/kg PE in.	0.56 kg CO_2 eq. /kg PE in.	**Process simulation**	N.D.	**Somoza-Tornos 2020**
	PO mix 1 kg	***Ethylene*** 0.505 kg	0.83 kWh/kg PO in.	N.D.	**Industrial**	BASF; Plastic Energy	**Jeswani 2021**
Pyrolysis to oil, for further cracking	**PE/PP mix** 1 kg	**Crude oil** 0.66 kg	0.63 kWh/kg PO in.	N.D.	**Industrial + Literature**	Multiple	**Xayachak 2023**
Pyrolysis to fuels	***PE flakes*** 1 kg	***Gasoline*** 0.34 kg ***Diesel*** 0.03 kg	1.71 kWh/kg PE in.	0.83 kg CO_2 eq. /kg PE in.	**Lab scale**	San Miguel *et al.* (2009)	**Iribarren 2012**
	PE/PP mix 1 kg	***Gasoline*** 0.05 kg ***Diesel*** 0.41 kg	0.63 kWh/kg PO in.	N.D.	**Industrial + Literature**	Multiple	**Xayachak 2023**

Table 13: Balances for pyrolyisis recycling of polyolefin

2.5 Compared balances of chemical recycling processes

The diversity and (in most cases) poor transparency of the data obtained from the literature make it impossible to even attempt to provide a global comparison for the chemical recycling processes for the plastics investigated in this report. However, a common feature of chemical recycling processes is that they are appear in most studies as less impacting, in terms of climate change, than incineration processes (**Rizos 2023**).
Results modelled from the available inventories and assumptions of the authors were found to be either inconsistent, unclear, or incomplete. The reader might find interesting to read the studies produced by **Meys 2020** and **Vollmer 2020**, which include comparisons of mechanical and chemical recycling of various polymers. However, the results from **Meys 2020** are mainly based on theoretical calculations, leading the results for chemical recycling to be very far from actual industrial values, while it is not clear where the data of **Vollmer 2020** come from. It is therefore not possible to provide for chemical recycling processes a comparison like those of figure 12 or table 1 proposed for mechanical recycling.

Next section explains in more details why such a comparison is considered mostly impossible.

3 Comparison between recycling processes for plastics

3.1 The impossibility of a comparison

It was seen in the previous chapters that the comparison between recycling processes, in terms of material, energy and environmental balances is difficult, even in the case of similar processes for different plastics or of almost similar processes for the same plastic. This is due to the variety of factors that make all studies hardly comparable:

- Not all studies refer to processes at a similar implementation level (e.g. lab-scale vs. industrial).
- Most studies are poorly transparent in terms of modelling assumptions.
- There are different functionalities assessed in the studies, some give data at the product level (e.g. energy used for 1 kg of recycled plastic obtained) others at the waste level (e.g. climate change impact for treating 1 kg waste).
- The system boundaries for studies may also differ, with studies starting from waste collection or from sorted bales, and others stopping either at small molecule (e.g. monomer) production or at recycled plastic pellets at factory gate.

It is therefore obvious that a meta-analysis of such disparate information can never lead to a ranking of processes, even when single aspects are considered. A simple example can illustrate this.

Let's assume two chemical recycling processes that can be operated at the same scale for converting 1) PLA waste into LA and 2) PE waste into ethylene.

Process 1 requires X kWh energy to obtain 1.2 kg LA from 1 kg PLA. Process 2 requires Y kWH energy to obtain 0.5 kg ethylene from 1 kg PE. These hypothetic yields are in good agreement with the ranges obtain in literature and shown in chapter 2.

If one wants to answer the question "which of these processes has the best energy balance", first question to be asked is if the two processes should be compared from a product perspective of from a waste perspective.

From a waste perspective (energy consumption per kg of treated waste), process 1 seems less energy consuming than process 2 if $X < Y$. But from a product perspective (energy consumption per kg of produced chemical), process 1 seems less energy consuming than process 2 if $X < 2.4\ Y$.

There is therefore obviously no simple answer to the question (at least when $Y < X < 2.4\ Y$). Even more, since the two processes have in fact nothing in common since they transform two different products A and B into two other different

products C and D, a comparison (and then the question) could only make sense in a context where A and B (or C and D) could substitute each other in a similar application.

Global reports about the state of the art of chemical recycling processes for plastics that are meant to provide insight for policies, such as **Hann 2020** or **Rizos 2023** mostly come to the same conclusion that no sound ranking could be made between recycling processes, and that the real issue would not be to recommend one type of recycling more than one other but to determine which type of recycling process and facilities should be favored to treat which type of waste (amount, nature, quality...). In fact, there should not be many instances where a real competition would exist between mechanical and chemical recycling, because thermomechanical recycling of waste into pellets would be more suited to treat single stream clean waste whereas chemical recycling processes of waste into chemicals could handle more contaminated waste streams (even if a minimum level of quality would also be required to enable recycling yields that would make the system economically viable).

3.2 The possibility of a comparison?

With a reduced scope, it can anyway be possible to compare recycling processes for plastic waste. Recent studies from TNO (Netherlands Organisation for Applied Scientific Research) try to achieve this, in order to evaluate the less impacting process for each type of plastic. In **Schwarz 2021**, a series of processes were evaluated with a LCA based-tool for different plastics. Figure 18 presents the results obtained (with a single-score perspective) for processes to treat PET waste and shows that all processes are preferable to incineration, even with energy recovery, but that the most two relevant processes for PET would be closed-loop mechanical recycling and depolymerization. The same was applied to other types of plastics, and results for the climate change indicator are also provided. The results of their evaluation appears to be very case specific, and the climate ranking of recycling processes is not the same for all types of plastics, though closed-loop mechanical recycling and (when possible) chemical depolymerization tend to be among the less impacting processes for almost all plastics.

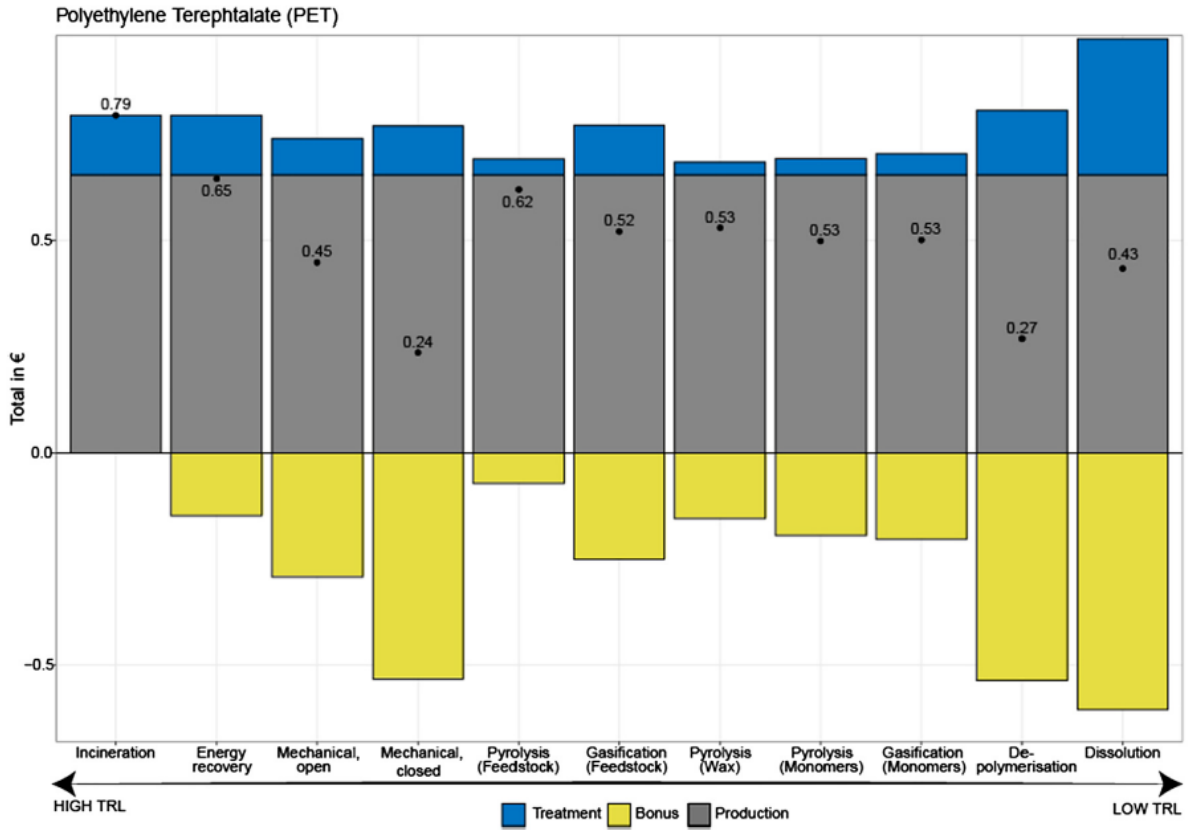


*Figure 18: Compared single score environmental impacts of PET waste treatment processes (from **Schwarz 2021**)*

Very recently, the same TNO team presented at LCM 2023 conference in September (**Schwarz 2023**) an updated version of this comparative study, that also includes a prospective evolution of the systems in a scenario that would contain climate effects to +1.5 °C. The conclusion of this prospective is that the relative ranking of waste treatment scenario could be affected by such changes of context. Indeed, climate change containment measures would include a significant growth of the share of renewable energies in the energy mixes, which means that the credits due to energy production avoidance in waste treatment processes with total or partial energy recovery (i.e., incineration and thermochemical recycling) will be lower because the substituted mix will have intrinsic lower impacts. This will obviously be in favor of chemical or thermomechanical recycling processes.

3.3 Comparison between the recycling processes

As it can be seen from the previous paragraphs, a comparison between different recycling processes for different types of plastic waste can only be attempted at a very qualitative level for a series of reasons. Table 14 below is an attempt to propose such a qualitative comparison, from a plastic-to-plastic perspective, based on the data and information collected throughout this work.

		Yield	Selectivity*	Quality**	Energy demand	Climate change footprint
Thermomechanical recycling	PET					
	PLA					
	PE/PP					
	PS					
Chemical recycling	PET					
	PLA					
Thermochemical recycling	PE/PP				***	***
	PS				***	***

**Selectivity = ability to treat low quality waste stream,*

***Quality of the plastic output,*

**** These processes are energy intensive, but their footprint is lowered by credits due to substitution of energy mix by energy recovery. As stated in 3.2 those credits are dependent on energy mix and a high renewable share would make those processes appear less interesting in terms of energy or climate balance.*

Table 14: Qualitative comparison of recycling processes of plastics

Only chemical (or thermochemical) processes can provide an output of a quality exactly similar to that of virgin material, and a degradation is unavoidable for thermomechanical recycling. Also, the ability of those processes to handle poor quality waste streams is slightly higher than that of mechanical recycling, even though the yields of the chemical processes can be lowered significantly with poor quality input.

In terms of yields, thermomechanical and chemical processes are preferable to thermochemical degradation processes. The impacts (climate and energy balances) are globally lower for mechanical processes than for (thermos)chemical processes. It has to be noticed that the balances for thermomechanical processes are affected by the credits due to energy recovery. Those processes appear therefore less impacting when operated in a context where the global energy mix has a high carbon footprint than in a context with a high share of renewable energy sources. Chemical recycling of PLA appears interesting from this comparison, with a potential for high yield and output quality with a moderate footprint.

Conclusion

A large variety of recycling processes for plastics exist, that have not all reached the same scale of implementation and TRL.

Three main types of processes can be found for plastic-to-plastic scenarios.

The first type is thermomechanical recycling. This process can concern all types of thermoplastics, and consists in melt processing sorted, cleaned and shredded waste streams into new plastic pellets that can be used by plastic transformation industry. Thermomechanical recycling implies in most cases some degradation of the material properties. However, since it preserves the polymeric nature of the initial material, this short-loop process has rather low impacts. A high quality of waste is required to obtain recycled pellets with a good quality, therefore waste collection and sorting operations are crucial to enable the viability of mechanical recycling.

The second type is chemical depolymerization. These processes convert the plastic waste into monomers that can be used by polymer chemistry industry to produce new polymers and plastics. This type of process is not suitable for all types of plastics; polyolefins for example can not be chemically depolymerized. In a plastic-to-plastic perspective, chemical depolymerization can be considered as a medium-loop process and may have low or medium impacts. A lower quality of the waste stream can be accepted than for mechanical recycling, however the contamination level should not be too high for the process to have yields high enough for enabling economic viability.

The third type is thermochemical degradation. Pyrolysis is the main type of thermochemical degradation for plastic waste. In pyrolysis, the plastic waste stream is converted into a mixture of small molecules. A fraction of this mixture can be transformed by chemical processes, possibly into monomers for a plastic-to-plastic strategy, and another fraction can only be valorised as energy. From a plastic-to-plastic perspective, thermochemical degradation is a long loop process, with some steps operated at high temperatures, and should therefore have higher impacts. All types of plastics can be treated by pyrolysis processes, including mixed waste streams of poor quality. However here again the quality of the stream will have consequences on the yields in molecules of interest and hence on the economic viability of the process.

Figure 19 summarizes the three types of recycling processes from a plastic-to-plastic perspective and illustrates the different sizes (number of steps) of the loops. It shows clearly that thermochemical degradation may be the least environmentally promising processes from a plastic-to-plastic perspective because they have the two drawbacks of poor yields and necessity of numerous subsequent process steps for reaching back plastics. On the other hand, the chemical depolymerization and thermomechanical recycling processes can give new plastics

with a lower amount of process steps and therefore have the potential for a better footprint.

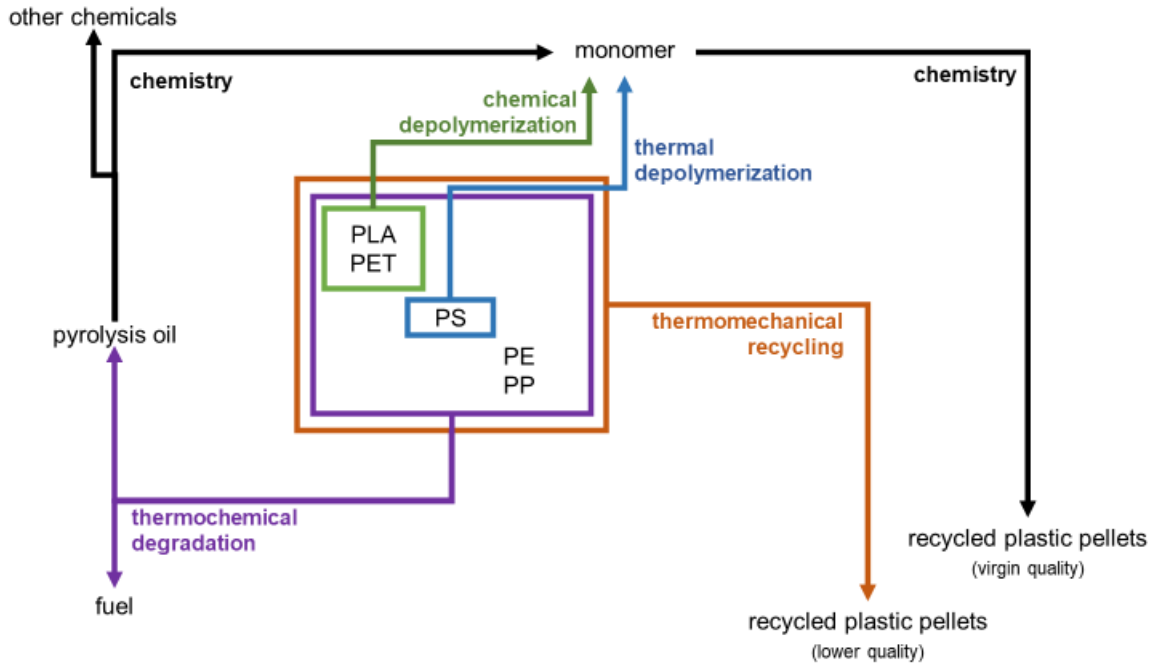


Figure 19: Plastic recycling technologies

LCA literature was searched for balance data about mechanical and chemical recycling of the targeted plastics. For each case, one representative process of current practices at the largest scale possible was selected and presented. When available, data from other sources were also presented for comparison purposes.

Due to its larger implementation and higher maturity level, data about mechanical recycling were easier to extract and were found to be globally more representative of industrial practices, while precise information at industrial scale of chemical recycling is scarce and scattered. According to the available data, the potential for a low footprint of chemical depolymerization processes may not have been reached yet, and process optimization may be necessary. In the current situation, it is anyway hardly possible to draw comparisons between the environmental relevance of each recycling path.

Though a global and quantitative comparison of all recycling processes for all plastics cannot be made, some general trends can be kept in mind.

- Recycling processes are almost always preferable to incineration with energy recovery, whatever the size of the recycling loop and the involved process steps. This will be more and more true in a context where the share of renewable energies in the consumption mixes will grow.
- Short-loop recycling strategies are likely to be more relevant from an environmental point of view than long-loop recycling strategies, those

short loop recycling strategies would include thermomechanical recycling but also chemical depolymerization processes.

- The best strategy for one type of plastic may not be the best strategy for one other type of plastic.

Disclaimer

One goal of this report was to provide simple and readable results in terms of balances. However, due to all factors already explained, the balance data supplied in this report (infographics, tables and histograms) must be interpreted with the greatest caution, especially those concerning chemical recycling.

- **Mass balances may hide additional undisclosed by-products and waste treatments.**
- **Energy balances are strongly sensitive to subjective assumptions of the authors about energy recovery scenarios and fuel usage.**
- **Climate change impacts and carbon balances here reported can be influenced by modelling assumptions and methodological choices from the authors of the studies (e.g., substitution considerations, energy recovery, allocation rules, system boundaries…), leading to poor comparability between studies.**

Though the general trends and the orders of magnitude of the results can be trusted with rather good confidence, it is thus strongly advised to check the sources of data presented in this report for any use of the absolute values reported.

References

Alderweireldt N., Kresovic U.
Indaver – 2021
Process for recovering styrene monomer from a styrene-containing polymer
Patent WO2021/180893A1.

Al-Itry R., Lamnawar K., Maazouz A.
Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy.
Polymer Degradation and Stability, 2012, 97, 1898-1914,
doi: 10.1016/j.polymdegradstab.2012.06.028.

Amorin N.; S., Rosa G., Alves J., Gonçalves S., Franchetti S., Fechine G.
Study of thermodegradation and thermostabilization of poly(lactide acid) using subsequent extrusion cycles.
Journal of Applied Polymer Science, 2014, 131,
doi: 10.1002/app.40023.

Antonopoulos I., Faraca G., Tonini D.,
Recycling of post-consumer plastic packaging waste in the EU: Recovery rates, material flows, and barriers,
Waste Management, Volume 126, 2021, Pages 694-705, ISSN 0956-053X,
https://doi.org/10.1016/j.wasman.2021.04.002

Aryan V., Daniel Maga, Pranav Majgaonkar, Ronny Hanich,
Valorisation of polylactic acid (PLA) waste: A comparative life cycle assessment of various solvent-based chemical recycling technologies,
Resources, Conservation and Recycling, Volume 172, 2021, 105670, ISSN 0921-3449,
https://doi.org/10.1016/j.resconrec.2021.105670.

Awaja F., Pavel D.
Recycling of PET.
European Polymer Journal, 2005, 41, 1453-1477,
doi: 10.1016/j.eurpolymj.2005.02.005.

Badia J.D., Strömberg E., Ribes-Greus A. Karlsson S.
Assessing the MALDI-TOF MS sample preparation procedure to analyze the influence of thermo-oxidative ageing and thermo-mechanical degradation on poly (Lactide).
European Polymer Journal, 2011, 47, 1416-1428,
doi: 10.1016/j.eurpolymj.2011.05.001.

Badia J.D., Ribes-Greus A.
Mechanical recycling of polylactide, upgrading trends and combination of valorization techniques.
European Polymer Journal, 2016, 84, 22-39,
doi: 10.1016/j.eurpolymj.2016.09.005.

Badia J. D., Gis Castel O., Teruel Juanes R., Ribes Greus A.
Recycling of Polylactide.
Encyclopedia of Renewable and Sustainable Materials, 2019, 282-295,
doi: 10.1016/B978-0-12-803581-8.10569-7.

Barboza E.S., Lopez D.R., Amico S.C., Ferreira C.A.,
Determination of a recyclability index for the PET glycolysis,
Resources, Conservation and Recycling, Volume 53, Issue 3, 2009, Pages 122-128, ISSN 0921-3449,
https://doi.org/10.1016/j.resconrec.2008.10.002.

Barnard E., Arias J. J. R., Thielemans W.
Chemolytic depolymerisation of PET: a review.
Green Chemistry, 2021, 23, 3765-3789,
doi: 10.1039/d1gc00887k.

BASF 2020.
Evaluation of pyrolysis with LCA - 3 case studies.
https://www.basf.com/global/en/who-we-are/sustainability/we-drive-sustainable-solutions/circular-economy/mass-balance-approach/chemcycling/lca-for-chemcycling/download-study.html

Bauer B., Tanne J., Spott T., Mayhew F., McInnis A.J., Leis M., Cardinal C., Greer T.
Resinergy – 2020
Microwave methods for converting hydrocarbon-based waste materials into oil and gas fuels.
Patent WO2020/006512A1

Benavides P.T., Pingping Sun, Jeongwoo Han, Jennifer B. Dunn, Michael Wang,
Life-cycle analysis of fuels from post-use non-recycled plastics,
Fuel, Volume 203, 2017, Pages 11-22, ISSN 0016-2361,
https://doi.org/10.1016/j.fuel.2017.04.070.

Botelho G., Queiros A., Liberal S., Gijsman P.
Studies on thermal and thermo-oxidative degradation of poly(ethylene terephthalate) and poly(butylene terephthalate).
Polymer Degradation and Stability, 2001, 74, 39-48,
doi: 10.1016/S0141-3910(01)00088-X.

Bordynuik J.W.
Plastic2Oil – 2015
System and process for converting plastics to petroleum products.
Patent US2015/001061A1.

Capone C., Di Landro L., Inzoli F., Penco M., Sartore L.
Thermal and mechanical degradation during polymer extrusion processing.
Polymer Engineering and Science, 2007, 47, 1813-1819,
doi: 10.1002/pen.20882.

Castro-Aguirre E., Iniguez Franco F., Samsudin H., Fang X., Auras R.
Poly(lactic acid)—Mass production, processing, industrial applications, and end of life.
Advanced Drug Delivery Reviews, 2016, 107, 333-366,
doi: 10.1016/j.addr.2016.03.010.

Cavinaw B., Crawford S., Lamaze S., Allen D., Christenson E., Rumford M.
Agylix Corporation.
Systems and methods for recycling waste plastics, including waste polystyrene
Patent US10301235B1, 2019.

Civancik-Uslu D., T.T. Nhu, Bart Van Gorp, Uros Kresovic, Macarena Larrain, Pieter Billen, Kim Ragaert, Steven De Meester, Jo Dewulf, Sophie Huysveld,
Moving from linear to circular household plastic packaging in Belgium: Prospective life cycle assessment of mechanical and thermochemical recycling,
Resources, Conservation and Recycling, Volume 171, 2021, 105633, ISSN 0921-3449,
https://doi.org/10.1016/j.resconrec.2021.105633.

Colin X., Verdu J.
Polymer degradation during processing.
Comptes Rendus Chimie, 2006, 9, 1380-1395,
doi: 10.1016/j.crci.2006.06.004.

Cornago S., Davide Rovelli, Carlo Brondi, Maurizio Crippa, Barbara Morico, Andrea Ballarino, Giovanni Dotelli,
Stochastic consequential Life Cycle Assessment of technology substitution in the case of a novel PET chemical recycling technology,
Journal of Cleaner Production, Volume 311, 2021, 127406, ISSN 0959-6526,
https://doi.org/10.1016/j.jclepro.2021.127406.

Cosate de Andrade, M.F., Souza, P.M.S., Cavalett, O. *et al.*
Life Cycle Assessment of Poly(Lactic Acid) (PLA): Comparison Between Chemical Recycling, Mechanical Recycling and Composting.
J Polym Environ **24**, 372–384 (2016).
https://doi.org/10.1007/s10924-016-0787-2

Côté R.
POLYSTYVERT – 2016
Processes for recycling polystyrene waste
Patent WO2016/049782A1

De Bie F., Ravard M., La Scola P., Veras R.
Planting the future of PLA - 2023
https://www.totalenergies-corbion.com/media/3vijlw5w/totalenergies-corbion-biobased-pla-whitepaper.pdf

Dong J., Yuanjun Tang, Ange Nzihou, Yong Chi,
Key factors influencing the environmental performance of pyrolysis, gasification and incineration Waste-to-Energy technologies,
Energy Conversion and Management, Volume 196, 2019, Pages 497-512, ISSN 0196-8904,
https://doi.org/10.1016/j.enconman.2019.06.016.

Dordinejad A. K., Sharif F., Ebrahimi M., Rashedi R.
Rheological and thermorheological assessment of polyethylene in multiple extrusion process.
Thermochimica Acta, 2018, 668, 19-27,
doi: 10.1016/j.tca.2018.08.010.

Doucet J., Laviolette J.P.
Pyrowave – 2018
Catalytic microwave depolymerisation of plastic for production of monomer and waxes.
Patent WO2018/018153A1

Faraca G., Veronica Martinez-Sanchez, Thomas F. Astrup,
Environmental life cycle cost assessment: Recycling of hard plastic waste collected at Danish recycling centres,
Resources, Conservation and Recycling, Volume 143, 2019, Pages 299-309, ISSN 0921-3449,
https://doi.org/10.1016/j.resconrec.2019.01.014.

Faulkner C., Vallieres P.
Production of circular styrene monomer.
Technip Energies brochure - 2023
https://www.technipenergies.com/sites/energies/files/2023-05/Brochure_TruStyrenyx.pdf

Federal Department of Foreign Affairs (Switzerland)
Switzerland leads the way in PET recycling
Article published online 26/01/2022
https://houseofswitzerland.org/swissstories/environment/switzerland-leads-way-pet-recycling

Franklin Associates, A Division of Eastern Research Group (ERG) (2018)
Life Cycle Impacts for postconsumer recycled resins : PET, HDPE, and PP

Gebre S. H., Sendeku M. G., Bahri M.
Recent Trends in the Pyrolysis of Non-Degradable Waste Plastics.
ChemistryOpen, 2021, 10, 1202-1226.
http://doi.org/10.1002/open.202100184

Gil A., Dimondo D., Rybicki R.
GreenMantra Recycling Technologies – 2017
Reactor For Continuously Treating Polymeric Material
Patent US2017/327663A1

Gileno L.A., Luiz Felipe Ramos Turci,
Life cycle assessment for PET-bottle recycling in Brazil: B2B and B2F routes,
Cleaner Environmental Systems, Volume 3, 2021, 100057, ISSN 2666-7894,
https://doi.org/10.1016/j.cesys.2021.100057.

Gomez Urgoiti M., Van Gansberghe F.
NOOSA - 2021
Method for recycling textile containing polylactic acid.
Patent WO2021-148549A1.

Gonçalves L. M. G., Rigolin T. R., Frenhe B. M., Bettini S. H. P.
On the Recycling of a Biodegradable Polymer Multiple Extrusion of Poly(Lactic Acid).
Materials Research, 2020, 23,
doi: 10.1590/1980-5373-MR-2020-0274.

Goshayeshi B., Abbas-Abadi M. S., Kusenberg M., Lemonidou A., Van Geem K. M.
Prospects of physical, mechanical, and advanced recycling of end-of-life polystyrenes: Towards full recyclability.
Current Opinion in Green and Sustainable Chemistry, 2023, 42, 100821,
doi : 10.1016/j.cogsc.2023.100821.

Grewell, D, Srinivasan, G, Cochran, E., 2014.
Depolymerization of post-consumer polylactic acid products.
J. Renewable Mater. 2 (3), 157–165.
DOI: 10.7569/JRM.2014.634112

Gupta M. C., Deshmukh V. G.
Thermal oxidative degradation of poly-lactic acid - Part II: Molecular weight and electronic spectra during isothermal heating.
Colloid and Polymer Science, 1982, 260, 514-517,
doi: 10.1007/BF01452999.
Guyot A.
Recent developments in the thermal degradation of polystyrene—A review.
Polymer Degradation and Stability, 1986, 15, 219-235,
doi: 10.1016/0141-3910(86)90052-2.

Hann S., Toby Connock.
Chemical recycling: State of play.
Report for CHEM Trust, 2020
https://www.eunomia.co.uk/reports-tools/final-report-chemical-recycling-state-of-play/

Hinsken H., Moss S., Pauquet J. R., Zweifel H.
Degradation of polyolefins during melt processing.
Polymer Degradation and Stability, 1991, 34, 279-293,
doi: 10.1016/0141-3910(91)90123-9.

Iribarren, D., Dufour, J. & Serrano, D.P.
Preliminary assessment of plastic waste valorization via sequential pyrolysis and catalytic reforming.
J Mater Cycles Waste Manag **14**, 301–307 (2012).
https://doi.org/10.1007/s10163-012-0069-6

Jang J. Y., Sadeghi K., Seo J.
Chain Extending Modification for Value Added Recycled PET: A Review.
Polymer Reviews, 2022, 62, 860-889,
doi: 10.1080/15583724.2022.2033765.

Jeswani H., Christian Krüger, Manfred Russ, Maike Horlacher, Florian Antony, Simon Hann, Adisa Azapagic,
Life cycle environmental impacts of chemical recycling via pyrolysis of mixed plastic waste in comparison with mechanical recycling and energy recovery,
Science of The Total Environment, Volume 769, 2021, 144483, ISSN 0048-9697,
https://doi.org/10.1016/j.scitotenv.2020.144483.

Kägi T., Mischa Zschokke, Cornelia Stettler, Carbotech AG (2017)
Life Cycle Inventories for Swiss Recycling Processes – Part Carbotech: Recycling of Carboard, Glass, PE, PET, Tinplate
https://carbotech.ch/cms/wp-content/uploads/Technical_Report_V1.0-2.pdf

Kamleitner F., Duscher B., Koch T., Knaus S., Archodoulaki M.

Upcycling of polypropylene—the influence of polyethylene impurities.
Polymer Engineering and Science, 2017, 57, 12, 1374-1381,
doi: 10.1002/pen.24522.

Klimke K., Braun H.
BOREALIS AG.
High melt strength polypropylene of improved quality.
Patent EP2679630A1, 2014.

Kopinke F. D., Remmier M., Mackenzie K., Moder M., Wachsen O.
Thermal decomposition of biodegradable polyesters–II. Poly(lactic acid).
Polymer Degradation and Stability, 1996, 53, 329-342,
doi: 10.1016/0141-3910(96)00102-4.

La Mantia F. P., Vinci M.
Recycling poly(ethyleneterephthalate).
Polymer Degradation and Stability, 1994, 45, 121-125,
doi: 10.1016/0141-3910(94)90187-2.

Lecomte H. A., Liggat J. J.
Degradation mechanism of diethylene glycol units in a terephthalate polymer.
Polymer Degradation and Stability, 2006, 91, 681-689,
doi: 10.1016/j.polymdegradstab.2005.05.028.

Ma Y., Agarwal U. S., Sikkema D. J., Lemstra P. J.
Solid-state polymerization of PET influence of nitrogen sweep and high vacuum,
Polymer, 2003, 44, 4085-4096,
doi: 10.1016/S0032-3861(03)00408-7.

Maga D., Markus Hiebel, Nils Thonemann,
Life cycle assessment of recycling options for polylactic acid,
Resources, Conservation and Recycling, Volume 149, 2019, Pages 86-96, ISSN 0921-3449,
https://doi.org/10.1016/j.resconrec.2019.05.018.

Maisels A., Hiller A., Simon F.-G.
Chemical Recycling for Plastic Waste: Status and Perspectives.
ChemBioEng Reviews, 2022, 9, 541-555,
doi: 10.1002/cben.202200024.

Martín-Lara M.A., J.A. Moreno, G. Garcia-Garcia, S. Arjandas, M. Calero,
Life cycle assessment of mechanical recycling of post-consumer polyethylene flexible films based on a real case in Spain,
Journal of Cleaner Production, Volume 365, 2022, 132625, ISSN 0959-6526,

https://doi.org/10.1016/j.jclepro.2022.132625.

McNamara D., Murray M.
CYNAR PLASTIC RECYCLING LIMITED – 2011
Conversion of waste plastics material to fuel.
Patent WO2011/077419A1.

McNeill I. C., Leiper H. A.
Degradation studies of some polyesters and polycarbonates 2. Polylactide: Degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer.
Polymer Degradation and Stability, 1985, 11, 309-326,
doi: 10.1016/0141-3910(85)90035-7.

McNeill I. C., Razumovskii L. P., Goldberg V. M., Zaikov G. E.
The thermo-oxidative degradation of polystyrene.
Polymer Degradation and Stability, 1994, 45, 47-55,
doi: 10.1016/0141-3910(94)90177-5.

Meys R., Felicitas Frick, Stefan Westhues, André Sternberg, Jürgen Klankermayer, André Bardow,
Towards a circular economy for plastic packaging wastes – the environmental potential of chemical recycling,
Resources, Conservation and Recycling, Volume 162, 2020, 105010, ISSN 0921-3449,
https://doi.org/10.1016/j.resconrec.2020.105010.

Montaudo G., Puglisi C., Samperi F.
Primary thermal degradation mechanisms of PET and PBT.
Polymer Degradation and Stability, 1993, 42, 13-28,
doi: 10.1016/0141-3910(93)90021-A.

Monteiro, A. da R. D., de Miranda, D. M. V., da Silva Pinto, J. C. C., Soto, J. J.,
Life Cycle Assessment of the Catalytic Pyrolysis of High-Density Polyethylene (HDPE) and High-Impact Polystyrene (HIPS).
Macromol. React. Eng. 2022, 16, 2200037.
https://doi.org/10.1002/mren.202200037

Nakatani, J., Fujii, M., Moriguchi, Y. *et al.*
Life-cycle assessment of domestic and transboundary recycling of post-consumer PET bottles.
Int J Life Cycle Assess **15**, 590–597 (2010).
https://doi.org/10.1007/s11367-010-0189-y

Nessi, S., Sinkko, T., Bulgheroni, C., Garbarino, E., Garcia-Gutierrez, P., Giuntoli, J., Konti, A., Orveillon, G., Sanye Mengual, E., Tonini, D., Pant, R., Marelli, L. and Ardente, F.,
Life Cycle Assessment (LCA) of alternative feedstocks for plastics production,
EUR 31085 EN, Publications Office of the European Union, Luxembourg, 2022, ISBN 978-92-76-52959-0,
doi:10.2760/234548, JRC127175.

Niaounakis M.
Recycling of biopolymers – The patent perspective.
European Polymer Journal, 2019, 114, 464-475,
doi: 10.1016/j.eurpolymj.2019.02.027.

Ormonde E., DeGuzman M., Yoneyama M., Lio S., Loechner U., Zhu X.
Plastics Recycling, Novembre 2022.

Parravicini M., Crippa M, Bertele M. V.,
Method and apparatus for the recycling of polymeric materials via depolymerization process.
Patent WO 2013/014650A1, 2013.

Patagonia (2005)
Patagonia's Common Threads Garment Recycling Program: A detailed analysis; 2005.

Pérez-Bravo,G.; Contreras-Larios, J.L.; Rodríguez, J.F.; Zeifert-Soares, B.; Angeles-Beltrán, D.; López-Medina, R.; Vázquez-Rodríguez, T.; Salmones-Blasquez, J.
Catalytic Pyrolysis Process to Produce Styrene from Waste Expanded Polystyrene Using a Semi-Batch Rotary Reactor.
Sustainability **2022**, 14, 14914.
https://doi.org/10.3390/su142214914

Piemonte, V., Sabatini, S. & Gironi, F.
Chemical Recycling of PLA: A Great Opportunity Towards the Sustainable Development?.
J Polym Environ **21**, 640–647 (2013).
https://doi.org/10.1007/s10924-013-0608-9

Pressley P.N., James W. Levis, Anders Damgaard, Morton A. Barlaz, Joseph F. DeCarolis,
Analysis of material recovery facilities for use in life-cycle assessment,
Waste Management, Volume 35, 2015, Pages 307-317, ISSN 0956-053X,

https://doi.org/10.1016/j.wasman.2014.09.012.

Ragaert K., Delva L., Van Geem K.
Mechanical and chemical recycling of solid plastic waste.
Waste management, 2017, 69, 24-58.
http://dx.doi.org/10.1016/j.wasman.2017.07.044

Remili C., Kaci M., Benhamida A., Bruzaud S., Grohen Y.
The effects of reprocessing cycles on the structure and properties of polystyrene/Cloisite15A nanocomposites.
Polymer Degradation and Stability, 2011, 96, 1489-1496,
doi: 10.1016/j.polymdegradstab.2011.05.005.

Rizos V., Patricia Urban, Edoardo Righetti, Amin Kassab,
Chemical recycling of plastics – Technologies, trends and policy implications,
CEPS In-Depth Analysis, 2023
https://www.ceps.eu/ceps-publications/chemical-recycling-of-plastics/

Romao W., Franco M.F., Corilo Y.E., Eberlin M.N., Spinacé M.A.S., De Paoli M.A.
Poly (ethylene terephthalate) thermo-mechanical and thermo-oxidative degradation mechanisms.
Polymer Degradation and Stability, 2009, 94, 1849-1859,
doi: 10.1016/j.polymdegradstab.2009.05.017.

Ronald Whitlock L., Porter R. S.
The source of degradation during extrusion of polystyrene.
Journal of Applied Polymer Science, 1973, 17, 2761-2770,
doi: 10.1002/app.1973.070170913.

Samperi F., Puglisi C., Alicata R., Montaudo G.
Thermal degradation of poly(ethylene terephthalate) at the processing temperature.
Polymer Degradation and Stability, 2004, 83, 3-10,
doi: 10.1016/S0141-3910(03)00166-6.

Scheirs J.
Overview of Commercial Pyrolysis Processes for Waste Plastics.
in Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels (Ed: J. Scheirs, W. Kaminsky), John Wiley & Sons Ltd., Chichester 2006, 383–434.

Schwarz A., T. Ligthart, D. Godoi Bizarro, P. De Wild, B. Vreugdenhill, Toon van Harmelen,
Plastic recycling in a circular economy; determining environmental performance through an LCA matrix model approach
Waste Management 121 (2021) 331–342,

https://doi.org/10.1016/j.wasman.2020.12.020

Schwarz A., Toon van Harmelen, Sietske Lensen, Sjoerd Herlaar, Paul Schouten, Paul Stegman,
Towards a circular economy for plastics through a modelling approach and transition LCA: PRISM (plastic recycling and impact scenario model),
The 11th International Conference On Life Cycle Management, Lille, 2023,

Shen L., Ernst Worrell, Martin K. Patel,
Open-loop recycling: A LCA case study of PET bottle-to-fibre recycling,
Resources, Conservation and Recycling, Volume 55, Issue 1, 2010, Pages 34-52, ISSN 0921-3449,
https://doi.org/10.1016/j.resconrec.2010.06.014.

Silva Spinacé M. A., De Paoli M. A.
Characterization of poly(ethylene terephtalate) after multiple processing cycles. *Journal of Applied Polymer Science, 2001, 80, 20-25,*
doi: 10.1002/1097-4628(20010404)80:1<20::AID-APP1069>3.0.CO;2-S.

Somoza-Tornos A., Andres Gonzalez-Garay, Carlos Pozo, Moisès Graells, Antonio Espuña, and Gonzalo Guillén-Gosálbez
Realizing the Potential High Benefits of Circular Economy in the Chemical Industry: Ethylene Monomer Recovery via Polyethylene Pyrolysis
ACS Sustainable Chemistry & Engineering **2020** *8* (9), 3561-3572
DOI: 10.1021/acssuschemeng.9b04835

Sun C., Wei S., Tan H., Huang Y., Zhang Y.
Progress in upcycling polylactic acid waste as an alternative carbon source: A review.
Chemical Engineering Journal, 2022, 446, 136881,
doi: 10.1016/j.cej.2022.136881

Thiounn T., Smith R., C.
Advances and approaches for chemical recycling of plastic waste.
Journal of Polymer Science, 2020, 58, 1347,-1364,
doi: 10.1002/pol.20190261.

Tonini, D., Garcia-Gutierrez, P., and Nessi, S., (2021)
Environmental effects of plastic waste recycling,
EUR 30668 EN, Publications Office of the European Union, Luxembourg, 2021, ISBN 978-92-76-41130-7,
doi:10.2760/6309, JRC122455.

Tournier V., Topham C. M., Gilles A., David B., Folgoas C., Moya-Leclair E., Kamionka E., Desrousseaux M.-L., Texier H., Gavalda S., Cot M., Guémard E., Dalibey M., Nomme J., Cioci G., Barbe S., Chateau M., André I., Duquesne S., Marty A.
An engineered PET depolymerase to break down and recycle plastic bottles.
Nature, 2020, 580, 216-233,
doi: 10.1038/s41586-020-2149-4.

Uekert T., J. S. DesVeaux, A. Singh, S. R. Nicholson, P. Lamers, T. Ghosh, J. E. McGeehan, A. C. Carpenter and G. T. Beckham,
Life cycle assessment of enzymatic poly(ethyleneterephthalate) recycling
Green Chem., 2022, 24, 6531–6543.
DOI: 10.1039/d2gc02162e

Vollmer I., M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes, B. M. Weckhuysen,
Beyond Mechanical Recycling: Giving New Life to Plastic Waste
Angew. Chem. Int. Ed. 2020, *59*, 15402.
doi.org/10.1002/anie.201915651

Welle F.
Twenty years of PET bottle to bottle recycling—An overview.
Resources Conservation and Recycling, 2011, 55, 865-875,
doi: 10.1016/j.resconrec.2011.04.009.

Wendelin G., Hackl M., Feichtinger K,
EREMA Engineering Recycling Maschinen und Anlagen Gesellschaft m.b.H.
Method for the pretreatment, reprocessing or recycling of thermoplastic material.
Patent WO2008058303 A1, 2008.

Xayachak Tu, Nawshad Haque, Deborah Lau, Raj Parthasarathy, Biplob Kumar Pramanik,
Assessing the environmental footprint of plastic pyrolysis and gasification: A life cycle inventory study,
Process Safety and Environmental Protection, Volume 173, 2023, Pages 592-603, ISSN 0957-5820,
https://doi.org/10.1016/j.psep.2023.03.061.

Xiao M., Xu Y., Peng T.,
SHANGHAI NEW SHANGHUA POLYMER.
Recrystallization method of polylactic acid and polylactic acid acquired thereby.
Patent CN101230129 A, 2008.

Yao J.Y., Wang Y.W., Muppaneni T., Shrestha R., Le Roy J., Figuli G.D., Freer E.
BIOCELLECTION – 2019
Methods for the decomposition of contaminated plastic waste
Patent WO2019/204687A1

Zayoud Azd, Hang Dao Thi, Marvin Kusenberg, Andreas Eschenbacher, Uros Kresovic, Nick Alderweireldt, Marko Djokic, Kevin M. Van Geem,
Pyrolysis of end-of-life polystyrene in a pilot-scale reactor: Maximizing styrene production,
Waste Management, Volume 139, 2022, Pages 85-95, ISSN 0956-053X,
https://doi.org/10.1016/j.wasman.2021.12.018.


MATERIA
NOVA
Materials
R&D Center