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Chapter

Mixed or Contaminated Waste Plastic Recycling through Microwave - Assisted Pyrolysis

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Abstract

A single type of thermoplastic polymer is easily recycled through a mechanical process, but this way can't be followed in the presence of mixed or contaminated plastic. In this case, one of the main followed solutions is a thermochemical process and among them, microwave-assisted pyrolysis is one of the emerging technologies. This chapter offers an update of the microwave-assisted pyrolysis of mixed or contaminated waste plastic as a very promising example of chemical recycling. Furthermore, some unpublished results in this field will be reported such as the pyrolysis of waste lead containing polyethylene coming from end cycle batteries or the pyrolysis of waste polypropylene from facemasks used for covid protection. Finally, some examples of pilot plants will be described and commented as well as several industrial cooperations.

Keywords: microwave, pyrolysis, waste mixed plastic, waste contaminated plastic, waste plastic disposal

1. Introduction

The goal of realizing the conditions for achieving a truly circular economy is one of the main challenges in which scientists are involved to solve the problems concerning both global warming and the end of mineral resources. Over the last twenty years, the number of companies involved in environmental issues is continuously increasing and now almost all companies are, even in a different way, involved to solve this problem. These resources also represent a strong driving force for the development of sustainable industrial processes.

The world plastic production in 2019 was 368.0×10^6 tons with an increase of 2.5% concerning for 2018 [1] while in the same year the European production was 57.9×10^6 tons among thermoplastic and thermosetting polymers.

Among them, polyolefins are the most produced and employed materials for applications in everyday life for industrial, domestic, and technological applications [1]. They are thermoplastic polymers and are mainly used for packaging, whose life cycle is very short which means they may be disposed of in a short time after their production. A less important part of them is employed to realize furniture, insulating materials, automotive parts, and so on and their life cycle is considerably longer (ten years or more).

Polymeric materials are easily recycled through mechanical processes, as reported in **Figure 1**, for the production of renewed objects prolonging the life of these plastic materials, avoiding their disposal through landfilling or combustion, and reducing

the use of raw materials. This is a very friendly and economic process, however, it may be applied only when a single plastic material is available or when the material is not contaminated or strongly deteriorated. In these cases, other routes such as thermochemical processes may be followed as an environmentally friendly procedure avoiding to send these materials to combustion or landfilling, so giving a contribution to realizing a circular economy and reducing the emission of greenhouse gases (GHG).

Thermochemical processes may supply fuels and chemicals using recycled or renewable feedstock as alternatives to oil-based raw materials [2]. These led to the development of new technologies able to carry out the optimal use of such resources minimizing the environmental impact and producing a limited amount of secondary waste. It means that waste disposal or contaminated plastic materials may be transformed into useful products. Among these processes, the microwaves technologies have taken large attention due to their high efficiency to supply the energy required for a plethora of industrial processes. The main performances on the use of microwave as correlated to a classical heating system are resumed in **Table 1**.



Figure 1.
Pathway to recycle thermoplastic materials.

Microwave heating		**Conventional heating**	
Advantages	Volumetric heating	**Detriments**	Surface heating
	Short reaction time (minutes)		Long reaction time (hours)
	High heating efficiency		Heating efficiency is usually low
	The low thermal conductivity of polymers may be overwhelmed: easy heating of polymers		Hard heating of polymers: their thermal conductivity is low
	The gas formed does not contain combustion gas		The gas formed is contaminated by combustion gas (Direct heating)
Detriments	Electrical power is required	**Advantages**	Every fuel source may be employed
	Microwave absorber is required		Additives are not required, some heating carrier are sometimes used

Table 1.
Correlation between microwave and conventional heating.

This chapter aims to offer a comprehensive description of new results reported to provide an updated description to the specialist and open this knowledge to a greater audience. So our intent is to contribute to extend the application of this technology to many other fields.

2. Previous results

Pyrolysis is the thermal decomposition of a material at a relatively elevated temperature under an inert atmosphere. It involves a change of the chemical composition of the waste polymer that will be converted into a solid, a liquid, and a gaseous product. These products will be directly used as solid, liquid, or gaseous fuels to produce energy or employed as raw materials for the synthesis of new products [3].

Pyrolysis of end-cycle plastic materials using the microwave as heating technology (Microwave-Assisted Pyrolysis: MAP) has been reviewed ten years ago [4–6]. The polymeric materials have a low efficiency to convert microwave radiation into heat (see **Table 1**), but if a microwave absorber is added, sometimes erroneously called a catalyst, the pyrolysis may run very efficiently. The absorbers are compounds showing a high efficiency to convert microwave into heat and the main types employed are silicon carbide, carbon, iron, and so on. Anyway, in the literature, it is possible to find a list of many different compounds able to convert MW into heat, each one with specific features.

In the previous review [4] was reported some preliminary results on the pyrolysis of several waste plastics such as High-Density Polyethylene (HDPE), Polypropylene (PP), Polystyrene (PS), Polyvinylchloride (PVC), Polyethylentherephtalate (PET), and end cycle tyre but these data were referred to 10 years ago.

3. Update on MAP of plastic waste

This chapter aims to report a comprehensive description of the new results obtained to provide an accessible description not only to specialized researchers but also to open this knowledge to a greater audience.

MAP of plastic wastes has emerged as a promising chemical method to displace waste plastic and generating fuels suitable to produce energy and chemical products. Several parameters such as the plastic origin and its composition, temperature, reaction time, MW power, MW absorber and eventually the catalyst present and its composition has been reported in the literature in different reviews during the last years [3, 7, 8]. The catalyst, if present, rapidly loses its activity due to the formation of char on its surface. Energy balance showed that 5 MJ of electric energy was required to process 1 kg of HDPE using a continuous MAP system (energy efficiency 89.6%). It is interesting to note that the requested energy could be generated from the gas products formed during pyrolysis (6.1 MJ), making the process self-sufficient from an energetic point of view.

Some of the main theoretical and experimental aspects of the microwave-materials interactions are reported alongside the issues related to a microwave pyrolytic process of materials [9]. Due to several parameters affecting the interactions between materials and microwaves a rigorous detection of the reaction temperature may be a hard task during MAP [10] both for its detection and uniformity of the distribution of temperature on the material during the overall pyrolytic run.

The MAP is furthermore a promising process available for other industrial applications allowing for energy recovery directly from plastic wastes. Moreover, it offers some interesting advantages, such as high energy efficiency, absence of waste

production, lower reaction temperature if correlated to classical heating processes. In the following parts are reported the MAP of synthetic plastic produced through the polymerization of monomer obtained from mineral oils together with citations of MAP of biomasses (polymers from natural source) to produce bio-gas, bio-oil, and bio-char.

3.1 Disposal of a single type of plastic

Disposal of a single type of plastic waste through pyrolysis is not the best choice when they are clean and not deteriorated, because they can be easily reused through mechanical recycling as reported in **Figure 1**. Mixed plastics may be hardly sent to a mechanical process because a large amount of expensive compatibilizers are required, due to the low miscibility of different plastics. Otherwise, if the plastics, even if of a single type, are contaminated or they have lost a large part of their performances, pyrolysis represents one the best choice. Waste or contaminated polyolefins were disposed through MAP using tyres or carbonaceous char as MW absorber [3, 11–15]. The presence of the absorber mixed with the char formed in the course of the pyrolysis process is not a problem because it may be easily recycled to the pyrolysis process or(depending on the absorber used) employed together with the char formed for several applications such as solid fuel, support for catalyst, filler for fiber-reinforced composites and so on. The study of MAP on single plastic is however important to understand the mechanism of the process, the nature and composition of the products, and the interaction among intermediates when pyrolysis of composites or mixed plastics is run.

3.1.1 Polyethylene (PE)

PE is the most common plastic used today, it is produced as High-density Polyethylene (HDPE) through Ziegler-Natta catalysis or Low-Density Polyethylene (LDPE) from a radical polymerization. Other classes of intermediate products (between HDPE and LDPE) are present on the market. PE is a polymer, with production over 100.0×10^6 tons/y accounting for 34% of the total plastic market. It is a polymer, primarily used for packaging (plastic bags and films), geomembranes and containers including bottles, tanks, and so on). Waste or contaminated PE may be disposed of through MAP using tyres or carbonaceous char as MW absorber. HDPE was converted into waxy products (yield 80.2 -83.9 wt. %) while the yield of gas was 15.7-19.2 wt. % and that one of solid was 0.4—0.6 wt. % [9, 10, 14] when standard apparatus was employed. However HDPE was converted into a low viscosity liquid by using a very low MW power, but a long time was required to obtain a complete conversion. It is possible to use a pyrolytic apparatus containing a system able to fractionate the vapor formed, improving the residence time of the waxy products in the oven. In these conditions, a low viscosity and density liquid was obtained and the overall pyrolysis was improved. In all cases, the time of the process was strongly reduced concerning processes using classical thermal heating. The liquid fraction from HDPE contained linear alkanes and 1-alkenes with negligible formation of branched, cyclic, or aromatic hydrocarbons.

MAP of HDPE was realized also using a bed of activated carbon [11] obtaining a liquid containing hydrocarbons with a carbon chain length profile close to that one of a diesel. The chain of HDPE was broken, across all operating temperatures, and a lighter liquid product with a narrower range of chain lengths was formed if compared to the traditional pyrolysis using a bed of traditional coke. High-temperature

pyrolysis of plastic has been also reported by Jang et al. [16] without any correlation with other results previously reported in the literature.

The MAP of PE using a mixed catalyst containing cracking active components (γ-Al_2O_3, amorphous aluminum silicate, fly ash, zeolite molecular sieve, natural mineral clay, and solid acid) together with an MW absorber (C-containing compounds, Si-containing compounds, Fe-containing compounds, and polymers) and coking inhibiting component (alkali metal salt, P-containing compounds, B-containing compounds, magnesium sulfate, diethylpolysiloxane and p-tert-Butyl catechol) were reported [17]. The use of in-situ or ex-situ catalysts such as NiO and HY zeolite is reported to improve the quality of the products formed [18].

3.1.2 Polypropylene (PP)

PP is a thermoplastic polymer obtained through stereospecific polymerization with properties close to those of PE, but slightly hard, and resistant to a higher temperature. It is white, non-polar, and used in a wide variety of applications. It is the second large produced plastic, after PE. PP has been pyrolyzed using tyres or carbonaceous char as MW absorber [14] obtaining a low density (0.746-0.760 g/mL) and viscosity (0.63-0.95 cP) liquid (yield 56.5-74.7 wt. %), a char (yield 9.1-12.0 wt. %) and a gaseous fraction (yield 13.3 - 34.4 wt. %) containing hydrogen and aliphatic hydrocarbons. Liquid from MAP of PP was formed as a mixture of methyl-branched alkane and alkenes, and sometimes aromatics. The composition was a function of pyrolysis conditions.

Similar results were later reported by Suriapparo et al. [19], using different MW absorbers such as graphite, aluminum, silicon carbide, activated carbon, lignin, and fly ash. The optimal conditions were an MW power of 450 W and a ratio of PP: graphite = 100: 1, but only an oil yield of 48 wt. % was reached. The oil had a heating value of 44.45 MJ/Kg and contained 50 wt. % of C_3-C_6 gaseous hydrocarbons. The reaction was repeated with 50 g of PP under the same conditions, obtaining an 83 % of energy recovery in the oil. Alkenes and cycloalkanes were the major compounds in the oil, but their relative yields varied significantly with different absorbers. The catalytic activity of the absorber was hypothesized even if the results may be explained with the different efficiency in the conversion of MW into heat and the transfer of the heat to the polymer. The MAP was also carried out in the same conditions using commercial PE and polyisoprene.

3.1.3 Polystyrene (PS)

PS is an amorphous, colorless, and transparent thermoplastic polymer synthesized from an aromatic alkene (styrene) through radical polymerization. PS can be solid or foamed, the PS used for general purpose is clear, hard, and brittle. It have a low-density and a high barrier to heat and noise when expanded (EPS) but a low barrier to oxygen and water vapor and a relatively low melting point. PS is one of the most widely used plastics, after PE and PP, it can be naturally transparent, but can be colored. It is employed as protective packaging, containers, lids, bottles, trays, tumblers, and so on. Reverse polymerization of waste PS was realized obtaining styrene and other aromatics through MAP, using tyres or carbonaceous char as MW absorber [20–25]: Tyres may be employed if the final use of the liquid is as a diesel fuel, carbon if the liquid formed (styrene) must be directly used to produce new PS. Working at atmospheric pressure a clear and low viscosity liquid containing styrene as the major product was always collected together with a low amount of char and gas. Using a MW power of 3 kW and 100 g of PS together with 47.3 g of

carbon, it gave a liquid (yield 86.5 wt. %) containing a higher amount of single-ring aromatic compounds, as evaluated by Gas Chromatographic-Mass Spectrometric analysis (GC–MS) (aromatics C_6–C_{10} 93.9%, among which styrene is 66.0%) a char (yield 9.8 wt. %) and a gas (yield 3.7 wt. %). Improvements in residence time, by using low MW power or a fractionating system directly inserted over the oven and before the collecting system, allowed to obtain a liquid with low viscosity and density even if the char yield was increased to 10.0%. If the process was realized at reduced pressure (21.3 KPa) the liquid product was formed with a yield of 84.3 wt. % containing the monomeric styrene in a concentration of 71.9 % (determined by GS-MS).

Waste PS was also pyrolyzed in the presence of aluminum as MW absorber, at temperatures as high as the melting point of aluminum, obtaining styrene and other substituted aromatic compounds [22]. The rate of MAP and yield of the products was found to depend on the size, shape, and form of the aluminum. The reaction was faster using the coil, slower for strips, and negligible for the cylindrical form. The products of the pyrolysis were found to contain 88 wt. % of liquid (substituted benzene together with polycyclic aromatics and condensed ring aromatics), 9–10 wt. % of gas, and a low amount of char.

A pyrolysis process was also run in a batch reactor for MAP using activated carbon [21]. The quality of the oil from pyrolysis of PS was assessed for the possible applicability of the liquid in fuel production. The best conditions were a MW power of 450 W and a polymer/activated carbon ratio of 10:1, resulting in an oil yield of 93.0 wt. %. The liquid contained alkenes 8.4 wt. %, α-methyl styrene 1.0 wt. %, condensed ring aromatics 23.2 wt. %, and benzene derivatives 26.8 wt. %. The C_9-C_{12} aromatics were 93.0 wt. % while it was not reported the amount of styrene (C_8H_8) in the liquid.

3.1.4 Poly(vynylchloride) (PVC)

PVC is another largely used polymer obtained through radical polymerization of vinyl chloride. It is employed in two basic forms: rigid and flexible. The main uses are in construction for pipes, doors, windows, non-food packaging, food-covering sheets, and cards. It can be made softer and more flexible by the addition of plasticizers. In this form, it is used in plumbing, electrical cable insulation, imitation leather, flooring, signage, phonograph records, inflatable products, and many applications where it replaces rubber. Together with cotton or linen, it has been used in the production of canvas. According to its thermodynamic stability, the pyrolysis of PVC was obtained with the initial loss of HCl followed by cracking the hydrocarbon chain, so the gas contains HCl and low molecular weight hydrocarbons (ethene and propene) while the main compounds present in the liquid fraction were aromatic hydrocarbons such as benzene, toluene, dialkylbenzenes and so on, formed through Diels Alder reactions involving polyunsaturated compounds formed as intermediates in the course of the MAP process.

3.1.5 Polyesters

The most widespread synthetic polyester fiber is obtained by polycondensation of ethylene glycol and terephthalic acid (Polyethylentherephtalate: PET). It is also mainly used to produce bottles devoted to contain sparkling water and carbonated soft drinks due to the low permeability to CO_2. PET may be also disposed of through pyrolysis with the formation of a gaseous fraction containing carbon dioxide (22.7%) and carbon monoxide (13.3%) due to decarboxylation and decarbonylation of the ester groups [26] while the liquid product contains aromatic

hydrocarbons (benzene and toluene) and oxygenated compounds (benzoic acid, acetaldehyde, and benzaldehyde). However, the yield of liquid product was lower and PET may be more efficiently recycled through microwave-assisted reverse polymerization (hydrolysis) in the presence of methanol obtaining a high yield of ethene glycol and dimethyl terephthalate the monomer employed for the synthesis of PET.

The microwave-assisted reverse polymerization (hydrolysis) of polycarbonate (PC) in the presence of NaOH using tetrahydrofuran/water as solvent has been also reported [27] obtaining bisphenol-A, the main monomer employed for the synthesis of PC.

3.1.6 Polylactic acid (PLA)

PLA is a thermoplastic polyester formally obtained by condensation of lactic acid. It can be prepared by ring-opening polymerization of lactide, the cyclic dimer of the lactic acid. PLA has become a popular material due to its production from a renewable resource (lactic acid is industrially produced by fermentation of glucose, fructose, or galactose using lactic acid bacteria). Its widespread application has been hindered by numerous physical and processing shortcomings. PLA is the most widely used plastic filament material in 3D printing.

A reverse polymerization of PLA may be realized through MAP using different MW absorbers (tyre, carbon, Fe), apparatus set-up, and MW power [28]. A liquid rich in 3,6-dimethyl-1,4-dioxane-2,5-dione (lactide, one of the starting monomer for the production of PLA) and other oxygenated organic compounds were formed. The pure form of l-lactide was separated from the collected liquid by crystallization, while the meso-form of lactide remained in the mother liquors and was identified through GC–MS analysis. Up to 27.7% of lactide was obtained and might be recovered. Furthermore, simple acids such as acetic and propionic acids (up to 17.1 %), carbonyl compounds, and fragments of PLA backbone randomly cleaved were present in the liquid collected.

When the pyrolysis of PLA was run in the presence of tyres (used as MW absorber) the products showed the presence of cross-reactions between the intermediates formed from PLA and tyres affecting both yield and characteristics of the liquid. Aromatic compounds were formed from tyres pyrolysis and they improved the solvent properties of the liquid, preventying the crystallization of lactide.

3.2 Mixed plastics

In 2017 a proposal on friendly management of waste/contaminated polymeric materials from differentiated municipal solid waste collection through microwave-assisted pyrolysis [29] was reported to enlighten the properties and possible use of the main products formed.

Zou et al. [30] in 2021 reported the pyrolysis of plastic wastes with SiC as an MW absorber and it is a new, continuous MAP process for fuel production. Higher pyrolysis temperatures promoted the cracking of wax and lighter and more stable hydrocarbons were formed. Talc as a filler in commercial polypropylene showed high cracking activity. Incorporating ZSM-5 catalysts in the waste using a space velocity of 10 h^{-1} and a pyrolysis temperature of 620°C a yield of liquid of 48.9 % was obtained and this product consisted of 73.5 % of gasoline-range hydrocarbons rich in aromatics (45.0 %) and isomerized aliphatic hydrocarbons (24.6 %). However, the catalyst rapidly lost its activity using a feedstock/catalyst ratio of 5:1.

Microwave-assisted catalytic pyrolysis of municipal solid waste was reported by Yu et al. in 2020 [31] using a catalyst able to be regenerated. The catalyst was

employed in a fluidized bed pyrolysis furnace with a microwave generator. Data were not reported on the summary of the Chinese paper.

An artificial mixture of cellulose, paraffin oil, kitchen waste, and garden waste that closely mimic municipal solid wastes (MSW) was pyrolyzed at different reaction conditions [32] using MAP. Ten different MW absorbing materials such as aluminum, activated carbon, garnet, iron, silica beads, cement, SiC, TiO_2, fly ash, and graphite was tested. MAP was run up to 600°C, and the effects of MSW/MW absorber ratio and composition of the model MSW mixture were reported. The MW absorber affected the yields of oil, gas, and char, and played a catalytic role in altering the selectivity towards the various components present in the liquid. The oil contained oxygenated compounds (furans, phenolics, cyclic-oxygenates) from the biomass present in MSW, aliphatic, and aromatic hydrocarbons (mono- and polycyclics). Aromatic hydrocarbons were mainly derived from lignin decomposition while aliphatic hydrocarbons were derived from cellulose and plastic pyrolysis. The highest yield of oil (53 wt. %) was achieved with a 1/1 wt./wt. ratio of MSW/graphite. The energy in the oil corresponded to energy recovery of nearly 95 % with an 85 % deoxygenation. Using a high ratio of MW absorber/MSW monoaromatics such as benzene, toluene, xylene and styrene, and C_8-C_{20} aliphatic hydrocarbons were formed with high selectivity, while polycyclic aromatics were obtained with low selectivity. Methane, ethene, propene, isobutene, and hydrogen were the major products in the gaseous phase, whose selectivities varied with MSW composition.

MSW containing about 40 % of food was treated through MAP at different MW power [33]. The maximum oil yield of 30.2 wt. % was obtained under the optimized pyrolysis conditions: 400°C, residence time 30 min and a nitrogen flow rate of 50 mL/min at the microwave power of 450 W. Surprisingly the liquid contained oxygen, sulfur, nitrogen, and phosphorous containing compounds: methylphosphine [CH_3PH_2] (the main compound), 2-ethoxyethylenamine (CH_3CH_2-O-CH_2CH_2-NH_2], 2-methoxyethylenamine [CH_3CH_2-O-CH_2CH_2-NH_2], 2-fluoropropane [C_3H_7F], (2-hydroxyethyl) (trimethylsilylmethylen)sulfide [Me_3Si-CH_2-S-CH_2CH_2OH], and 1,3-bis(2-hydroxymethylen)urea [OC(NH-$CH_2OH)_2$] were identified and quantified by GC–MS analysis. The heating value of the oil was 23.94 MJ/kg.

3.3 Plastic composites

The MAP of some plastic composites such as end cycle tyres [34–39], multilayer packaging beverages, corn derived plastic bags, biomasses and so on have also been reported.

3.3.1 Tyre

Waste tyres are well known to have relevant disposal or reprocessing problems under environmental and economic sustainable conditions and their disposal is a challenge for industrial and academic research. Mechanical recycling to produce renewed tyres or granular tyres (employed in several fields such as athletics track, road paving, and so on) are followed but these processes use only a fraction of tyres to be disposed of. In this contest, pyrolysis represents a modern valid alternative to generate value-added products. Anyway improvements in the heat transfer technology are crucial to optimize the efficiency of the process itself. The use of MAP is one of the most promising heating technologies for their pyrolysis, due to MAP's ability to heat quickly and directly any MW absorbing material. Tyre contains a high amount of MW absorbing materials such as metal wires,

metal oxides, and carbon, and they quickly absorb MW and turn it into heat [12–19]. The process was performed in a short time comparing with traditional heating techniques [2]. Typical products were a char (yield 40.6-65.0 wt. %), a liquid (yield 20.7-44.0 wt. %) and a gas (yield 9.0-27.4 wt. %). MAP variables such as MW power, reaction time (15-100 min) and tyre mass, may strongly affect the properties of the products. The char was characterized through chemical (ultimate analysis and ion coupled plasma-mass spectroscopy (ICP-MS)), morphological (BET surface area, scanning electron microscopy), and X-ray diffraction (XRD) analyses. It contains a large amount of amorphous carbon (up to 92.0%) and inorganic compounds formed from additives employed in tyres formulation. XRD analyses of crystalline phases of char showed a marked MW effect: different crystalline ZnS forms, spharelite or wurtzite were identified. The presence of these compounds suggested that tyres were heated to a temperature higher than that one usually accounted. The liquid was a low viscosity oil (<2.9 cP, with a large amount of single-ring aromatic hydrocarbons) while the gas contains light hydrocarbons, hydrogen and only traces of N_2. The three products collected had a high calorific value, respectively 34 MJ/kg for solid, 45 MJ/kg for liquid, and 46 MJ/kg for the gas fraction. The most performing conditions were achieved using an MW power of 3 kW per 0.2 kg of tyres even if these conditions were not optimized.

The char from MAP of waste tyres contains iron and carbon. The iron may be separated using an electromagnet and sold as armonic steel (iron) while the carbon can be directly reused to produce new tyres, or used in many other production processes: as a pigment for the production of plastics, or textile printing, for printer toners, etc. It was also evaluated for Oxygen Reduction Reaction (ORR) in electrocatalysis [40]. The presence of different metals together with high carbon in char may produce synergic catalytic effects which are necessary for ORR. The char obtained from microwave-assisted pyrolysis of waste tyres represents a low-cost and friendly source of metals need for the preparation of the cell cathode for ORR.

The liquid is a fuel oil with low sulfur content (< 1%), formed in about 35% of the tyre treated. It contains aliphatic and aromatic hydrocarbons and may be used as marine diesel fuel or sent to a refining treatment to obtain any kind of fuel.

The gas contains hydrogen and low molecular weight hydrocarbons and may be employed as fuel gas or directly used to produce the electricity required for the process [41].

3.3.2 Multilayer packaging beverage

Multilayer packaging beverages are containers of composite material usually manufactured using five layers of materials: LDPE, Ink, Board, Aluminiun (Al), LDPE [42]. The most famous product is Tetrapack©. At the end of their life cycle multilayer packing beverages contaminated by the liquid present in the container, may be displaced through MAP using different MW absorbers (none, chopped tyre, carbon, and iron powder) and apparatus set-ups. Board was pyrolyzed forming water containing bio-oil where alcohols, aldehydes, acids, and anhydrosugars were present, according to pyrolysis conditions. LDPE was converted as reported in chapter 3.1.1, into a high viscosity liquid (wax), solid at room temperature, except when a fractionating system was directly connected to the pyrolysis oven. In these last conditions linear alkanes, alkenes, cyclic, and aromatic hydrocarbons were formed. Al was always recovered as unscratched samples.

3.3.3 Corn derived plastic bags

Europe introduced measures on the management of waste packaging in 2005 through the revision of Directive 94/62/EC and the introduction of the norm EN13432:2000 where it was specified the characteristics of bio-materials to be employed for plastic bags. These directives were adopted in Italy in 2011 and, as a consequence, the polyethylene base shopping bags were forbidden and replaced by bio-degradable materials. Bio-plastics are materials obtained from a vegetable source such as corn and they are largely used, especially those derived from corn starch with the aim to reduce world pollution. Their production requires starch destructuring, complexation, blending with specific synthetic and/or natural polymers, and the addition of compatibilizers, plasticizers, and other additives [43, 44]. This great variability of processing methods brings different types and grades of bio-polymers with a wide range of properties which allows their use in various fields [45].

Corn-derived plastic bags (CDP) are biodegradable and they may be disposed of through anaerobic digestion, however their energy and chemical content, required for their production, will be largely lost, only biogas was sometimes recovered. Furthermore, the biodegradation process is too long with respect to the time required for the biodegradation of the biomass present inside the container, usually derived from a waste collection. For this reason CDPs must be initially separated and then separately bio-degraded. In a greener process, these wastes may be employed for energy production with the recovery of their thermal content, but the atom economy of the process is very poor because the chemical content of CDP is lost. MAP of CDP was performed to evaluate the possibility to efficiently dispose of this waste obtaining a liquid useful as a source of chemicals and/or fuels. MAP was performed using different MW power, MW absorbers (carbon or Fe), and apparatus obtaining a liquid, a char, and a gas in amount depending on the pyrolysis conditions. Liquids were always separated into three phases: upper, middle, and bottom and deeply characterized. They contained a large amount of aromatic acid, phthalates, and their derivatives in the upper fraction; water (70 wt. %), organic acids, alcohols, anhydro-sugars, and their pyrolysis products were present in this fraction; bottom fraction showed close properties and composition than the upper fractions. The same classes of compounds were present in upper and bottom phases but in the last ones, these compounds were oligomers of those present in the upper fractions. Working with more drastic conditions bottom fraction was reduced while char yield was increased. MAP converted a waste CDP, even contaminated, obtaining some chemicals or even fuel thus avoiding to send them to anaerobic digestion for their transformation into carbon dioxide, methane, water, and a residue with a very low recovery of chemicals or energy. MAP process may represent a green solution to dispose of CDP recovering a liquid useful as a source of chemicals or employed to produce fuels. Furthermore, this process avoids the contamination of the soil improvement obtained by an anaerobic digestion with the residue of plasticizers present in CDP.

3.3.4 Waste electric and electronic equipment (WEEE)

The collection of waste electric and electronic equipment (WEEE) is largely and rapidly increasing, and even if WEEE is recycled today there are still valuable residues left after recycling, ending up in landfills. MAP may be a valuable way to recycle these components. Six different fractions (from light dust to particles sized of 7-12 mm) were pyrolyzed, producing an oil, a gas, and a solid residue [46]. A mass reduction was observed as a function of process time, independently on the reaction temperature for all of the WEEE treated.

WEEE from the envelope of end-life computers was pyrolyzed using different absorbers and set-ups in a multimode batch reactor [47]. A large amount of the liquid fraction (yield 76.6 wt. %) was obtained together with a strong reduction of the solid residue (yield 14.2 wt. %). The liquid fraction was characterized using Fourier Transform-Infrared Spectroscopy-Attenuated Total Reflection (FT-IR ATR), Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR), and quantitative GC–MS analysis. The liquid showed a low density, viscosity and contained a high concentration of useful chemicals such as styrene (up to 117.7 mg/mL), xylenes (up to 25.6 mg/mL of p-xylene) while halogenated compounds were absent or present in undetectable amounts.

Waste printed circuit boards (a fraction of WEEE) were also pyrolyzed using carbonaceous absorbers such as graphite or activated carbon [48]. Char was the main product (58 wt. %) and the presence of a high amount of absorber reduces the yield of tar and gas. Char contained phenolic compounds and phenylphosphates in significant amounts. CO_2 was the major component in the gas fraction, while the concentration of H_2 in the gas was increased when activated carbon was used as an absorber. The major metal-containing compounds present in char were Cu, Pb, Ti, while a lower amount of Bi, Fe, and Ca were present.

MAP of WEEE with bromine-containing compounds as flame retardant was also performed with special attention to the fate of these compounds. Conversion is increased with increasing temperature, reaching 93.3 wt. % at 650°C [49]. High pyrolysis temperature enhanced the transfer of bromine containing compounds to pyrolysis gas while the presence of K_2CO_3, Na_2CO_3 and NaOH mixed with the WEEE formed KBr and NaBr reducing the presence of HBr in the gas. Increasing heating time did not exhibit a remarkable influence on pyrolysis conversion: Working at 350°C, the main compounds in the liquid were phenols (91.1 %) while at 650°C, polycyclic and monocyclic aromatic hydrocarbons (except phenols) increased to 20.5 % and 19.0 %, respectively. Meanwhile, the non-condensable gases were composed of CO_2, CO, CH_4, and H_2 and they improved significantly with increasing temperature. Working in the presence of ZSM-5 and kaolin as catalysts, the monocyclic aromatic hydrocarbons (except phenols) and C_{11}-C_{20} compounds in the oil was increased while non-condensable gas was reduced.

A review of existing classical pyrolysis techniques for recycling of plastics in WEEE with special attention to the recovery of the products obtained (monomers, hydrocarbons, phenols, etc.) was reported [50]. Special attention was devoted to the processes to remove bromine containing compounds in the starting materials such as solvent extraction, supercritical fluid technology, and so on. Co-pyrolysis was also investigated and plastic wastes were displaced without the use of solvents or catalysts. The catalysts were employed to affect the distribution of the products and to enhance the removal of bromine containing compounds from pyrolysis oils.

4. Metal recovery from waste/contaminated plastics through MAP

Metal containing plastic has been treated with MAP to recover the metal and recycle all the other components like a solid, a liquid and a gas.

a. Several metals are present in waste or contaminated plastics, for instance, lead is present in the envelope of lead-acid battery realized using HDPE as the material of the container. At the end of life of the lead-acid battery the Pb of the electrodes and H_2SO_4 are recovered and recycled while the envelope must be disposed of as a contaminated HDPE because it contains Pb. This contaminated plastic may be pyrolyzed using a MAP process using carbon as an MW absorber. In the course of the process gas is formed (containing hydrogen and

low molecular weight hydrocarbons) together with a liquid (containing a small amount of water, and aliphatic hydrocarbons close to those reported in paragraph 3.1.1 on the MAP of HDPE). The char contains the MW absorber, the low amount of carbon formed from HDPE, and the lead present as a contaminant [51] and this char may be recycled as an MW absorber. For each recycle of the char, the concentration of lead is slightly increased every time. When an appropriate concentration of lead was reached the MW absorber was sent to a process for the extraction of the lead present, for instance through acid or metallurgical treatment, then the MW absorber may be recycled or in the case of carbon, used as a solid fuel together with the carbon formed from HDPE. In **Figure 2** is reported a schematic representation of the process.

b. An analogous process was employed to recover precious metals (i.e. Ag) present in some painted materials at the end of the life cycle of painted (for instance in the painted car bodywork). The plastic painted materials were pyrolyzed through MAP collecting a liquid employed as a fuel, a gas that may be burned to produce energy while the precious metal remained in the char together with the MW absorber. The char was recycled several times, up to an appropriate concentration of the precious metals was present in the char. At this point, the precious metal was recovered through a metallurgical process.

c. Using an analogous methodology the printed circuit board, a class of WEEE, has been treated to pyrolyze the plastic material recovering an oil containing a large amount of phenols [46] and a residue where are present, in a high amount, several metal containing compounds such as Cu, Pb, Ti, and minor amounts of other metal containing compounds including Bi, Fe and Ca.

d. Another application of MAP for the recovery of metal containing plastics is represented by pyrolysis of waste tyres. In this MAP [52], as reported in paragraph 3.3.1, harmonic steel (iron) present as a reinforcing material in tyre (about 5-10% of the tyre), remains in the char, from which it was recovered with an electrical

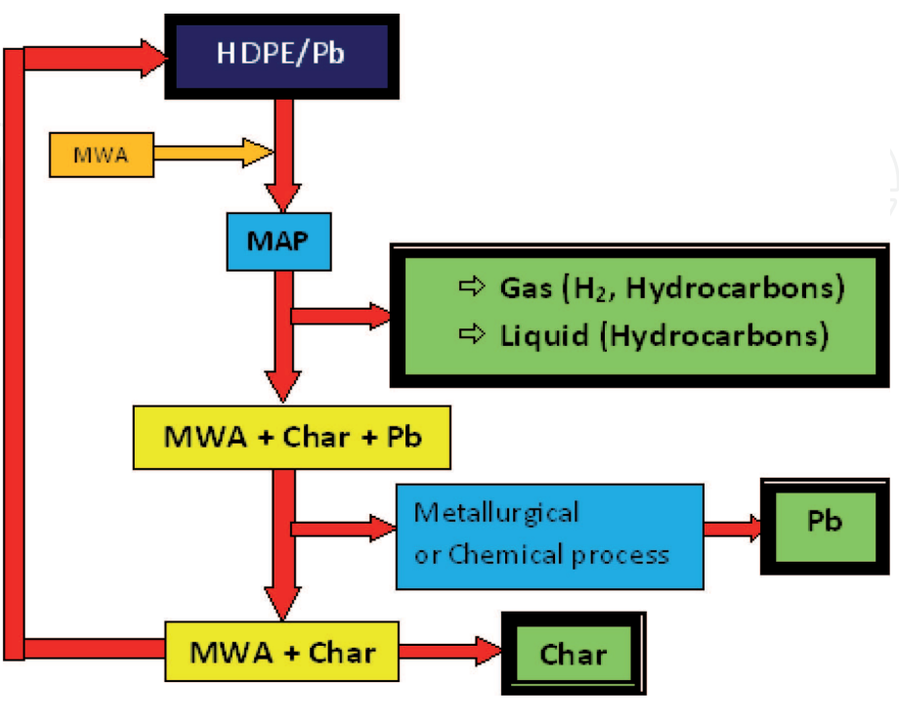


Figure 2.
A schematic representation on the MAP of lead containing HDPE to recover lead. MWA: Microwave absorber.

magnet and sent to a metallurgical process to enter in a new cycle of utilization. The char formed during the pyrolysis of tyre (recycled carbon, rCB) may be used to prepare new tyres or may be employed to prepare anode for Oxygen Reduction Reaction (ORR) [40] as previously suggested in paragraph 3.3.1.

5. Some industrial applications

a. Environmental Waste International (https://www.ewi.ca/tyre.html):

This company, since 1992, located in Whitby – Ontario (Canada), designs specialized eco-friendly waste reduction solutions and systems, using patented Reverse Polymerization processes and proprietary Microwave Delivery Systems. The recycle of scrap tyres has been a huge priority for EWI since 1994, demonstrating its capabilities. The results show the realization of a continuous feed system and its operation. EWI was able to prove the economic tyre recycling projections.

b. Molectra (https://wastemanagementreview.com.au/a-rubberised-archetype-molectra-technologies/):

This company developed a series of machines and a technique to process tyres extracting rubber in a fine powder format, which is unique (the name of the company means MOLECularTRAnsformation). The process comprises mechanical, chemical, and MW treatments. The residual carbon is pure (97.4 %) and can be crushed to form carbon black, which is used to manufacture new tyres, plastics, paints, inks, and batteries. Alternatively, the carbon can be converted into activated carbon for water purification, gold extraction, and air filtration. Another clever development is the inclusion of fertilizers and soil microbes into the char. The capacities can be 2-10 tons/h of processed tyres.

c. SBC (https://www.sbiofuel.com/downloads.html):

SBC pursues industrialization and commercialization of its proprietary and patented technology; the utilization of MAP of any material of hydrocarbon origin, being it any biomass, plastic, or rubber. The product strategies differ as a function of the markets and according to the maturity of technologies.

d. Tyrebirth s.r.l. - Italy (https://www.tyrebirth.com/en/):

Tyrebirth has developed, following proprietary patents [38, 53, 54] a very high-efficient recycling process that allows the creation of high-quality products through the MAP of end-of-life tyres. The Tyrebirth process produces solid, liquid, and gaseous products:

i. Solid - carbon black (rCB) - about 40% of the tyres treated. It has very high performances, it is dry, unpolluted and with quality characteristics 95% close to virgin carbon black. The rCB can be directly reused to produce new tyres, or used in many other production processes: as a pigment for the production of plastics, or textile printing, for printer toners, and so on.

ii. Solid - harmonic steel - about 10% of the production. This product has strong market demand. The steel is easily separated and delivered to steelwork for reuse.

iii. Liquid - Fuel Oil with low sulfur content (< 1%) - about 35% of the tyres treated. The liquid product is a low sulfur diesel marine oil and can be used in ships' diesel engines, in thermal plants for the production of electricity, and other specific installations.

iv. The gas – a mixture containing LPG gases and hydrogen. It is about 15% of the tyres treated. It may be used to produce more than 70% of the plant's electric energy required through cogeneration. The capacity of the plant is 540 Kg/h. Some pictures of the plant are reported in the following **Figure 3**.

e. Techwave s.r.l. - Italy (https://www.techwave.it/)

Techwave follows an innovative technological solution using proprietary patents of the MAP process [35, 39] to recover the material and energy content of waste plastic obtaining new materials from waste or contaminated plastics. The process is innovative, energetically sustainable, and has a low environmental impact. The innovation of the process is the use of microwave to supply the energy required by the process and a MW absorber, obtaining uniform heating of the material avoiding the problems of classical thermal heating. Another characteristic of the plant is its compactness because it may be installed in two standard containers (**Figure 4**).

f. Pyrowave - Canada (https://www.pyrowave.com/en/)

Pyrowave provides a unique technology using a MAP process [55] to regenerate post-consumer plastics by breaking them down into intermediate products that are used to make new plastics identical to virgin plastics, restoring their full value. Pyrowave paves the way to a truly circular economy of plastics. The regeneration of plastics allows for infinite recycling and avoids the Green House Gases associated with the extraction of virgin material.

g. Industrial co-operations

Some co-operation has been realized among companies and some important firms or institutions for chemical recycling of synthetic polymers, even if some of them, at this time, do not plan to use the microwave to supply the energy



Figure 3.
A picture of the Tyrebirth plant (by curtesy of Tyrebirth s.r.l.)

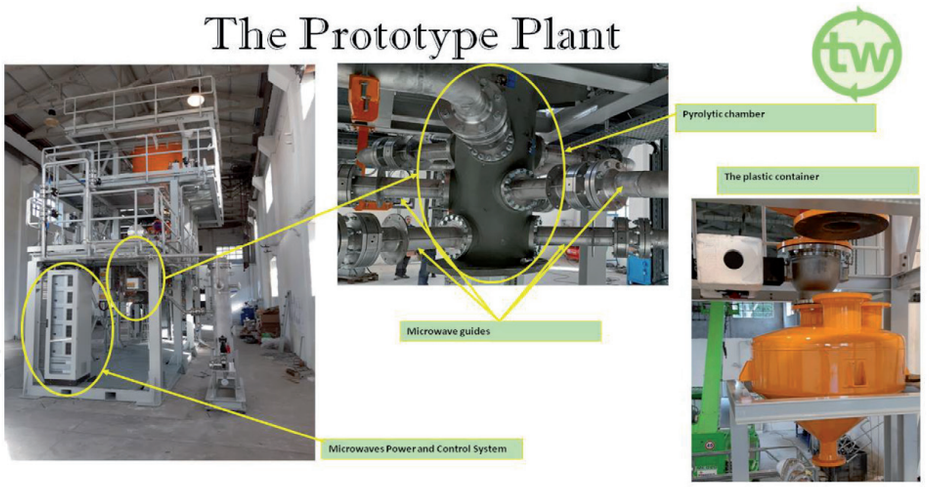


Figure 4.
Some picture of the prototype plant of Techwave s.r.l. (by curtesy of Techwave s.r.l.)

for the process, but the use of MW may lead to a better improvement of the process itself.

i. Montreal-based specialty recycling company Polystyvert (for the chemical recycling of polystyrene throw solvent dissolution) has closed a round of funding to facilitate the development of full-scale PS recycling plant [56]. Proceeds will be used to facilitate the development of a full-scale plant – a strategic milestone for the company to demonstrate the high level of purity reached by their products.

ii. AmSty, the largest PS producer in the Americas, and Agilyx Corporation a wholly-owned subsidiary of Agilyx AS (Euronext Growh – Oslo: "AGLX"), a pioneer in the advanced recycling of post-use plastics, announced an agreement to explore the development of a jointly owned advanced recycling facility of a 50–100 tons/ already in use at the parties' Regenyx joint venture where post-use PS products are converted back into virgin-equivalent styrene monomer.

iii. Versalis (Eni's chemical company) and AGR (an Italian company) have signed an agreement to develop technological innovations and new products and applications with recycled rubber [57].

iv. ReVital Polymers, Pyrowave and INEOS Styrolution are realizing a North American PS recycling consortium [58] to launch a closed-loop for recycling single-serve PS packaging using recycling technology pioneered by Pyrowave (a MAP process) obtaining styrene monomer used for manufacturing new PS products.

v. SABIC and Plastic Energy are set to start construction of world's first commercial unit to significantly upscale production of certified circular polymers derived from used plastic [59].

vi. BASF, Quantafuel, and REMONDIS have signed a Memorandum of Understanding (MoU) to jointly evaluate cooperation in chemical recycling including a joint investment into a pyrolysis plant for mixed plastic waste [60].

REMONDIS supplies suitable plastic waste to the plant and BASF uses the resulting pyrolysis oil as feedstock in its production.

vii. Neste successfully processed 400 tons of liquefied plastic waste at its refinery in Finland this fall (2021), an amount corresponding to the annual amount of plastic waste generated by 20,000 average European citizens [61]. Neste's target is to process over 1 x 10^6 ton of waste plastic annually from 2030 onwards.

viii. Techwave has evaluated the possibility to pyrolyze facemasks used for Covid19 pandemia in one of its microwave ovens using the MAP and a microwave absorber [62]. The facemasks were converted into the classical three products of a MAP (liquid, small amount of solid, and gas) having a composition close to those reported in the pyrolysis of PP. The possible contamination was absent in the products formed due to the pyrolysis conditions adopted.

ix. The Fraunhofer Institute UMSICHT, with SABIC and Procter & Gamble (P&G) start a collaboration to demonstrate the chemical recycling of used facemasks using a dedicated research pyrolysis plant [63]. The masks were first automatically shredded and then thermochemically converted to pyrolysis oil. Any residual pollutants or pathogens, such as the Coronavirus were absent in the products. The pyrolysis oil was employed by SABIC as feedstock for the production of new PP resin obtaining a high-quality PP.

x. The Techwave plant may improve the KuWert project [64] because the MAP-Techwave plant may be installed in two standard containers, so it may be installed on the ocean platform of the KuWert project or, more interestingly, on a ship devoted to collect the plastic present in the ocean [65]. In this last option, the ship may sail where a large amount of plastics are present, collect them, and immediately introduced into the pyrolysis plant present on board. In this way the waste plastics will be converted into useful materials, part of them employed to supply the energy required by the plant and the ship while the remaining fuel may be sold on the market to obtain the revenue need for the activity. After that the waste plastic may be immediately eliminated, avoiding the cost for their transport and only the final products may be sent to the market of raw materials.

xi. EEW Energy from Waste together with DSD plans to develop a new plant for processing mixed plastics and sorting residues [66] through chemical recycling. The process will be developped by the end of this year (2021) to process up to 200,000 tons/y of plastic waste.

xii. Borealis starts a new project for an increase on supply of chemically recycled feedstock for the production of more circular base chemicals and polyolefin-based products [67]. This research is carried out with project partner Stena Recycling and provided a successful feasibility study and final investment decision, operations are expected to begin in 2024.

xiii. Dow a global leader in materials science, and Mura Technology, the global pioneer of an advanced plastic recycling solution, announced a partnership

to keep plastic waste out of the environment [68]. The collaboration will support the rapid scaling of Mura's new HydroPRS™ (Hydrothermal Plastic Recycling Solution). This process can recycle all forms of plastic – including multi-layer, flexible plastics with the first 20,000 tons/y line expected to be operational in 2022.

xiv. LyondellBasell successfully starts up a new pilot Molecular Recycling Facility (*MoReTec)* at its Ferrara, Italy, site [69]. The pilot plant is capable of processing between 5 and 10 kg/h of household plastic waste.

xv. Repsol, Axens, and IFPEN, have joined forces to develop the pioneering and patented Rewind™ Mix process [70]: It purifies the plastics pyrolysis oils allowing the direct and undiluted processing in existing petrochemical plants for the production of circular plastics. Repsol, Axens, a worldwide technology provider and IFPEN, the renowned French research and innovation player in the field of energy, have developed a pioneering and patented process to enhance the chemical recycling of plastic waste and boost circular materials production. Pyrolysis is one of the most promising pathways for the chemical recycling of plastic waste, which otherwise the Rewind™ Mix process removes impurities such as silicon, chlorine, diolefins, and metals from the plastics pyrolysis oils produced, allowing the direct use as undiluted feed to petrochemical units.

xvi. Chemical recycling, has been developed by ExxonMobil to molecularly convert difficult-to-recycle plastics into the virgin-quality raw material used to make a wide range of valuable new products and potentially repeat the process over and over again [71]. The facility will have an initial capacity of 25,000 tons/y of plastic waste, with plans to scale up to 33,000 tons/y shortly.

xvii. DEMETO project: a Modular, scalable and high-performance DE-polymerization by MicrowavE TechnolOgy [72]. Based on an internationally patented technology, the project foresees to bring at industrial level (through a completely functional pilot plant) an innovative process, based on applying a new microwave technology to a well-known chemical reaction: the reverse polymerization (alkaline hydrolysis depolymerization) of PET.

6. Conclusions

This review shows several MAP processes proposed for friendly and economical disposal of waste/contaminated plastics to reduce the carbon footprint and obtain valuable products useful to close the cycle of a circular economy.

MAP is a very interesting way because it does not produce waste from chemical recycling of plastics but produces three classes of product: a char, an oil and a gas every one available as fuel or the source of new materials for the synthesis of new products. The process is self-sustainable from an energetic point of view rendering the process economically sustainable.

The interest of industrial companies in this field is improving day by day, as reported in the last part of the chapter because this is an important aspect for the realization of a truly circular economy and the reduction of the Green House Gas in the atmosphere.

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