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Technical and environmental performances of alternative treatments for challenging plastics waste

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ABSTRACT

The recovery of resources from streams of mixed plastics waste is a technological and economic challenge since they contain various (and generally non-compatible) polymers, different (and often hazardous) additives, as well as multilayer structures and fiber-reinforced composites. Only a too limited part of these plastics - such as those coming from waste of electric and electronic equipment (WEEE), end-of-life vehicles (ELV) and construction and demolition waste (C&DW) - can be treated by mechanical techniques in the conventional recycling facilities, and a still smaller part is reintroduced into the market. Some innovative treatments have been recently proposed and appear suitable for these challenging waste streams. The paper describes technical characteristics of some of them, and compares their environmental performances with those of currently adopted management options. An environmental life cycle assessment was developed by taking into account the substitutability factor of obtained products and technological readiness level of the analyzed resource recovery processes. The focus is on new treatments of dissolution/precipitation, supercritical fluid extraction, catalytic pyrolysis, and waste-to-energy (WtE) equipped with carbon capture and storage unit (CCS). The results highlight the promising performances of some of these new options, quantify their potential environmental advantages, and suggest to take them into account in the definition of sustainable management schemes for the examined challenging plastics wastes. In particular, physical recycling by dissolution/precipitation process applied to one tonne of WEEE plastics, not treatable by mechanical recycling, can save up to about 2 $t_{CO2,eq.}$ with respect to landfill disposal and WtE with CCS, and more than 3 $t_{CO2,eq.}$ with respect to WtE without CCS. The performances of WtE with CCS appear of interest, particularly for WEEE and ELV mixed plastics, allowing to save up to 0.5 $t_{CO2,eq.}$ and 1.7 $t_{CO2,eq.}$, with respect to pyrolysis and WtE without CCS, respectively.

1. Introduction

The annual generation of some important streams of plastics waste, such as those coming from WEEE (waste of electronic and electric equipment), ELV (end-of-life vehicles) and C&DW (construction and demolition waste), is continuously increasing. Recent studies estimate that, only in Europe, the officially collected annual amounts are about 0.7 Mt/y, 1 Mt/y, and 1.7 Mt/y for plastics coming from WEEE, ELV and C&DW, respectively (Ardolino et al., 2021; Cardamone et al., 2022; CPA-EC, 2020a, b, c). Only a small part of them is sent to resource recovery facilities (13.5% for WEEE plastics and 2.6% for ELV plastics), while there is a too large recourse to waste exportation (up to 75% of collected WEEE plastics), which often implies improper management procedures in not-specialized treatment facilities, with severe risks for human health and environment (Forti et al., 2020; Cardamone et al., 2021; 2022). The poor sustainability of the management of these "challenging" plastics waste streams is due to technological difficulties and high costs of their mechanical recycling treatment. The latter is

Abbreviations: ABS, Acrylonitrile–Butadiene–Styrene; BAT-AEPLs, Best Available Technique - Associated Environmental Performance Levels; BFR, Brominated Flame Retardant; CCS, Carbon Capture and Storage; CCUS, Carbon Capture and Utilization or Storage; C&DW, Construction and Demolition Waste; D.A.F., Dry Ash Free; DecaBDE, Decabromodiphenyl ether; ELV, End-of-Life Vehicles; ELVP, Plastics fraction from ELV; EPS, Expanded PolyStyrene; HIPS, High Impact Polystyrene; LHV, Low Heating Value; PC, Polycarbonate; PC+ABS, Blends of Polycarbonate and Acrylonitrile–Butadiene–Styrene; PMMA, Poly(methyl methacrylate); SFE, Supercritical Fluid Extraction; TBBPA, Tetrabromobisphenol A; TBPE, 1,2-bistribromophenoxyethane; TRL, Technological Readiness Level; VOC, Volatile Organic Compounds; WEEE, Waste of Electrical and Electronic Equipment; WEEP, Plastics fraction from WEEE; WtE, Waste-to-Energy.

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particularly suitable for simple polymers, as polyolefins and low brominated styrenics (Beigbeder et al., 2013), but it shows important limitations for mixed plastics waste. In particular, it is not able to treat multilayer packaging, fiber-reinforced composites, and complex plastic mixtures (Ragaert et al., 2017). It cannot be used for plastics with hazardous additives, such ABS and PS with brominated flame retardants (BFR) from WEEE, PE and PP with additives and non-plastic fractions from ELV, and PVC rich of plasticizers and stabilizers from C&DW (Wagner and Schlummer, 2020). Moreover, mechanically recycled polymers can build-up non-polymeric residues, mainly pigments and additives necessary to comply with safety standards or to provide resistance to microbial degradation or ultra-violet stability. This implies that a part of recycled materials is obtained from mixed plastics rich of additives and contaminants that, if not efficiently removed, generate risks for the environment as well as for the health of waste operators and users of recycled products (Lahl and Zeschmar-Lahl, 2012; Ionas et al., 2014; Fellner and Brunner, 2021). Finally, mechanical recycling produces downgrading of polymer quality after one or multiple rounds of recycling, eventually reaching the point where the resin cannot be mechanically recycled again (Schyns and Shave, 2021). This means that plastics waste can be recycled only a limited number of times and often the final outcome should be more properly defined as a "down-cycled" material, with a weak possibility to access the market.

In a life cycle perspective, these considerations indicate that (direct) environmental burdens related to the mechanical recycling chain can become greater than those saved by the generation of new products (avoided burdens). The substitutability factor, defined as the functionality provided by the recovered resource compared to that of the conventional one (Vadenbo et al., 2017), becomes too low. This can make mechanical recycling not sustainable from the economic and environmental points of view, as demonstrated by the scandals of plastics waste exported to developing countries (Hook and Reed, 2018). Hence, there is a huge necessity to go beyond the traditional recycling by finding other processes able to minimize health and ecological risks and to provide the best value-creating treatment option. These alternative processes could work as complementary options, able to manage the waste streams that cannot be mechanically treated due to the presence of hazardous substances, or since the obtainable down-cycled products would have a poor market response.

Suschem (2020) provided an overview of these alternative processes, indicating the priority sectors, where innovative solutions are needed, and the types of polymers for which a value chain should be created: the crucial role of challenging plastics coming from WEEE, ELV and C&DW was highlighted. This is confirmed by Lase et al. (2021), which investigated current and future management schemes for small electronic equipments in Belgium and the Netherlands, identifying the stages where improvements could increase plastic recycling rates. Possible alternative management schemes for WEEE and ELV plastics (Ardolino et al., 2021; Cardamone et al., 2022) were compared by means of a Life Cycle Assessment (LCA), by analyzing future European scenarios where novel processes of physical and chemical recycling will be implemented. Other interesting comparisons between alternative treatment options were developed by Vollmer et al. (2020) - which considered five polymers coming from packaging and WEEE sectors, but including only plastics with low levels of hazardous additives - and by Schwarz et al. (2021) - which developed an LCA model for 25 plastics wastes, but without considering the specific feasibility of selected processes for each polymer.

This paper analyzes some of these innovative treatments - dissolution/precipitation, supercritical fluid extraction, catalytic pyrolysis, and waste-to-energy (WtE) equipped with carbon capture and storage unit (CCS) - all potentially complementary or alternative to the current options of mechanical recycling, energy recovery by combustion, and disposal into sanitary landfill. It is the first time that treatments suitable for each of the main polymers from WEEE, ELV and C&DW plastics were identified and compared. The selection of suitable management options was made based on the capability to treat waste polymers, and taking into account the type and content of their hazardous additives. Another innovative aspect is that the comparison was developed by an attributional life cycle assessment (LCA), which took into account the substitutability factor of obtained products (as proposed by Demets et al., 2021) and the TRL, technology readiness level (Mankins, 1995; 2009), of the analyzed resource recovery processes. Moreover, the study is based on a set of high-quality data, mostly provided by international companies active in industrial recycling of plastics waste and involved in a dedicated European H2020 project (Nontox, 2021).

2. A taxonomy of processes for challenging plastics waste valorization

The resource recovery processes suitable for challenging waste plastics, both those currently adopted and those available on the market in a close future, can be classified in different ways. A largely used classification identifies four categories (ASTM, 2006; Schyns and Shave, 2021; Davidson et al., 2021). *Primary recycling* or *closed-loop recycling*, which is generally related to mono-stream (pre- and post-consumer) plastics, allows to save the plastics in the same loop, that means recycling them to products with the same properties as the previous ones. *Secondary recycling* or *open-loop recycling*, which is related to largest part of post-consumer plastics, requires sorting of plastics waste streams, reduction of polymer waste size, followed by extrusion: the plastics are recycled in an open-loop, that means that they are generally used in lower value products, since the obtained recyclate is of worse quality than the original one. *Tertiary recycling* or *chemical recycling* includes all the processes that chemically modify polymeric waste to obtain high added-value materials, such as the related monomers or feedstock. Finally, *quaternary recycling* indicates the energy recovery by thermochemical processes, mostly combustion occurring in dedicated plants or waste-to-energy (WtE) units for municipal solid waste.

This classification does not take into account the existing diversity of processes belonging to the same category, in terms of operating parameters, environmental performances (e.g., energy consumption or generation, type and entity of emissions), but also the TRL of the related technologies. The taxonomy proposed in Fig. 1 considers the industrial maturity of each (traditional and emerging) processes, together with the involved mechanism (mechanical/physical/chemical recycling or thermochemical route), and the typology of the main outcome (new polymers, chemical building blocks, oils, or energy).

The scheme does not include biological recycling options (ISO, 2008), since they are applied to a still negligible amount of biodegradable waste plastics, and only limited data are available in the scientific and technical literature. The scheme necessarily does not include management options that do not imply any resource recovery, such as the disposal into sanitary landfill and the substandard treatments of open dumping and open burning (Forti et al., 2020; Cardamone et al., 2021). Finally, it does not consider the techniques of plastics waste sorting, such as those of magnetic, eddy current and vibrational separation, which are crucial preliminary steps for most of the analyzed options but not conversion and remanufacturing processes (Demets, 2022). The following paragraphs essentially describe the main available options for the valorization of the target plastics waste, also defining their current TRL and main challenges for their further utilization.

2.1. Mechanical recycling

It is the traditional Plastic Waste-to-New Materials process, which does not change the basic structure of the materials. Even though the process has the highest level of TRL (9), continuous improvements in each steps - sorting and baling, grinding, purification and separation, densification (compounding, additivation and pelletizing) - and in their combination in the recycling chain are continuously investigated and implemented in order to overcome the current constraints (Ragaert

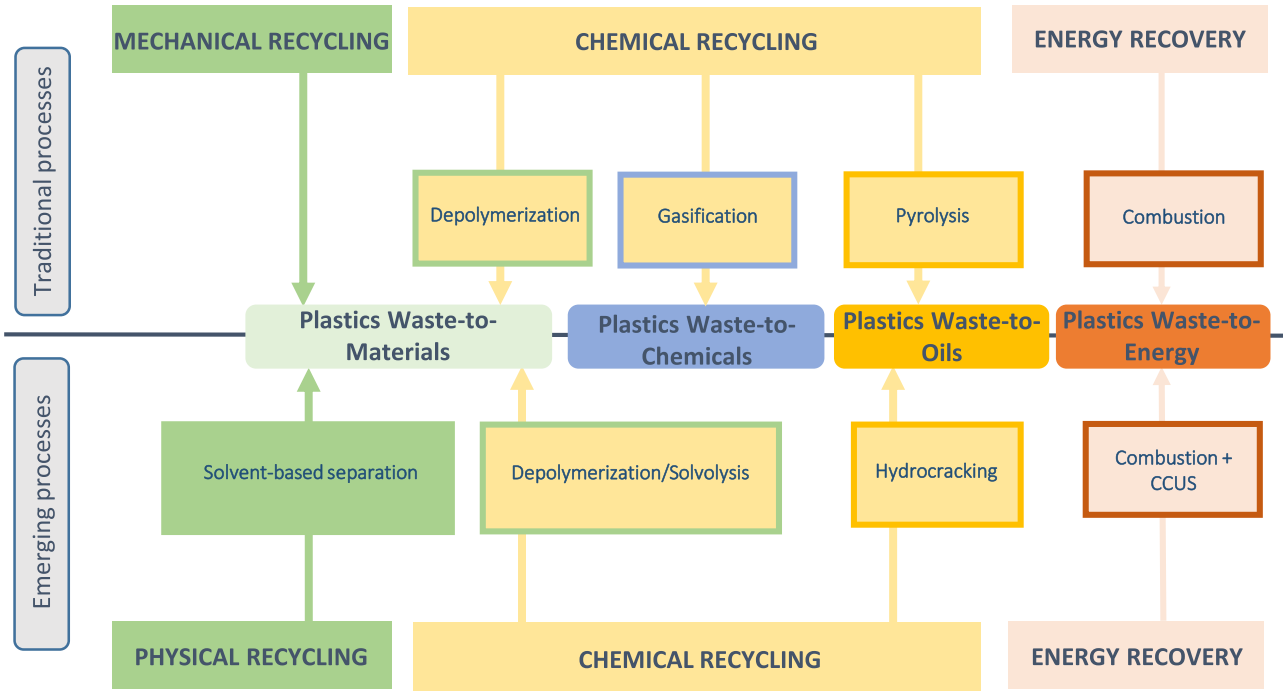

Fig. 1. A taxonomy of processes available for challenging plastics waste valorization.

et al., 2017; Schyns and Shave, 2021). Each type of plastics waste responds differently to the process depending on its chemical structure and composition, mechanical behavior, and thermal properties. The contaminations of a polymer waste significantly affect the quality of the recycled products. In most cases, as those of multilayer materials, these contaminants are other polymers that cannot be separated by sorting treatments. Further contaminants that complicate the mechanical recycling, even if present just as trace elements, include small degradation products and additives, like flame retardants, volatile organic compounds, phthalates, stabilizers, paints, coatings. These substances could be not completely soluble and then lead to phase separation with detrimental effect on mechanical properties. Finally, mechanical recycling has strong limitations with temperature-sensitive plastics, composites, and plastics that do not flow at elevated temperatures, as thermosets (Garcia and Robertson, 2017). The consequence is that only 9% of plastics waste globally collected between 1950 and 2015 has been recycled, of which only 10% has been recycled multiple times (Geyer et al., 2017). Currently, few types of plastics are largely treated and recovered by mechanical processes: PET, polyethylenes (LDPE, LLDPE, MDPE, HDPE), and PP, mainly coming from packaging sector (Plastic Europe 2020; Garcia and Robertson, 2017). With reference to the challenging plastics waste streams of interest for this study, mechanical recycling is successfully applied to not-brominated polyolefins and styrene plastics (PE, PP, ABS and PS/HIPS) from WEEE, and to really limited amounts of polymers from ELV and C&DW.

2.2. Chemical recycling

It is a group of thermal and/or chemical processes and technologies that are able to break bonds of plastics waste to obtain constituents parts such as monomers and oligomers, or gaseous, liquid and solid mixes of hydrocarbons (Davidson et al., 2021). They can be classified (Fig. 1) into the sub-groups of solvolysis, including chemically induced depolymerization reactions taking place in a solvent, and thermolysis, including various thermal treatment methods (depolymerization, pyrolysis, gasification, hydrocracking) able to induce different decomposition reactions (Shamsuyeva and Endres, 2021). The main goal is depolymerizing the polymers into the mother monomers, which can be used to synthesize new polymers (Plastic Waste-to-New Materials), even though it is often appealing the production of chemical building blocks (Plastic Waste-to-Chemicals, mainly by gasification) and that of oil products (Plastic Waste-to-Oils, mainly by pyrolysis). In general, chemical recycling processes require specific scientific expertise and significant investments for their industrial implementation. Most of them are not yet completely mature or economically competitive or not yet demonstrated at commercial scale operation, hence are still intensively investigated (Vollmer et al., 2020; Suschem, 2020; Schwarz et al., 2021).

Solvolysis. It is used to break down certain plastics into monomers with the support of a solvent. The obtained monomers can be polymerized together with virgin raw components and further processed into plastics. It is applicable to polymers with heteroatoms in their backbone and cannot be used to break carbon-carbon bonds. The specific processes are named based on the cleavage agent used, and include hydrolysis, alcoholysis (glycolysis and methanolysis), phosphorolysis, ammonolysis and aminolysis. Ether, ester and acid amide bonds can be cleaved this way. During the decomposition, a mixture of monomers, oligomers, solvents and residues is created, and the use of specific catalysts can improve the yield and selectivity (Suschem, 2020). The main challenge appears to increase the robustness of the processes to deal with higher content of contaminants. The TRL is rather low, with lowest values (3–4) for hydrolysis and highest values (4–5) for glycolysis (Schwarz et al., 2021; Suschem, 2020).

Depolymerization. It is the process where polymer chemistry is used to reverse polymerization reactions to yield the component monomers and oligomers of plastic, to be used in further polymerization reactions (Vollmer et al., 2020). The process can be applied only to a high-purity feedstock, in order to break the bonds of the polymers to form a monomer or a mixture of monomers or oligomers, with a rather high yield and selectivity at relatively low temperatures (Suschem, 2020). The catalytic depolymerization is the process where the breaking of

long-chain polymers to form monomers and oligomers is enhanced by one or more catalysts. The most suited polymers for depolymerization are PS (Dement'ev et al., 2019) and poly-methylmethacrylate (PMMA) (Godiya et al., 2019). It can also occur that other side products form, due to secondary reactions or interactions with a reactive medium present during depolymerization. This Plastic Waste-to-New Materials process is strongly affected by the purity of the input stream. It is likely that new or improved sorting technologies, based on measurable differences in various properties of commercial polymers (not only density but also electrostatics, wettability or spectral signatures, and more) will make easier to obtain high-purity waste stream, and then the possible implementation of depolymerization process (Rahimi and García, 2017). The TRL strongly depends on the specific process and input polymer, ranging from low (3–4) to medium (5–6) values (Schwarz et al., 2021; Agilyx, 2021; Suschem, 2020).

Pyrolysis. Pyrolysis involves the breaking of the polymer chains, in absence of any type of oxidant. Plastics waste is heated under an inert atmosphere (made of nitrogen or flue gasses) up to moderate temperatures (generally 350–550 °C), to obtain permanent (non-condensable) gasses, liquids (paraffins, olefins, naphthenes and aromatics), and solid residues (char), depending on waste composition and reactor temperature profile. Pyrolysis of waste plastics, even simple in concept, generally yields low-value mixtures of hydrocarbons having a wide compositional range, which can extend from light alkane gasses to coke, i.e. ranging from C5 to C28 or more. It is therefore frequent the utilization of a catalyst - able to reduce the operating temperature and residence time as well as to narrow the distribution of products (Scheirs, 2006) - so that plastics waste can be converted to marketable products, such as diesel fuel or gasoline (Haig et al., 2013). The choice or design of a dedicated catalyst, together with the optimization of the polymer-to-catalyst ratio, is crucial (Hafeez et al., 2019; Nanda and Berruti, 2020). Pyrolysis is likely the most widely researched plastics conversion process. Recent results (Esposito et al., 2020; Vollmer et al., 2020) seem to confirm the great potentiality of the process, even when applied to challenging plastics waste coming from WEEE. Anyway, there is still a lack of exhaustive and reliable answers about the optimization of process complexity (in particular, the effects that temperature profile, heating rate, and residence time of the specific reactor can have on the yield and quality of gasoline and diesel grade fuels from plastics) as well as plant scalability (the typical range of throughput capacities is 5000–20,000 t/y (Haig et al., 2013; AECOM & Fichtner Consulting Engineers 2021). Other challenges for a larger utilization of catalytic pyrolysis are the implementation of dehalogenation procedures to prevent or remove hazardous and corrosive compounds that can be generated during the process as well as the safety aspects (Suschem, 2020). The current TRL is medium (6–7), with lower values for units dedicated to challenging plastics waste, even though the great effort of applied research carried out by several industrial companies suggests a possible fast increase of the technology maturity (McKinsey, 2018; Vollmer et al., 2020; Schwarz et al., 2021).

Gasification. Gasification converts plastics waste into a fuel gas, called syngas, through a series of reactions taking place in a reducing atmosphere and higher temperatures (900–1100 °C). The process breaks the polymer chains, and the obtained syngas contains large amounts of CO and H_2, together with smaller contents of CH_4. The composition and possible utilization of the gaseous products largely depends on the gasifying agent, which can be air, oxygen-enriched air, steam or carbon dioxide (Lopez et al., 2018). It can be used in a wide range of applications, aiming at energy generation or production of energy carriers and drop-in-chemicals Arena, 2012; AECOM & Fichtner Consulting Engineers 2021). Gasification process flexibility is greater than that of other thermochemical conversion processes, which allows to jointly valorizing plastics of different composition or mixtures or plastics with other feedstock. This means that gasification can be potentially applied where plastics waste cannot be treated by mechanical recycling or pyrolysis (Suschem, 2020). Its high input and output process flexibility allows classifying gasification as Plastic Waste-to-Energy, to-Chemicals or to-Oil. The so-called advanced gasification technologies (AGTs) aim at waste conversion into aviation fuel, diesel, hydrogen, methane and other hydrocarbons (Thunman et al., 2018; AECOM & Fichtner Consulting Engineers 2021; IEA, 2018). Some of their configurations could be equipped with a carbon capture and storage (CCS) technology, to acquire the potential for hydrogen and hydrocarbons production with a net negative release of carbon dioxide (AECOM & Fichtner Consulting Engineers 2021). However, advanced gasification technologies are still away from commercialization. The wide variety of existing gasification technologies and syngas cleaning methods, without an adequate selection and validation of just some of them, is an index that the technology is not yet mature (IEA, 2018). The main challenge is an appropriate definition of design and process criteria for hot syngas cleaning to remove mainly tars, but also alkaline compounds, heavy metals and halogens (Suschem, 2020; Boccia et al., 2021). A wide commercialization of gasification technology for mixed plastics waste also needs a better understanding of the impact of feedstock quality and variability on process performance, the implementation of significant scale-up of each component of the whole plant, and reliable assessments of cost and performance risk (in terms of availability). These are the main reasons for which the current TRL is medium-high (6–8), hence comparable to that of pyrolysis (Schwarz et al., 2021; AECOM & Fichtner Consulting Engineers 2021; Suschem, 2020), as confirmed by the limited number of gasification plants fed with mixed plastics waste (JGC, 2019; Marie-Rose et al., 2014), some of which are still suffering for operating problems (IEA, 2018).

Hydrocracking. It is the process where heat and pressure (roughly 70 bar, anyway in the range 30–100 bar) are used in an inert atmosphere, with the presence of a catalyst to break the carbon-carbon bonds in plastics waste, and with a subsequent addition of hydrogen to produce solid, liquid and gaseous hydrocarbons (Davidson et al., 2021). The process is also known as hydropyrolysis, and generally classified as a Plastic Waste-to-Oil process, since a rather good-quality naphtha can be produced. The plastics waste stream is initially liquefied by means of a low-temperature pyrolysis and filtered to remove non-distillable material. The obtained liquid is sent over a bed of metal catalyst, such as Ni/S or NiMo/S (Ragaert et al., 2017). It is considered a promising process, able to operate at reduced temperatures (375–400 °C) and to limit coke formation through radical capping of its precursors: both these potential advantages should increase the catalyst lifetime (Vollmer et al., 2020; Miller et al., 2006). It is expected that the addition of hydrogen improves significantly the product quality, i.e. a higher H/C ratio and lower aromatic content, promoting the formation of more saturated hydrocarbons (alkanes (paraffin) instead of alkenes). Experiments for different types of catalysts revealed that hydrogen could help in the treatment of plastics waste with heteroatoms, Br included (Akah et al., 2015). Main disadvantages relate to the high operating costs (due to the high cost of hydrogen) and investment costs (mainly due to operation at elevated pressures). There are also investigations about the possibility to use helium or argon instead of nitrogen (in the traditional pyrolysis process) and ethylene, propylene or carbon dioxide instead of hydrogen. In general, the utilization of a reactive gas reduces the formation of coke and necessarily affects the yield and composition of products (Lee et al., 2017). The main challenge is the optimization of investment and operating costs. The price competition of obtained oil with crude derived petroleum still hinders commercial viability, and slows down the scale-up pathway (Vollmer et al., 2020; Solis and Silveira, 2020). The TRL is consequently medium (5–6).

2.3. Physical recycling

It is a group of emerging recycling processes where the recovered polymers remain largely unaffected and can be reformulated into plastics. They require a rather high expertise in polymer chemistry even though do not fall into the classification of chemical recycling, since no

bonds are cleaved and the chemical structure of the polymer chains remains unchanged (Zhao et al., 2018). There are two main alternatives: the selective dissolution process by using traditional solvents (dissolution/precipitation) or a supercritical fluid (supercritical fluid extraction).

Dissolution/precipitation. It is a process where a plastic waste containing additives and impurities of other polymers or materials is dissolved. A solvent is chosen to selectively dissolve the desired polymer. Ideally, when a solvent is able to dissolve either the target polymer or all the other polymers except the target one, it is perfect for selective dissolution. Unwanted additives are filtered out and the desired polymer is selectively crystallized or precipitated. The dissolution phenomenon is affected by the type of polymers and solvents but also by the polymer molecular weight, dissolution temperature and time, polymer concentration (Zhao et al., 2018). Dissolution/precipitation is a batch, physical process where the plastic only changes its physical state from solid to liquid, and this can be reversed again (CreaCycle GmbH, 2021). However, chemical fundamental knowledge is needed to understand the solvent/polymer interaction, solvent design and solvent recovery (Ragaert et al., 2017). The process can be carried out in two ways: i) by using a single solvent, which is then removed by evaporation, while the polymer is crystallized to be recovered; ii) by using a strong solvent, which has a positive solubility to the target polymer, and then a weak solvent (also called, anti-solvent), which has a negative solubility to the target polymer, used to precipitate the polymer, which can be recovered by filtration. In any case, it is necessary a solvent removal step, which can be energy consuming. The polymers undergo final phases of extrusion and granulation (Wagner and Schlummer, 2020), while the soluble impurities and additives (such as BFRs, phthalates, and stabilizers) are separated from the remaining solution by means of a distillation process (Schlummer et al., 2016). The obtained solvent/anti-solvent solution is recovered by a specific process and the extracted flame retardants can be treated by thermo-chemical processes (Ardolino et al., 2021). One of these processes is the CreaSolv® patented by Fraunhofer Institute (CreaCycle GmbH, 2021), which is able to treat most of the mentioned challenging plastics waste streams. In particular: brominated ABS, PS/HIPS and PC+ABS from WEEE; PE and PP from ELV, contaminated by additives and non-plastic fractions; PVC and EPS from C&DW plastics, contaminated with phthalates, stabilizers, and BFRs. The removal efficiency of hazardous substances was measured as high as 98%, with a polymer recovery efficiency of approximately 97% (Ardolino et al., 2021; Cardamone et al., 2022). The main challenges of this promising type of recycling is the reduction of energy (and time) consumption related to the separation of solvent/anti-solvent mixture before re-use and the complete removal of solvents to avoid any negative effect on polymer properties (Vollmer et al., 2020; Ardolino et al., 2021). It is also crucial the validation of the process at commercial scale in a reasonable time. The current level of technological maturity is medium (TRL=5–7), depending on the input polymer: it can be estimated as equal to 5 for ABS from WEEE and PVC from C&DW (for which a pilot unit is in operation), and up to 7 for EPS (for which a demonstration plant already exists).

Supercritical fluid extraction. The supercritical fluid extraction (SFE) aims at extracting undesired components from different medias utilizing supercritical fluids, exploiting their characteristics (such as density, similar to that of liquids; viscosity, comparable to that of a gas; and diffusivity, which is between those of liquids and gasses) to deeply and quickly penetrate the solid matrices (Manjare and Dhingra, 2019). SFE finds many applications, such as extraction of volatile organic compounds (VOCs) and flame retardants from plastic waste, debinding of ceramic and metals components, degreasing of spent catalysts, regeneration of molecular sieves (Jänisch, 2018). It can be also used for the precipitation stage of a dissolution/precipitation process, where the polymers are dissolved in solvents and then extracted by supercritical fluids subsequently (Zhao et al., 2018). SFE potentially offers important advantages with reference to classical solvents method, such as improvement in mass transfer, better extraction time and efficiency, minimal residues in the final product, and no residues of organic waste (Ben Said et al., 2016). Their use in physical recycling is increasing in recent years. Supercritical carbon dioxide is the most widely used supercritical fluid because it is non-poisonous, non-polluting, and relatively cheap. Moreover, it usually allows fast diffusion due to its low viscosity, easy separation from the extract and high selectivity for the extraction of non-polar compounds, while its selectivity for polar compounds can be enhanced utilizing an appropriate co-solvent (Manjare and Dhingra, 2019). When applied to the extraction of undesired compounds from plastic polymers, sc-CO_2 is directly injected in the extruder during polymers reprocessing. The level of industrial maturity is at TRL=5, since an optimization of operating parameters, validation of suitable removal efficiencies of main contaminants (such as VOCs and BFRs), and the development of an appropriate scale-up process are still necessary.

2.4. Energy recovery by thermochemical route

The thermochemical route includes all processes that break polymer bonds by means of thermal energy, which can be carried out under inert (pyrolysis) or reactive atmosphere (hydrocracking, gasification, and combustion). These processes can produce new chemicals or oils, as mentioned above, but also recover large part of the chemical energy of plastics waste (Arena, 2012; Lopez et al., 2017). In this case, combustion process in waste-to-energy (WtE) units is the most utilized option in all the challenging plastics waste management scheme, even though it shortens the material's lifespan and hence it is not aligned with the principles of a circular economy (Solis and Silveira, 2020).

Combustion is the well-known and technically reliable Plastic Waste-to-Energy process of complete oxidation of plastic wastes under an oxidant atmosphere, characterized by an appropriate excess of oxygen with reference to that necessary for stoichiometric combustion. Also known as incineration, it is largely utilized for plastic fraction from WEEE, ELVs and C&DW having a high content of additive and flame retardants or being characterized by the presence of different engineering polymers. It is currently the preferred, and in several cases mandatory, option for resource recovery from the residues of plastic fraction sorting that cannot be mechanically recycled (EERA-European Electronic Recyclers Association 2018). This is due to its high efficiency in destroying toxic organic substances, and its ability to concentrate inorganic pollutants, which can then be reused or immobilized in safe disposal sites (Fellner and Brunner, 2021). On the other hand, thermochemical oxidation has the main constraint of carbon dioxide emissions, which greatly worsens its environmental performances. The possibility of a strong reduction of these emissions by means of carbon capture technology could give a new and still more important role to the WtE route (Ghiat and Al-Ansari, 2021; IEA, 2020). Fellner and Brunner (2021) recently estimated that the ambitious new plastics recycling targets (e.g. from 22.5% to 55% for plastics packaging) of European Community (EC) should lead to an increase of recycling cost up to over 1.2 k€/t, so that the CO_2 reduction cost via plastic recycling can be estimated equals to about 1 k€/t_{CO2}. The upgrading of the WtE units with an updated carbon capture technology (Yoro et al., 2021; Kamran and Park, 2021) could allow treatment of plastics waste at lower costs, together with a carbon capture of 90%. In other words, carbon dioxide savings could be obtained with half of the cost required by mechanical recycling (i.e. 0.5 k€/t_{CO2}), maintaining the peculiar characteristics of destruction of toxic organic substances (Fellner and Brunner, 2021). This suggests that WtE equipped with carbon capture and utilization or storage (CCUS) unit could be in a relatively close future an important and sustainable alternative to treat large part of plastics waste (Bisinella et al., 2021). CCUS technology still needs further developments before a reliable implementation in a high number of existing WtE units, but its TRL is fast improving and rather high (8).

2.5. Advantages and disadvantages of challenging plastics waste valorization processes

Data and information reported in the previous paragraphs, and those contained in recent review articles (Vollmer et al., 2020; Suschem, 2020; Solis and Silveira, 2020; Shamsuyeva and Endres, 2021; Schwarz et al., 2021; Davidson et al., 2021) were used to draw a summary of main advantages and disadvantages of the four categories of valorization processes: mechanical, chemical and physical recycling, and energy recovery. As mentioned above, processes belonging to the same group can be different in terms of input parameters, output products and levels of industrial maturity, as reported in Fig. 1. Table 1 compares their characteristics at the current state-of-the-art, distinguishing specific processes belonging to the same category. A list of main patents related to the recalled emerging recycling processes is reported in ANNEX A.

3. The methodological approach to compare alternative options

The proposed approach aims at comparing conventional and innovative treatments, which are suitable for an efficient valorization of important challenging waste plastics. An analytical comparison was implemented only between really alternative options, that means those that can rather well manage the same type of polymeric waste. Some important challenging plastic waste streams were selected, as reported in Table 2 together with their origin (WEEE, ELV and C&DW) and peculiar aspects of their composition. The approach focuses on the single polymers, as already made by (Schwarz et al., 2021), in order to estimate their specific contribution to the environmental performance of the technically reliable treatments that were selected. Therefore, the comparison was made only between processes that are really in competition, excluding those that cannot in any way be applied to the specific polymeric waste. Data reported in Table 1 and discussed above were used to select the resource recovery process to be compared. Depolymerization and solvolysis were excluded because only suitable for treatment of homogenous and not-contaminated plastics waste, while a crucial characteristics of the target challenging plastics waste is their heterogeneity and the presence of hazardous additives. Gasification was not considered, in spite of its great potentialities, since the plants in operation that treat mixed plastics waste are still few and most of them are at a demonstrative scale (IEA, 2018). Hydrocracking was excluded because of limited available data and the current too high cost of hydrogen (Suschem, 2020; Solis and Silveira, 2020). The analysis considered the treatments listed in Table 2 - mechanical recycling, energy recovery by combustion, disposal into sanitary landfills but also catalytic pyrolysis, dissolution/precipitation and supercritical fluid extraction – only when suitable for each specific type of plastics waste.

Environmental performances of the waste plastics treatments reported in the right column of Table 2 were quantified by means of an LCA developed in compliance with the international standard ISO 14,044 (ISO, 2006). An attributional, process-based approach was utilized. The functional unit was the management of 1 tonne of the selected polymers, having the composition peculiarities reported in Table 2. The system boundaries were those of a "gate-to-gate" analysis: the input gate being that of mixed plastic obtained downstream of the WEEE/ELV/C&DW separate collection and dismantling; and the final gate that of recovered resources (Fig. 2).

The allocation problem was approached by means of the system expansion methodology, by identifying the avoided burdens related to products, which are replaced on the markets by the obtained co-products, and including their replacement in the model. The adopted procedure (Vadenbo et al., 2017), quantifies the substitution potential γ of an available market product (virgin plastics, crude oil, energy) with a secondary resource (decontaminated plastics, recovered oil, energy), as the product of four parameters: U, the potential physical amount of the secondary resource; η, the recovery efficiency of this resource; α, the substitutability factor, i.e. the functionality provided by the recovered resource compared to that of the conventional resource; π, the market response, which is the share of secondary resource that can effectively displace the available product on the market. A fifth parameter, τ, was also considered (only in the sensitivity analysis) to take into account the different TRLs assigned to each of the management options (and reported in Fig. 2) in order "to correct" the obtained values of avoided burdens. τ was assumed equal to 1 for processes with TRL=9, and then proportionally lower (0.89 (=8/9), 0.78, 0.67 and 0.56) for those with TRL equal to 8, 7, 6 and 5, respectively. Processes with TRL<5 were not considered at all (τ=0).

The function of the system under analysis indicates a crucial role of the quality of recycled materials. A substitution of virgin grade with recycled polymers on one-to-one basis is rare, since recycled plastics have generally lower technical properties, greatly affected by the composition of the input waste streams and possible final application of recycled polymers. This increases the necessity of a reliable assessment of the substitutability factor α, which quantifies the (functional) performance of the recycled polymer with reference to that of the virgin one. Following the approach proposed by Demets et al. (2021), α was evaluated based on two key parameters, one for its mechanical properties and another one for its processability (Ardolino et al., 2021; Cardamone et al., 2022), by taking into account data in commercial technical sheets for virgin polymers and those obtained during the mentioned H2020 project (Nontox, 2021) for recycled polymers. The same H2020 consortium of thirteen important institutions and private companies contributed to provide amounts, composition, and process performance data so making high the quality of data utilized in the LCA. An extended analysis of scientific and technical studies allowed to complete the set of environmental burdens, those directly generated by the system under analysis (direct burdens) and those avoided to the environment due to the products generated by the system (avoided burdens). The burdens generated by all other processes that interact directly with the system and allow it to work properly (indirect burdens) were instead obtained from Ecoinvent databank v.3.6 (Ecoinvent, 2021). Environmental burdens related to the infrastructures were not included. The procedure for environmental burdens evaluation was supported by specific material flow analyses (MFAs), as already made in similar papers (Ardolino et al., 2021; 2020). The most important of these MFAs are reported in ANNEX B.

Impact 2002+ (Jolliet et al., 2003) was selected as LCIA methodology, in agreement with recent studies focused on the same types of challenging plastics waste (Ardolino et al., 2021; Cardamone et al., 2021; 2022). It was implemented with the support of the software package SimaPro© 9.1.1.7 (SimaPro, 2021), coupled with the Ecoinvent database. A list of assumptions used for Life Cycle Inventory (LCI) modeling of the analyzed treatments is reported in Table 3. In particular, sanitary landfilling was taken as the worst case reference for all the selected polymeric wastes, since it doesn't allow any recovery, and in the case of contaminated plastics it also implies huge release of contaminant into the environment. Degradation and emission of BFRs in the air and water along landfill lifetime were accounted, by assuming specific annual emission factors and collection efficiencies. Moreover, as detailed in the last column of Table 3, the environmental burdens related to the management of each selected polymer were quantified as a "separate share" (Ardolino et al., 2020). The key performances of each specific management option (e.g., the net electric efficiency of combustion or the polymer recovery efficiency of dissolution/precipitation) were assumed to be constant and equal to those of the reference unit while some other parameters (e.g., the recovered energy and carbon dioxide emissions for combustion or the substitutability factor for products obtained by dissolution/precipitation) were affected by the specific characteristics of the selected polymeric waste. LCI tables for each polymer can be found in ANNEX C. The study has to be considered valid within the set of assumed specific conditions and hypotheses.

Table 1
Pros and cons of the valorization processes for challenging plastics waste, based on data from some recent reviews: Vollmer et al., 2020; Suschem, 2020; Solis and Silveira, 2020; Shamsuyeva and Endres, 2021; Schwarz et al., 2021; Davidson et al., 2021.

Characteristics	Mechanical Recycling	Chemical Recycling					Physical Recycling		Energy recovery
		Solvolysis	Depolymerization	Pyrolysis	Gasification	Hydrocracking	Dissolution/ precipitation	Supercritical fluid extraction	Combustion
Range of treatable polymer types	Limited (not-contaminated PE, PET, PP, PS/HIPS, ABS)	Limited	Very limited	Wide	Wide	Wide	Limited	Limited	Very Wide
Possibility of multiple input valorization	Low (mainly specific binary mixtures)	Very Low	Very Low	High	High	Potentially High	Medium (a minimum content of target polymers is required)	Low	Very High
Sensitivity to feedstock contamination	High	Very High	Very High	Very Low	Very Low	Very Low	Low	Medium	Very Low
Quality of obtained resource	Medium (depends on the quality of input stream)	High	High	Medium	Medium	Potentially High	High	High	High
Expected market response	Medium (depends on the quality of output material)	Potentially High	Potentially High	Potentially High	Potentially High	Potentially High	Potentially High	Potentially High	High
Contribution to the circular economy	Medium-High (depends on the quality of output material)	High	High	High	Potentially High	High	High	High	Very Low
TRL	High (9)	Low (3–4 hydrolysis and 4–5 glycolysis)	Low – Medium (3–6), depending on the target polymer and specific process	Medium (6–7)	Medium-high (6–8)	Medium (5–6)	Medium (5–7) depending on target polymers	Medium (5)	High (9)
Complexity of required technology	Low	High	High	High	High	High	Medium-High	High	High, but well-known
Process decentralization	Possible	Possible	Possible	Possible but expensive	Possible but expensive	Possible but expensive	Possible	Possible	Difficult and very expensive
Cost	Low	High	High	High	High	Very High (due to operating conditions and the use of hydrogen).	Medium-High	Medium-High	Medium-High (large scale plants can be used)

Table 2
The single polymers analyzed in a life cycle perspective, with the indication of their waste stream source and composition, together with the analyzed management options.

Challenging polymers		Main source	Composition	Analyzed treatments
Low density polymers <1 kg/L	**NoBr-PP**	**WEEE**	~0 Br level; LHV = 42,500 MJ/t; Carbon content = 84%.	Mechanical Recycling; Energy Recovery by combustion (with/without CCS); Disposal into sanitary landfills.
	NoBr-ABS		<2000 ppm Br; LHV = 36,500 MJ/t; Carbon content = 83%.	
	NoBr-HIPS		<2000 ppm Br; LHV = 38,600 MJ/t; Carbon content = 90%.	
	PE (with high VOC content)	**ELV**	49,600 ppm VOCs; LHV = 42,500 MJ/t; Carbon content = 84%.	Physical Recycling by Supercritical fluid extraction; Energy Recovery by combustion (with/without CCS);Disposal into sanitary landfills
	PP		200 ppm Br; 600 ppm VOCs: LHV = 42,500 MJ/t; Carbon content = 84%.	Physical Recycling by Dissolution/Precipitation; Energy Recovery by combustion (with/without CCS); Disposal into sanitary landfills.
High density polymers >1 kg/L	**Br-ABS** (with high Br content)	**WEEE**	30,000 ppm Br (BFR composition: 75% TBBPA, 13% DecaBDE and 12% TBPE); LHV = 34,800 MJ/t; Carbon content = 79%.	Physical Recycling by Dissolution/Precipitation; Energy Recovery by combustion (with/without CCS); Disposal into sanitary landfills.
	Br-HIPS (with high Br content)	**WEEE**	30,000 ppm Br (BFR composition: 75% TBBPA, 13% DecaBDE and 12% TBPE); LHV = 36,800 MJ/t; Carbon content = 86%.	
	PC	**WEEE**	<2000 ppm Br; LHV = 27,400 MJ/t;Carbon content = 63%.	
	PVC	**C&DW**	Plasticizers (e.g. Phthalates) content = 17.5%; Stabilizers content (e.g. Lead and Cadmium) = 3%; LHV = 17,600 MJ/t; Carbon content = 38%.	Physical Recycling by Dissolution/Precipitation+Upgrading; Energy Recovery by combustion (with/without CCS); Disposal into sanitary landfills.
Mixed polymers (no treatable with other processes)		**WEEE**	Mixed WEEP with glass fibers; Br=25,000 ppm; LHV=28,500 MJ/t; Carbon content = 60%.	Catalytic Pyrolysis; Energy Recovery by combustion (with/without CCS).
		ELV	Mixed ELVP; Br=5000 ppm; LHV=34,600 MJ/t; Carbon content = 72%.	

4. Life cycle impact assessment of alternative treatments options

The life cycle impact assessment compared management options that are technically suitable for each of the selected polymeric wastes. Therefore, results refer to the environmental performances of processes for light and heavy plastics waste from WEEE (Fig. 3), plastics waste from ELV (Fig. 4), mixed plastics from WEEE and ELV (Fig. 5), and PVC from C&DW (Fig. 6). Analyses of normalized results extended to all the impact categories (Ardolino et al., 2021; Cardamone et al., 2021; 2022) indicated Global Warming and Carcinogens as the most relevant ones. The LCIA results were accordingly reported with reference to these categories.

Mechanical recycling shows the best environmental performances among the available treatments for light polymers from WEEE (Fig. 3, top), both in terms of Global Warming and Carcinogens, savings from 1 to 4 $t_{CO2,\ eq}$ and from 100 to 1000 $kg_{C2H3Cl,\ eq}$, with respect to landfill disposal and WtE with/without CCS. The environmental advantages of mechanical recycling when applied to not-brominated styrenics are explained by the high avoided impacts. These were determined, for PS/HIPS, by the elevated substitutability factor (0.99), and, for ABS, by the high direct emissions related to the production of virgin polymer (mainly hydrocarbons, fossil carbon dioxide, and methane). With reference to the same light and not-brominated WEEE plastics (top of Fig. 3), it should be also noted that the performances of energy recovery by combustion and landfill disposal are not affected by the specific polymer, since the properties necessary to environmental burden quantifications (such as, carbon content and Low Heating Value) are rather similar.

Dissolution/precipitation process shows good environmental performances among treatments applicable to heavy polymers from WEEE (Fig. 3, bottom). It can save up to 2 $t_{CO2,\ eq.}$, with respect to landfill disposal and WtE equipped with CCS, and more than 3 $t_{CO2,\ eq.}$, with respect to WtE without CCS. The same process allows to save up to about 2000 $kg_{C2H3Cl,\ eq.}$, with reference to landfill, and between 100 and 700 $kg_{C2H3Cl,\ eq.}$, with reference to any type of WtE units. These good performances are mainly related to treatment of PC (in terms of Global Warming) or to that of brominated ABS (in terms of Carcinogens). This is mainly due to the high direct impacts deriving from the production of virgin PC and ABS. The performance of WtE with CCS is comparatively lower, even though just for a limited extent. There is instead a great (negative) difference when the performances of the dissolution/precipitation are compared with those of conventional WtE without CCS (for Global Warming) or with landfill disposal (for Carcinogens). This is due to the high direct emissions associated to thermal treatments without CCS (mainly fossil CO_2) and landfill disposal (mainly DecaBDE and its lower congeners). In particular, it should be noted that ABS and PS/HIPS have huge contents of BFR (30,000 ppm of Br and then about 43,000 ppm of BFR) and then imply high emissions into the atmosphere along landfill lifetime (363 g of higher brominated PBDEs, 1623 g of lower brominated PBDEs and 11,451 g of TBBPA for each tonne of polymers).

The analyzed innovative processes of physical recycling show good performances when used as option for ELV plastics (Fig. 4): those made of PE from fuel tanks (treated by supercritical fluid extraction), and those made of PP (treated by dissolution/precipitation).

It was estimated that, with reference to the conventional WtE, the supercritical extraction can save almost 2 $t_{CO2,\ eq.}$ and 120 $kg_{C2H3Cl,\ eq.}$ for each tonne of PE treated. When compared to WtE equipped with CCS, it shows similar performances in terms of global warming and high savings in terms of carcinogens (again 120 $kg_{C2H3Cl,\ eq.}$ for each tonne of PE treated). This good performance could be further improved by implementing a system with the internal recirculation and reutilization of CO_2, since its consumption and release are the main direct burdens. Dissolution/precipitation shows good performances in terms of Carcinogens, saving up to 80 $kg_{C2H3Cl,eq.}$ for each tonne of treated PP from ELV, with reference to both landfill disposal and WtE (with or without CCS).

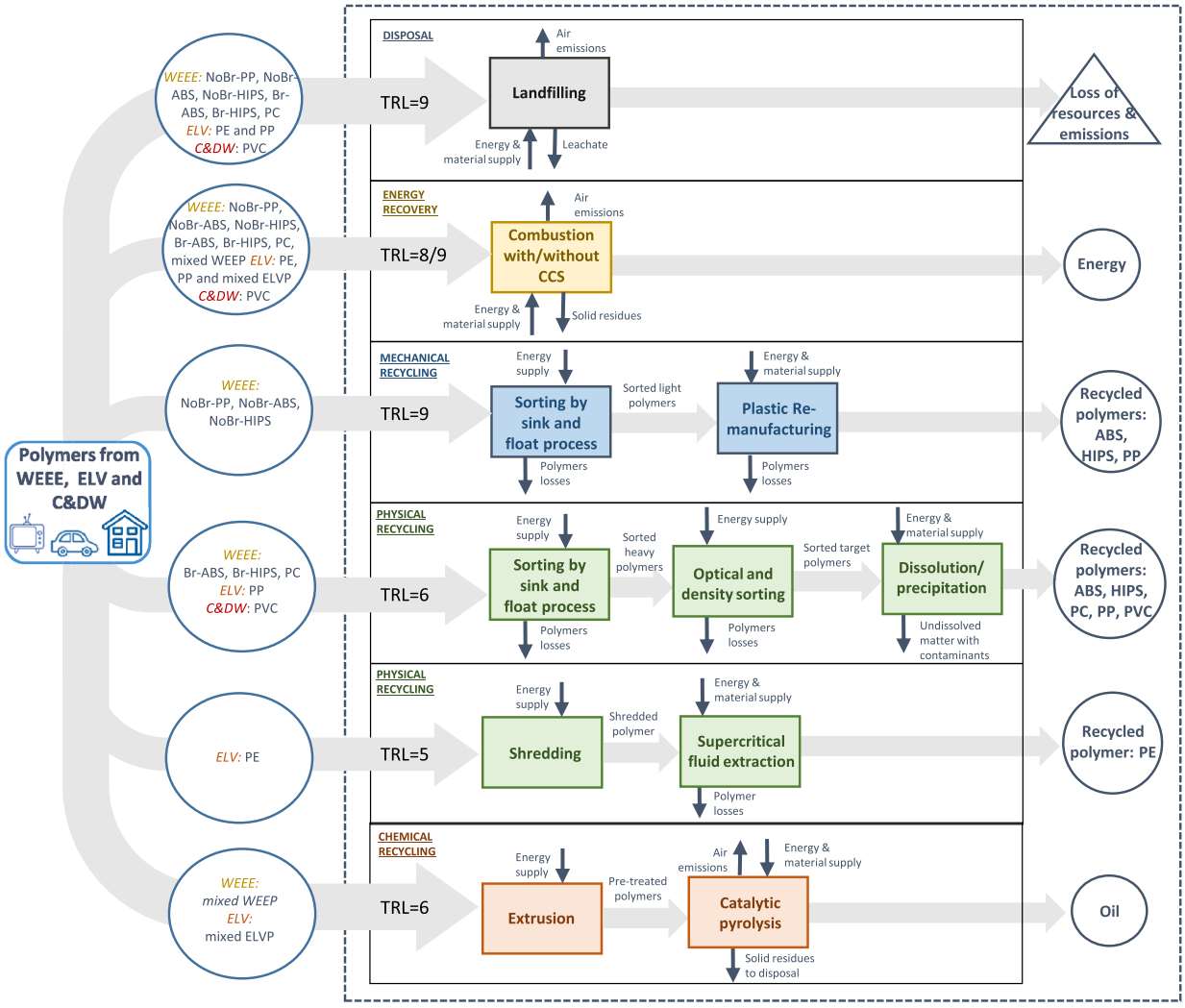

Fig. 2. System boundaries of the LCA study, with the indication of the alternative options for specific types of challenging plastics waste, and the related TRL.

On the other hand, WtE equipped with CCS has better environmental performances in terms of Global Warming, since dissolution/precipitation is penalized by direct burdens related to energy consumptions, which are higher than those avoided by saved production of virgin polymers.

Mixed plastics waste from WEEE and ELV plastics cannot be sent to any type of mechanical or physical recycling processes, since their complex composition includes different polymers (typically more than six) together with glass or carbon fibers. The alternative processes analyzed for this plastics waste are resource recovery by WtE (with or without CCS) and catalytic pyrolysis. Fig. 5 indicates that catalytic pyrolysis shows Global Warming performances better than those of WtE without CCS (saving about 1.3 $t_{CO2,eq.}$) but worsen than those of WtE with CCS (for about 0.5 $t_{CO2,eq.}$). Furthermore, it shows Carcinogens performances worsen than both the combustion processes, up to a (limited) increase of 10 $kg_{C2H3Cl,eq.}$, as a consequence of energy consumptions (mainly for ELVP) and larger amounts of solid residues that have to be disposed (mainly for WEEP). This suggests that WtE could be more sustainable than catalytic pyrolysis, at the current state-of-the-art, particularly in the case of configurations with CCS.

Finally, Fig. 6 indicates that PVC recovered by dissolution/precipitation plays a key role, making negative (that means sustainable for the environment) both the estimated potential impacts, as a result of avoided direct emissions (mainly dioxins, hydrocarbons and fossil carbon dioxide) connected with virgin PVC production. In particular, dissolution/precipitation of PVC collected from C&DW is always preferable to the disposal into landfill and to both combustion processes in terms of Carcinogens, when instead its performances in terms of Global Warming are better only than those of WtE without CCS.

4.1. Sensitivity analysis

A sensitivity analysis was developed following the approach proposed by Clavreul et al. (2012), and already used in similar studies (Cardamone et al., 2021; Ardolino et al., 2021). Some key parameters were varied in reasonable ranges, based on information received by the partners of the H2020 project (Nontox, 2021) or provided by scientific literature (Haig et al., 2013; IEA, 2020; Bisinella et al., 2021): electric energy consumptions of dissolution/precipitation process (+/- 25%); carbon dioxide consumption of SFE (+/- 100 kg); light sweet crude oil yield of pyrolysis process (+/−10% for WEEP; −10% for ELVP); net energy efficiency of WtE+CCS (+/- 3%). All these variations generally imply a rather limited effect on potential impacts, mainly in terms of Carcinogens midpoint category. The potential variation of energy efficiency of WTE+CCS units appears instead a crucial parameter, with variations up to 700% for Global Warming. The detail of the whole analysis is reported in ANNEX D.

As anticipated above, the study took also into account the different TRLs assigned to the selected management options, with the aim of considering the potentially weak reliability of estimated avoided

Table 3
Main assumptions made for the comparative assessment of the alternative treatments options for the selected challenging plastics waste.

Strategy	Treatment	TRL	Main LCI assumptions
Disposal	**Sanitary Landfill**	9	Landfill lifetime: 100 years. Air emission factors for DecaBDE and TBBPA: $1.0 \bullet 10^{-5}$ for plastic waste unloading and 0.016 as annual release during landfill lifetime. Degradation of DecaBDE in its low bromine congeners, having a half-life of 1 year has been assumed. BFR emissions were collected by a landfill gas capture system, with 55% of efficiency. Annual emission factor in leachate for DecaBDE and TBBPA: 0.0004. Leachate is sent to a waste water treatment plant with a BFR removal efficiency of 71%. Fossil carbon degradation: 3%, released as landfill gas, with a composition = 55%volCH_4–45%volCO_2. Landfill gas collection efficiency: 55%.
Energy Recovery	**Combustion without CCS**	9	24% net electrical efficiency (European energy mix has been utilised for avoided burdens accounting). Average BAT-AEPLs for air emission and consumption levels.
	Combustion with CCS	8	17% net electrical efficiency (European energy mix has been utilised for avoided burdens accounting). Adapted values of BAT-AEPLs for air emission and consumption levels.
Recycling	**Mechanical recycling**	9	Sink and float: 94% sorting efficiency; 25 kWh/t electricity consumption. *Re*-manufacturing: 95% efficiency; 360 kWh/t electricity consumption. Substitutability: PP=0.75, ABS=0.76, HIPS=0.99.
	Physical Recycling-Dissolution/ precipitation with/without upgrading	6	Efficiencies: 93% preliminary sorting (sink and float + density and optical phases), 97% polymers recovery, 98% Br removal (WEEE); 92% preliminary sorting (sink and float + density and optical phases), 97% polymers recovery, 98% Br/VOCs removal (ELV); 94% preliminary sorting, 90% polymers recovery, 99.8% Plasticizers/Stabilizers removal (C&DW). Consumptions: 20 kg/t solvents and additives; Substitutability factor: ABS=0.58, HIPS=0.65, PC=0.58 (WEEE); PP=0.8 (ELV); PVC = 0.88 with upgrading (C&DW).
	Physical Recycling-Supercritical fluid extraction	5	Efficiencies: 96% polymers recovery; 79% VOCs removal. Consumptions: ratio sc-CO_2/waste plastics = $60\%_w/40\%_w$. Substitutability factor: PE=0.85 (ELV).
	Catalytic Pyrolysis	6	WEEE plastics Catalyst amount: 5%. $Yield_{D.A.F.}$ gas/liquid/solid =10/76/14 gross and 0/70/14 net. Product LHV: 31.3 MJ/kg_{gas} and 37.9 MJ/kg_{Oil}. Required energy: 2800 MJ/t heat and 550 kWh/t electricity (internal recovery of 82% and 99%). Substitutability factor for Oil: 1. ELV plastics Catalyst amount: 5% $Yield_{D.A.F.}$ gas/liquid/solid =12/85/3 gross and 0/80/3 net. Product LHV: 35.4 MJ/kg_{gas} and 40.7 MJ/kg_{Oil}. Required energy: 4860 MJ/t heat and 560 kWh/t electricity (internal recovery of 49% and 100%). Substitutability factor for Oil: 1

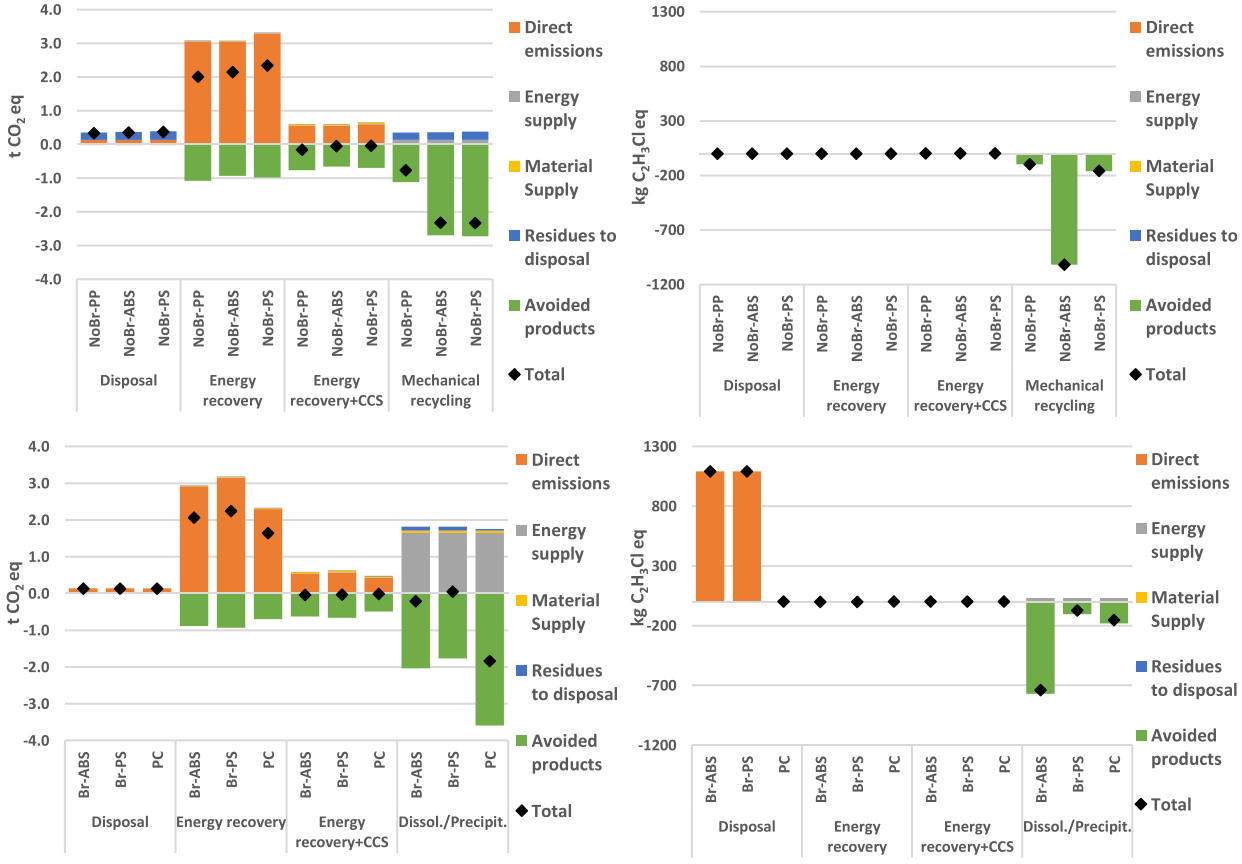

Fig. 3. Life cycle assessment of environmental performances in terms of impact categories of global warming (left) and carcinogens (right) related to alternative options to treat light (top) and heavy (bottom) plastics from WEEE.

burdens. A fifth parameter, τ, was added to the procedure proposed by Vadenbo et al. (2017), assuming that τ is equal to 1 for processes with TRL=9, and gradually lower for those with TRL between 8 and 5, in other words as a kind of penalty for lower TRLs. The results, reported in Fig. 7, confirmed that innovative treatments, such as energy recovery with CCS or dissolution/precipitation, are always preferable to the

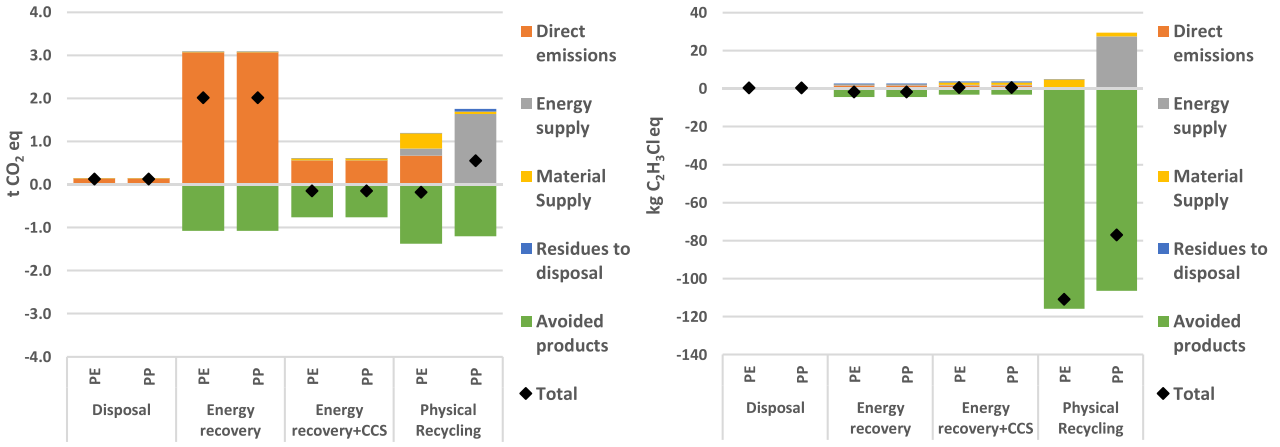

Fig. 4. Life cycle assessment of environmental performances in terms of impact categories of global warming (left) and carcinogens (right) related to alternative options to treat light waste plastics from ELV.

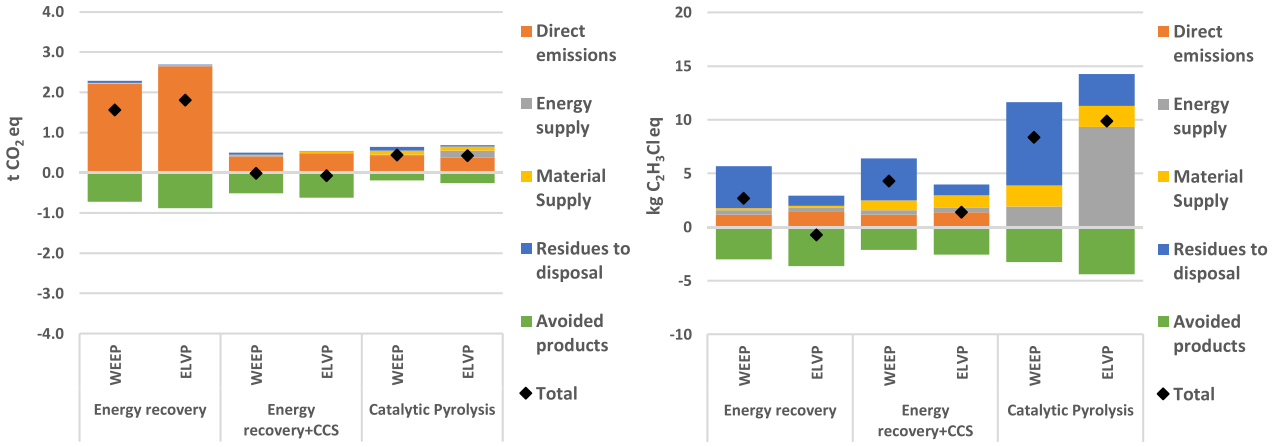

Fig. 5. Life cycle assessment of environmental performances in terms of impact categories of global warming (left) and carcinogens (right) related to alternative options to treat mixed waste plastics from WEEE and ELV.

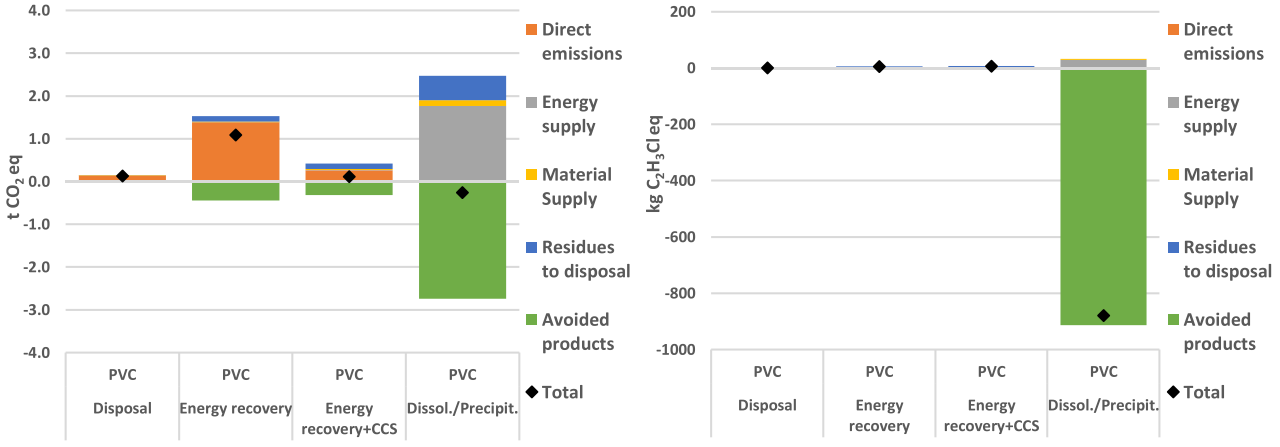

Fig. 6. Life cycle assessment of environmental performances in terms of impact categories of global warming (left) and carcinogens (right) related to alternative options to treat PVC from C&DW.

current management options, thanks to polymer recovery (for physical recycling) or the limited greenhouse gas emissions (for WtE+CCS). It is difficult to individuate a clearly better treatment between these options, since the results are always rather close to each other and the comparison is easily affected by limited variation of some parameters, such as the energy efficiency of WtE+CCS or the electric energy consumption of dissolution/precipitation.

The largest variations relate to the physical recycling processes (for which the role of avoided burdens is always crucial), but only in a few cases these variations overturn the results obtained in the base case.

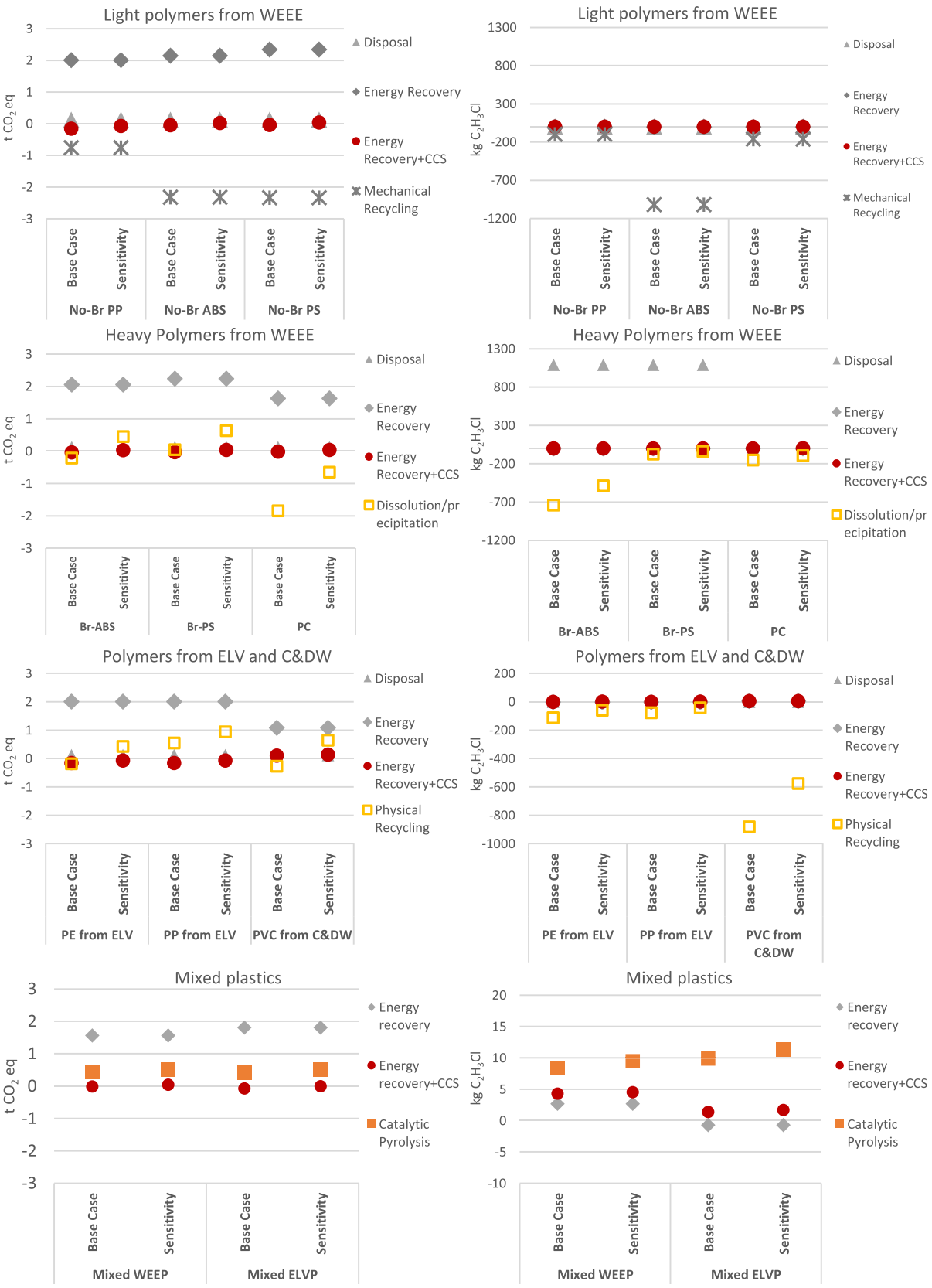

Fig. 7. Sensitivity analysis on the effect of TRL of emerging technologies for challenging plastics waste valorization.

Dissolution/precipitation process shows the largest differences between base case and sensitivity case, for Br-PS (1138%) and PVC (−348%, respectively), as reported in Table D. 2 of Annex D. Variations related to performances of catalytic pyrolysis are instead rather limited.

5. Conclusions

The study reports the state-of-the art of available options for plastics waste valorization, and proposes a taxonomy of conventional and emerging treatments, with a focus on those suitable for challenging plastics waste coming from WEEE, ELV and C&DW.

A life cycle impact assessment analyzed the environmental performances of considered treatments, by taking into account the peculiar composition of selected plastics waste streams, including their content of contaminants, such as BFRs, VOCs and plasticizers. An attributional, process-based approach compared only management options which are technically suitable for each analyzed plastics waste. The generated (direct and indirect) environmental burdens were estimated based on data mostly provided by international companies involved in industrial recycling. These high-quality data were also used to estimate avoided burdens, with a particular attention to the substitutability factor of obtained recovered resources and TRL of each management options.

The LCA results, reported in terms of the impact categories of Global Warming and Carcinogens, identify and quantify environmental advantages allowed by the adoption of the analyzed innovative physical and chemical recycling processes.

With reference to light and not-brominated polymers from WEEE, the results show great advantages obtainable by mechanical recycling: one or more tonnes of $CO_{2,eq.}$, and from 100 to 1000 kg of $C_2H_3Cl_{,eq}$ can be saved for each tonne of treated polymers, when compared to energy recovery by combustion or disposal into sanitary landfill.

Physical recycling by supercritical extraction and, above all, dissolution/precipitation, shows good performances when applied to polymers not suitable for mechanical recycling, such as ABS, PS/HIPS and PC from heavy fraction of WEEE plastics; PE from fuel tanks and PP from ELV plastics; and PVC from C&DW plastics. In particular, dissolution/precipitation process applied to WEEE plastics can save up to about 2 $t_{CO2,eq.}$ with respect to landfill disposal and combustion equipped with CCS, and more than 3 $t_{CO2,eq.}$ with respect to combustion without CCS.

Catalytic pyrolysis applied to mixed plastic waste from WEEE and ELV shows better Global Warming performances than those of combustion without CCS (saving about 1.3 $t_{CO2,eq.}$), and worsen performances than those of combustion with CCS (for about 0.5 $t_{CO2,eq.}$).

Overall, the analyzed emerging treatments appear suitable solutions for the management of the challenging plastics waste coming from WEEE, ELV and C&DW. Depending on the specific characteristics of the different plastics waste streams, they could be complementary to mechanical recycling and alternative to conventional incineration and landfilling, leading in some cases to strong environmental advantages. On the other hand, the commercial viability and development potential of the innovative recovery processes will depend also on economic aspects, which have just mentioned here. They depend on several different factors, such as the specific process and/or technology, optimal scale of the plant, its localization, existing economic incentives, local legislation, etc. Future work will take all of them into account in an accurate techno-economic study.

CRediT authorship contribution statement

Umberto Arena: Conceptualization, Validation, Supervision, Writing – review & editing. **Filomena Ardolino:** Conceptualization, Methodology, Investigation, Software, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Annexes associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2022.106379.

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