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Chapter

Microwave-Assisted Pyrolysis Process: From a Laboratory Scale to an Industrial Plant

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Abstract

One of the great challenges for the European Union (EU) is the “Circular Economy Package,” and to achieve this goal, materials at the end of their life cycle must be recycled using a sustainable process. In this way, as a thermochemical treatment, pyrolysis represents a significant opportunity so long it leads to the recovery of both energy and chemical content of mixed, contaminated, or deteriorated plastics. An excellent history of an academic-industrial adventure started in 2008 at the Department of Chemistry of the University of Florence demonstrates the possibility of employing microwaves to recycle plastics to preserve their energy and chemical content. After that, Techwave started industrialization of the process in 2019, realizing a small-scale prototype followed by a full-scale pilot plant using different plastic materials (e.g., polystyrene, acrylonitrile-butadiene-styrene (ABS), and polypropylene). Nowadays, the plant may process 90 kg/h of plastics with a low formation of char and gas and an interesting amount of liquid useful as a source of chemicals or fuel because it has an LHV of 35–43 kJ/kg. The Microwave-Assisted Pyrolysis (MAP) is an industrial novelty in plastic recycling, and it looks very promising for a much more modern and innovative plastic waste recovery system.

Keywords: plastic, recycle, pyrolysis, microwave, polystyrene, ABS, polypropylene

1. Introduction

A real circular economy may be realized if products at the end of their life cycle are reutilized or transformed into raw materials giving them the possibility for another life. The energy balance among the content of the new products and that one required by the transformation must be positive; that is, the process must require less energy of those present in the products; otherwise, the process will have a deleterious effect on the environment. More positive is the balance less will be the contamination. This goal 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. These recycled sources also represent a strong driving force for developing sustainable

industrial processes. Many industrial firms are now involved in environmental issues, and they are, even in a different way, engaged in solving this problem [1].

The world plastic production in 2019 was 368.0×10^6 tons with an increase of 2.5% concerning for 2018 [2] while in the same year, the European production was 57.9×10^6 tons between thermoplastic and thermosetting polymers. Among them, polyolefins are the most produced and employed material in everyday life for industrial, domestic, and technological applications [3]. They are thermoplastic polymers and are mainly used for packaging; their life cycle is very short, which means they must be disposed of in a short time after their production. A less important amount of them is employed to realize furniture, insulating materials, automotive parts, and so on, and their life cycle is considerably longer (10 years or more).

A very recent study by the Organization for Economic Co-operation and Development (OCSE) was published in the “Global Plastic Outlook” [4] where it is reported that less than 10% of plastics are recycled around the world. Considering that the world production is estimated to be 460.0×10^6 tons, higher than the total waste (353.0×10^6 tons) produced in the same year, many actions are required to dispose of these plastics.

Mechanical recycle of polymeric materials is easily through environmental-friendly and economic processes, as reported in **Figure 1**. In this way, renewed objects are realized by recycled plastic materials avoiding disposal of these plastics through landfilling or combustion and reducing the use of mineral oil for their production. This process, however, may be applied only when a single plastic material is available, and it is not contaminated or strongly deteriorated. In the other cases, different environmentally friendly routes may be followed, such as thermochemical processes, thus contributing to the realization of a circular economy and reducing the emission of greenhouse gases

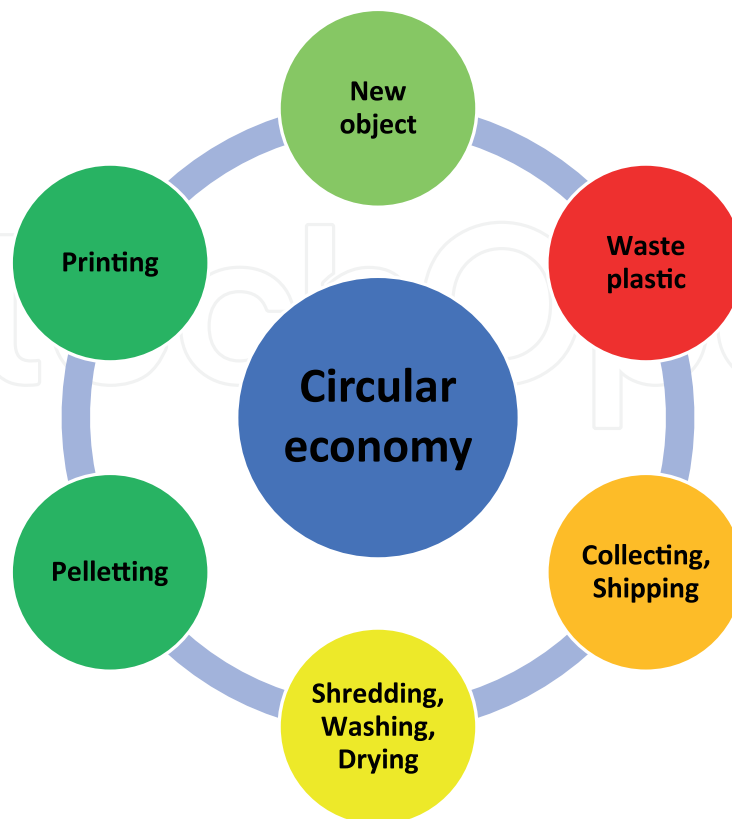


Figure 1.
Pathway for mechanical recycling of thermoplastic materials.

(GHG). Polymer thermochemical processes may supply fuels and chemicals using end life plastic materials as a feedstock, and it may be an alternative to oil-based raw materials [5]. These research studies led to the development of new technologies able to convert waste into resources minimizing the environmental impact of their treatment, avoiding the production of by-products, or limiting the amount of secondary waste.

Chemical recycling technologies [1, 6] are likely to play a crucial role in the transition toward a circular economy and close the recycling of materials giving compounds such as hydrocarbons, available for the production of new compounds. These technologies are able to remove hazardous substances, eventually present in the waste, thus giving new recycled feedstocks. Agreements with materials and chemical producers the use of raw materials from secondary sources are necessary for developing sustainable, feasible, and cost-efficient chemical recycling.

Among chemical recycling technologies, pyrolysis is one of the most important, also referred to as thermolysis or chemical recycling. It represents the transformation of organic materials, under the effect of heat, in the absence of oxygen. Depending on the process conditions, pyrolysis typically yields a mixture of molecules in the form of liquid or wax as the main products. This liquid or wax can be refined to obtain chemicals or fuels, as well as solid and gas may be used for the production of energy.

In this way, waste or contaminated plastic materials may be transformed into oil for industrial purposes, reducing the request and the environmental impact of mineral oil. The potential for recycling is enormous. In 2018, in Europe, plastic production reached almost 62.0×10^6 tons, and all this plastic should be utilized at the end of its life cycle, in one way or the others. For the oil industry, the use of waste plastic as an alternative feedstock represents a new business.

From a chemical point of view, pyrolyzed plastics are a good raw base material for the oil industry so long the remaining impurities are removed from the plastics, and the oil can be used as feedstock for oil refineries. Pyrolysis involves the use of heat and anoxic conditions to break down plastic waste into compounds containing smaller molecules, yielding valuable hydrocarbons in the form of liquid, waxes, and gases. The end products of pyrolysis can be monomers, heating oil, refinery feedstock, transportation fuels, and chemicals.

Chemical recycling can be mainly used to recycle mixed post-consumer plastic waste when sorting single components is not economical. That is, pyrolysis is a very flexible method that allows the use of various feedstocks. Another method of chemical recycling is gasification. This process converts carbonaceous materials into gases. The main product of gasification is synthesis gas (syngas: CO, and H₂), which can be further processed into various final products such as gasoline, diesel, methanol, and synthetic methane. Among these processes, the microwave technologies have taken large attention due to their high efficiency in supplying the energy required for a plethora of industrial processes. The main performances of the use of microwaves as correlated to a classical heating system are resumed in **Table 1**. Some examples of products obtained from pyrolysis of different polymers using Microwave-Assisted Pyrolysis (MAP) are reported in **Table 2**.

This chapter aims to offer a comprehensive description of the path from laboratory research to the realization of an industrial plant able to transform up to 2,000 Kg/d of waste plastic into valuable products. These products are available to synthesize new plastic materials, and they may be certified as renewed plastics. However, for plastic waste-based pyrolysis products to become a reality on an industrial scale, ardent development in technologies, value chains, and supporting legislation is needed. Despite these hurdles, the missing links in the plastic recycling loop can be addressed and eventually fixed to establish an actual circular economy for plastics.

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 carriers are sometimes used

Table 1.
Correlation between microwave and conventional heating.

Polymer	Products yield (Min-max) %			Ref.
	Solid	Liquid	Gas	
PE	0.4–0.6	80.2–83.9	15.7–19.2	[3, 7]
PP	9.1–12.0	56.5–74.4	13.3–34.4	[3, 5]
PS	0.9–16.7	73.5–96.1	3.0–9.8	[8–10]
PVC	13.9–53.2	10.2–70.8	13.3–75.8	[11]
PET*	15.6	41.3	38.7	[12]
PLA	2.6–7.6	28.4–57.7	38.5–69.0	[13]
Tyre	40.6–65.0	20.7–44.0	9.0–27.4	[14–17]
WEEE	14.2	76.6	9.2	[18]
MPB	24.9–59.9	31.1–43.7	9.0–42.5	[19]
CDP	11.1–30.1	22.3–47.6	28.7–46.2	[20]

PE: Polyethylene; PP: Polypropylene; PS: Polystyrene, PVC: Poly(vinyl chloride); PET: Poly(ethylene terephthalate); PLA: Poly(lactic acid); WEEE: Waste electric and electronic equipment; MPB: Multilayer packaging beverage; CDP: Corn-derived plastic bag. Pyrolysis using classic thermal heating.

Table 2.
Products obtained from microwave-assisted pyrolysis of plastics.

A circular economy is one of the drivers boosting chemical recycling because it may realize, more and more, so reusing all waste materials. Chemical recycling, such as pyrolysis, is therefore needed, but legislative issues are required for this big challenge of improving the development of this technology.

2. Scale-up of the MAP process

2.1 Preliminary studies of MAP process

Techwave s.r.l. is an Italian start-up established to realize an industrial plant from a patent able to transform, by means of microwave, plastic complex polymers into their original components, ready for a new use. The process is based on an Italian proprietary patent [21] of Cooperativa Autotrasportatori Fiorentini (CAF Scrl-Italy) developed and filed by a research team of Department of Organic Chemistry – University of Florence – Italy, in 2011, and converted into a European patent [3] acquired by Techwave in 2018.

Experiments were started in 2008 at the Department of Organic Chemistry “Ugo Schiff,” University of Florence, where a set of trials were performed on tires and various types of plastic materials, ranging from polystyrene (PS) to polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), poly(vinyl chloride) (PVC), and their mixtures [22]. Similar experiments were also performed on Waste Electric and Electronic Equipment (WEEE) [18].

Pyrolysis studies were initially performed on a laboratory scale (**Figure 2**). The experiments were carried out on a batch oven, and 100–300 g/h of materials were processed. The oven was equipped with four external MW generators, each having an absorption of electric power of 2 KW capable of delivering up to 6 KW of microwave power inside the oven, operating at the frequency of 2.45 GHz.

During the experimental trial, many arrangements were tested to determine the influence of several parameters on the quantity and quality of the three products formed: a liquid, an uncondensable gas, and a char. In particular, it was verified how some critical factors such as the residence time inside the pyrolytic oven, the temperature reached, and the type of downstream fractionating system would affect the amount and the composition of the three products of the reaction. The liquid may be employed for the synthesis of new polymeric products (**Figure 3**), while the gas and char may be used as fuel or employed for other uses [1].

This first study showed MAP as a suitable technique for cracking various types of plastic even if they may be highly contaminated and absolutely heterogeneous. The results obtained led to the publication of various scientific papers and process patents

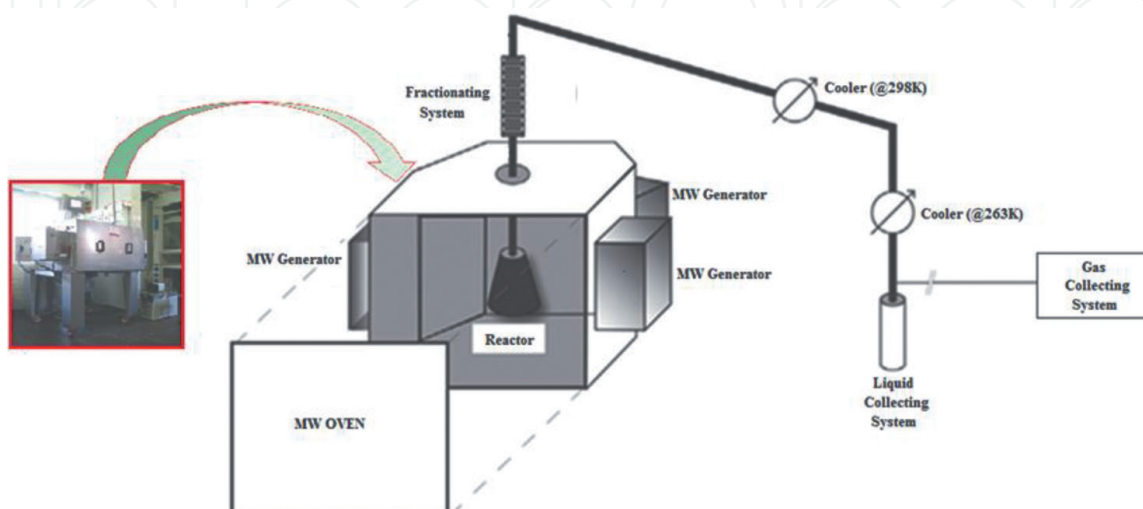


Figure 2.
Laboratory MW oven.

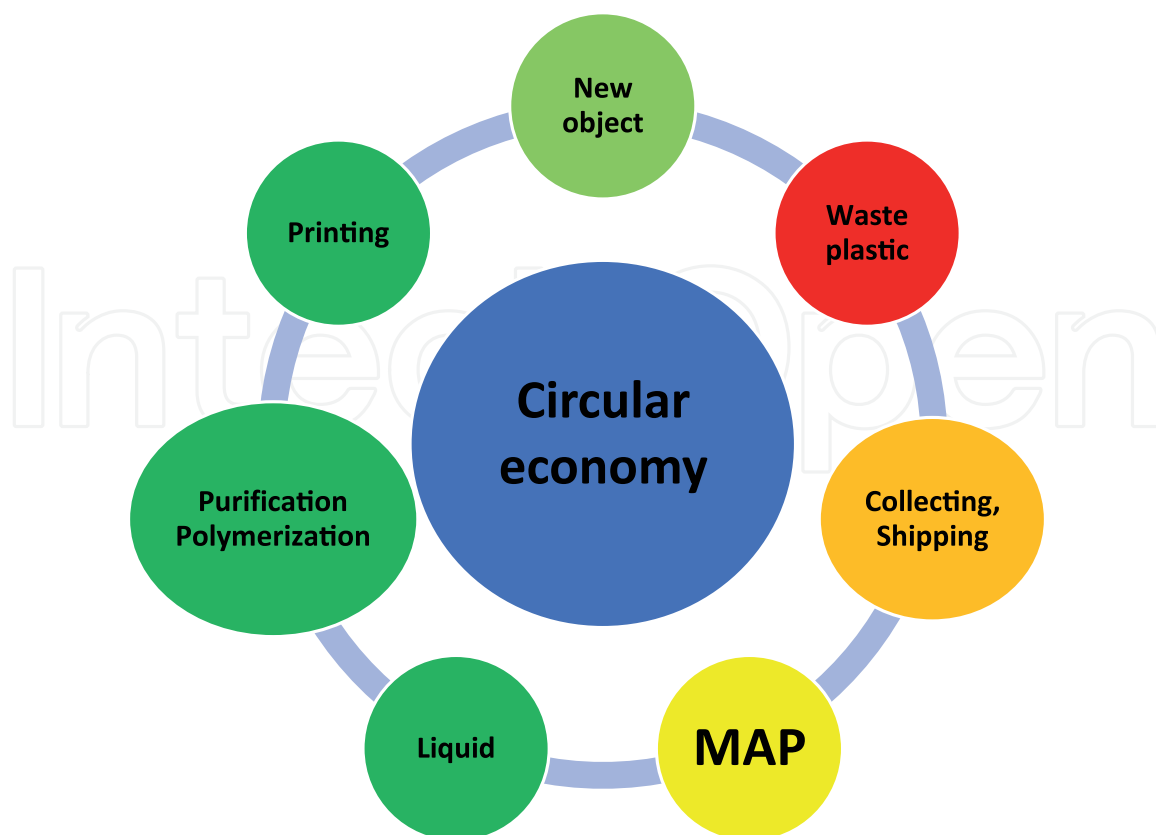


Figure 3.
The circular economy using a MAP process for polymeric waste materials.

(Table 2) and the identification of the guidelines for the scale-up of MAP technology to an industrial level [1].

2.2 The pre-industrial prototype

Therefore, a first development phase was run for this purpose, to design and then build a prototype that allows the scale-up of the MAP process, enabling the transition from the experimental laboratory studies carried out until today to a pre-industrial phase. The idea, born at the University of Florence and initially funded by one of Techwave's future partners, was materialized in 2016 with the construction of the first pre-industrial prototype (Figure 4).

This prototype was initially designed for the treatment of End Life Tires (ELTs) and was able to process [14–17] whole tire (approx. 8 kg) in 30 minutes. The prototype was equipped with electric heating to bring the material to the optimum temperature for the absorption of microwaves and four external MW generators, each supplied with electric power of 1 KW and able to deliver up to 3.2 KW of microwave power inside the oven, operating at the frequency of 2.45 GHz. Later with the birth of Techwave in 2018, it was decided to continue the scale-up of the MAP process by extending the technology to other waste plastic materials, even if mixed or contaminated. The results obtained during the first testing phase are described in the following paragraph.

2.3 Experiment with pre-industrial prototype for scale-up of MAP

The purpose of this initial phase was the validation of the data reported on the laboratory scale, both in qualitative and quantitative terms, from the pyrolysis of



Figure 4.
Pre-industrial prototype.

plastic wastes. It also aimed to determine the operating parameters necessary to treat flows of various types of plastic materials at the end of their life cycle, and PS was chosen as the first example. Polystyrene, like all plastics, is unable to absorb microwave energy and convert it into heat. It must therefore be blended with a microwave absorber to realize the pyrolysis. The materials used as a microwave absorber are commonly carbon or iron powder.

The experiments were carried out using expanded polystyrene (EPS) as starting material and focused on analyzing the ratio between the amount of polystyrene processed and the microwave power used. Therefore, an energy density close to that foreseen in the prototype was used to acquire the information necessary for the design. The process was also studied to correlate the overall yield of the process and the composition of the products to the operating parameters. The data obtained are reported in **Table 3**.

In all experiments, polystyrene was mostly converted into a liquid using mainly iron powder as a microwave absorber. Working at low power, the energy is not enough to start the pyrolysis process (EXP 1–3). Even by preheating the pyrolysis chamber through electrical resistances, the liquid yield is low (EXP 4). Instead, it can be noted that under the same reaction conditions, but using carbon as an absorber, the liquid increases considerably (EXP 5) confirming carbon as a better MW absorber. To obtain good yields of the liquid, it was necessary to increase the power (EXP 6–12), working with a ratio microwave power/PS of approx. 4.8–9.6 kW/kg. Analyses carried out on the liquid samples of the most significant tests showed aromatic hydrocarbons as the main compounds, among which single-ring aromatic compounds such as styrene, toluene, ethylbenzene, and α -methylstyrene were present in very high amounts. Styrene was the compound present in the highest percentage (approx. 55–70%). The results confirmed the previous studies carried out at the laboratory level [8–10], albeit working with a considerably lower MW power than that one previously employed in laboratory experiments (4.8–9.6 vs. 30 kW/kg), and made it possible to develop the application of the MAP process of PS on an industrial scale.

2.4 The industrial prototype plant

The experiments with the pre-industrial prototype were run to collect process information for the realization of the industrial plant. Thanks to the collaboration between Cognito Engineering srl and the Department of Chemistry of the University of Florence, in 2019, Techwave built its first experimental industrial prototype following the scheme reported in **Figure 5**. The plant was installed in its factory in Massa (Italy) (**Figures 6–8**).

Exp. N.	PS (kg)	MW Abs*	PS/ Abs	MW power (kW)	Total time (min)	Electrical time (min)	MW time (min)	Liquid (%)	Gas (%)	Solid (%)	Styrene in liquid (%)
1	1.26	Fe	2.0	1.2	30	0	30	0.0	0.0	0.0	0.0
2	1.26	Fe	2.0	1.2	62	20	42	0.0	0.0	0.0	0.0
3	1.26	Fe	2.0	2.4	90	28	62	0.0	0.0	0.0	0.0
4	1.13	Fe	1.8	2.4	80 ^a	80	60	25.2	56.6	18.2	56.5
5	0.75	C	2.0	2.4	60 ^a	60	45	82.4	15.3	2.3	57.5
6	1.13	Fe	2.0	4.8	90	0	90	64.6	24.8	10.6	69.5
7	1.01	C	2.3	4.8	60	0	60	56.7	24.4	18.9	55.6
8	0.98	Fe	2.0	4.8	80	25	55	71.9	17.9	10.2	55.5
9	0.98	Fe	2.0	4.8	90	90	60	71.9	18.9	9.2	54.7
10	0.49	Fe	1.9	4.8	75	75	30	44.1	24.3	31.6	62.1
11	0.49	Fe	1.9	4.8	90	90	45	62.9	21.8	15.3	59.6
12	0.98	Fe	2.0	4.8	80	80	45	55.6	22.4	21.9	68.2

*MW Abs: Microwave absorber.

^aElectrical and MW heating work at the same time.

Table 3.
MAP of PS: operating parameters.

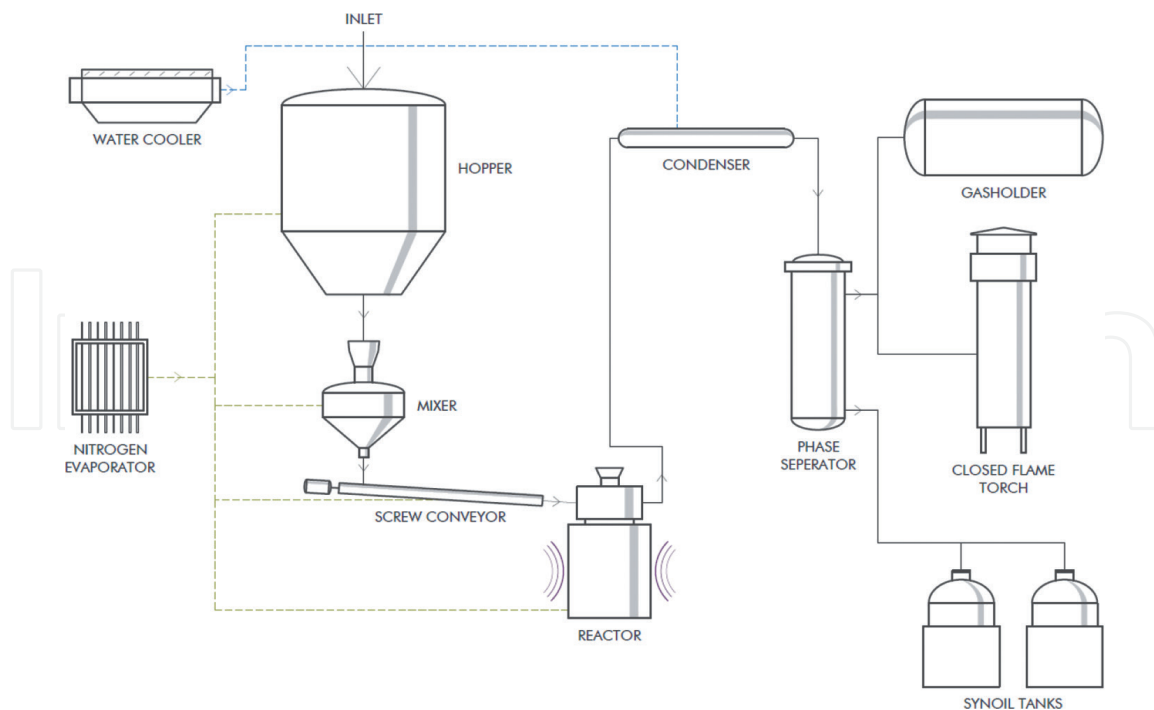


Figure 5.
Flow diagram of MAP process.



Figure 6.
Industrial prototype plant.



Figure 7.
Plastic container located in the upper part of the prototype.

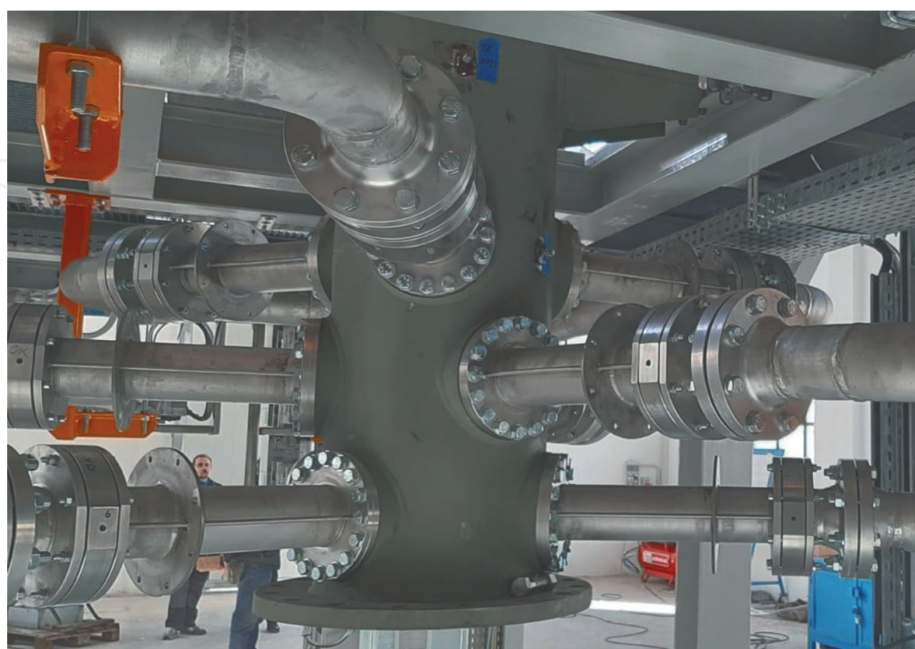


Figure 8.
MW oven located in the bottom part of the prototype with, in front, the microwave guide.

The prototype was realized considering its possible introduction in two standard containers for easy shipping, even if its dimension may be strongly scaled up if required. Taking into account the dimension, it may be installed on one small ship. Waste plastic materials are largely present in the sea [23], and they may be collected and immediately disposed of through this plant or another plant close to this. The products formed may be employed to produce the energy required, while the excess may be sold on the market. Furthermore, a plant of this dimension may be installed in a municipal collecting and selection center of waste plastics, where it may be employed to pyrolyze the mixed plastics collected, avoiding their sending to a disposal plant. The prototype may be useful also for a large hospital to dispose of the contaminated waste plastics. The pyrolysis products do not contain dangerous contaminants because the biological products are destroyed during the process as reported in the literature [24, 25] while the chemicals formed may be sold for their commercial uses. In 2020, the plant started testing operations using EPS, ABS, or PP as plastic materials. Tests were carried out for 1 year, improving the results step by step, both in terms of plant efficiency and the quality of the secondary raw materials produced. The description of the tests carried out and the results obtained are reported in the following paragraphs.

2.5 Experiment with industrial prototype plant

The description shows how the tests for the MAP process were run in the industrial prototype with the plant working in semi-batch mode. The amount of plastic and carbon black for a single test was taken from the storage area. The carbon black required for the absorption of the microwave was manually introduced into the pyrolysis reactor, while the plastic material was added through the plastic loading system.

Experiments were carried out in an inert atmosphere (nitrogen), realized through various vacuum/nitrogen cycles. The carrier gas was not used to avoid the dilution of the uncondensable gas with the carrier gas. At the end of the purge operations, the plastic material was loaded into the pyrolysis reactor by a screw conveyor and the electrical resistances were switched on to preheat the reactor. Then, they were switched off, and the microwave generators were switched on.

The plastic thermal degradation formed hydrocarbon vapors conveyed to a cooling system. The higher boiling fraction was condensed and collected in the bottom of the cooling system, while the low boiling fraction, together with uncondensable gas, was sent to a torch. During the pyrolysis, further amounts of plastic material were added to the reactor constantly. At the end of the process, the microwave generators were switched off. When the plant was returned to room temperature, vacuum/nitrogen cycles were repeated as described above. At the end of this operation, the solid fraction was collected from the bottom of the reactor. The process was completed, and a new pyrolysis cycle could be started.

In the experiment, the microwave launch system was studied and modified several times until it reached the optimal configuration. The experiments let to identify and refine some operational parameters of the MAP process for improving the yields and quality of pyrolysis products. **Table 4** reports the operating parameters of the most significant tests. Microwave power is critical in MAP as it must provide enough energy to break the polymer bonds and start the thermal degradation process. Comparing the data in **Table 4**, an increase in MW power allowed to treat a double amount of plastic with the same reaction time (PS1, PS3, and PS4).

Entry ^a	Plastic ^b (kg)	Power (KW)	Time (min)	Liquid (wt%)	Gas (wt%)	Solid (wt%)
PS1	8	6;12 ^c	210;15 ^c	94	4	2
PS2	32	12	310	95	3	2
PS3	20	12	280	89	6	5
PS4	38	18	272	98	1	1
ABS1	75	18	221	67	23	10
ABS2	69	18	225	68	28	4
PP1	61	18	237	81	12	7
PP2	70	18	230	86	7	6

^aPS: Polystyrene; ABS: Acrylonitrile/Butadiene/Styrene rubber; PP: Polypropylene;

^bAbsorber 1.8 kg (in all tests);

^c6 KW for 210 min then 12 KW for 15 min.

Table 4.
Operating parameters of the most significant tests.

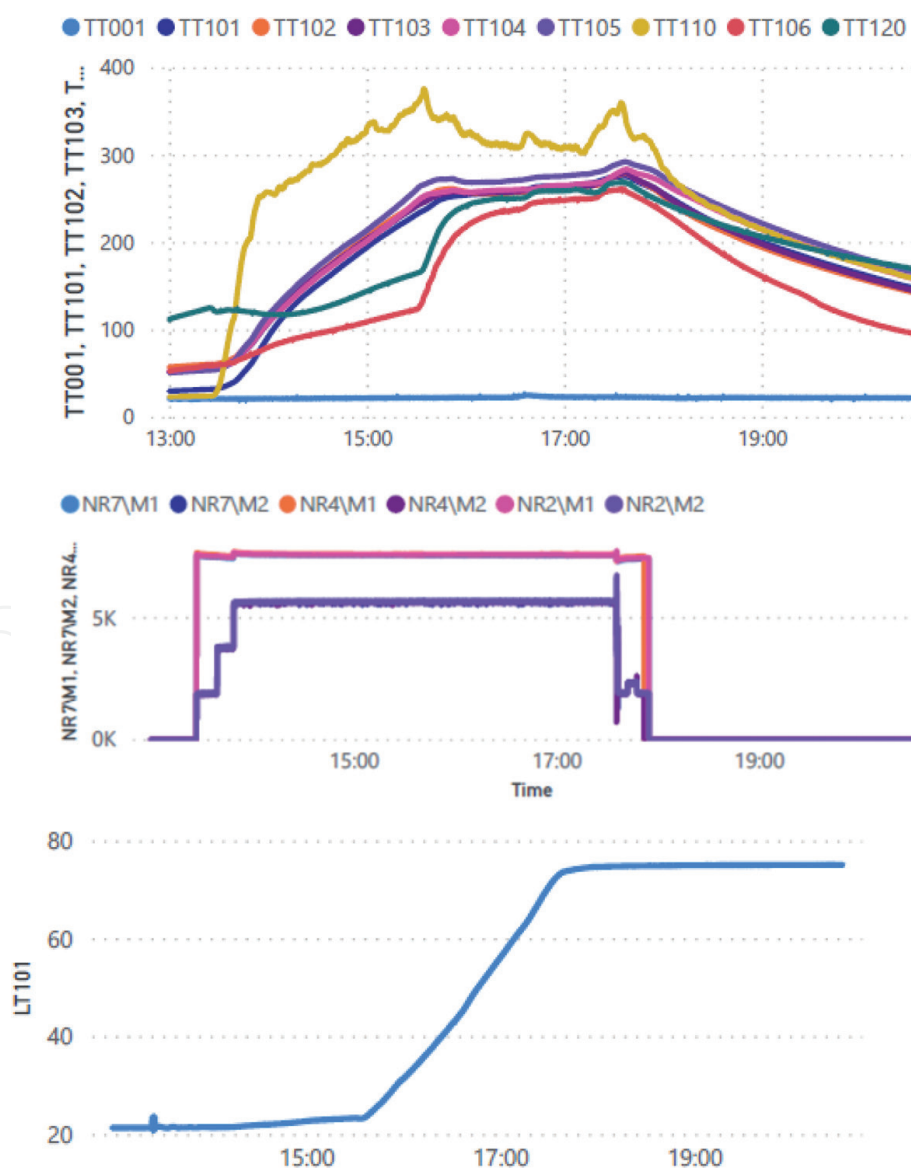


Figure 9.
From top to bottom: temperatures log, microwave power log, and level liquid log produced in MAP of ABS2.

Once the microwave launch system was fine-tuned, the design of experiments (DOE) was planned to optimize the plant productivity, using various types of plastic materials (PS, ABS or PP, **Table 4**). By way of example, the logs of temperatures, microwave power, and liquid level produced during the MAP of experiment ABS2 are reported in **Figure 9** to describe the evolution of the pyrolysis process. Although the temperature plays an important role, this parameter is detected with high uncertainty in microwave pyrolysis [26]. For this reason, the process was followed by monitoring the temperatures recorded by the probes located in several areas of the plant.

The probes from TT101 to TT105 were arranged on the reactor from top to bottom: on the bottom of the reactor was the TT110 probe. The temperature of the vapors generated during pyrolysis was recorded by the TT106 on the condensation pipeline, located after the exit from the reactor. The TT120 probe monitors the electrical resistances of the preheating reactor. All the probe temperatures were referenced to the TT001 corresponding to the ambient temperature.

When the reactor was heated at the prefixed temperature by the electrical resistances, these resistances were switched off while the microwave generators were turned on. Following the curves of the temperature probes on the reactor, it was possible to see how the temperature rose suddenly. During this phase, the carbon black absorbed the microwaves and transferred the heat to the plastic material, which starts to melt. As the process went on, the temperature curves of the reactor reached a value corresponding to the start of the thermal degradation of plastics and consequent generation of hydrocarbon vapors, as could be seen from the TT106 curve. At the same time, the LT101 level curve increased due to the condensation of the vapors and liquid was collected.

When the plant was in full operation, the TT101–106 curves remained constant, and the level LT101 of the liquid in the container continuously grew until the microwave generators were switched off, so the system was cooled, and all temperatures started to decrease when the industrial plant works in the best operating conditions, let to treat 33 kg/h of waste plastic.

3. Analysis of feedstock and products of the MAP process

As described above, the plant can carry out the MAP process of waste plastic materials at the end of its life cycle, from which three types of products were obtained (liquid, solid, and gas). During the experiment, samples were collected for each type of material for their characterizations. These analyses provided useful information to establish the quality and commercial value of the products formed. The following paragraphs report for each type of polymer tested, a description of analysis results, both for the starting material and the products obtained from the MAP.

3.1 Plastic materials used in MAP process

For each plastic material evaluated during the experiments, thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) were carried out to obtain information on the polymer composition, stability and consequently predict the yield of the pyrolysis products. Specifically, TGA and DSC are two thermal analyses used to characterize polymers. TGA variations measure the weight loss of a sample subject to a constant increase in temperature to quantify the products formed, including gaseous emissions, while DSC measures phase transitions such as melting point and glass transition temperature.

3.1.1 Expanded polystyrene (EPS)

The polystyrene sample was shredded before being analyzed (**Figure 10**). Two thermal ramps were employed for the TGA/FTIR analysis, the first at a rising temperature of 20°C/min in an inert atmosphere followed by an isotherm in an oxygen atmosphere. The thermogram shows a single weight loss of 99.8 wt % related to the organic part of the polymer and a final residue equal to 0.2% attributed to inorganic impurities present (**Figure 11**).

The FT-IR spectrum of the gas released during the degradation of the polymeric component is reported in **Figure 12**. The spectrum of the gas released at a



Figure 10.
EPS sample before (left) and after (right) shredding for TGA analysis.

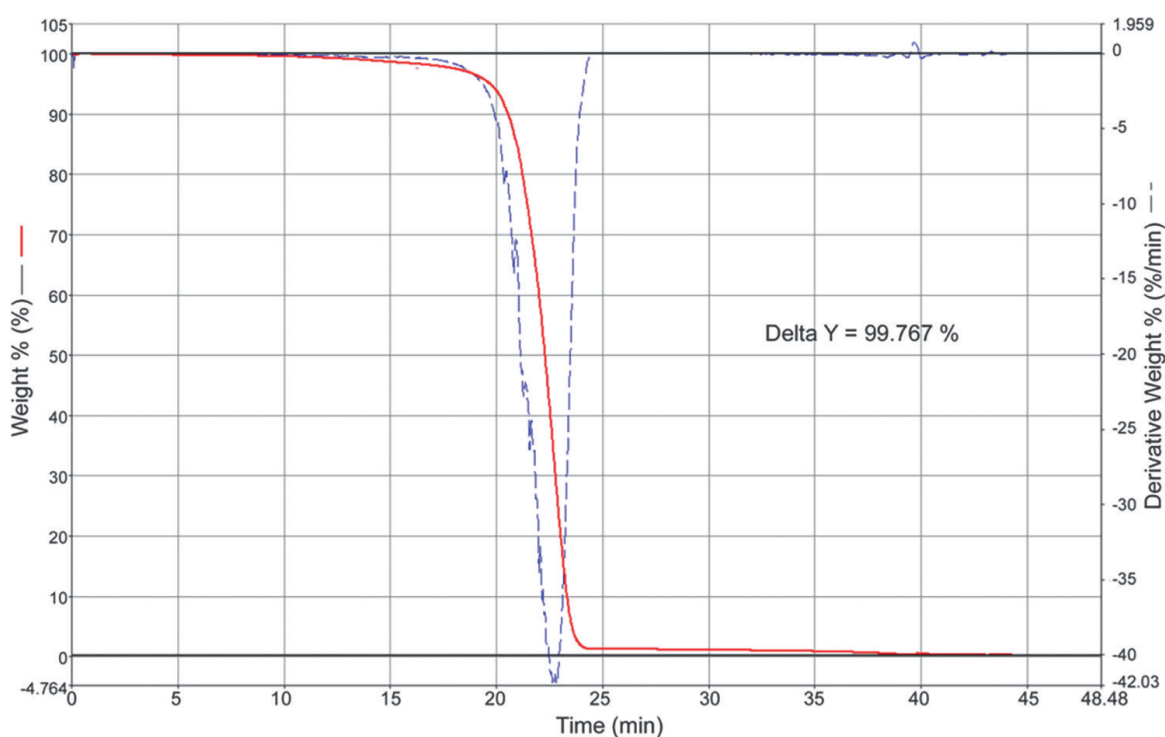


Figure 11.
TGA analysis of EPS.

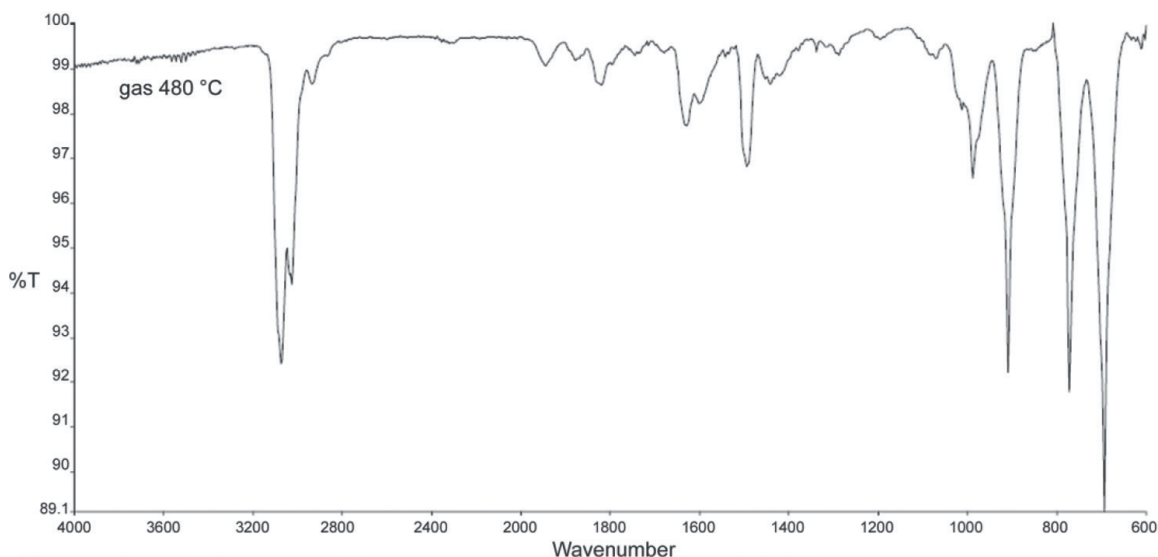


Figure 12.
FT-IR spectrum of the gases released during the TGA analysis of EPS.

temperature of 480°C shows the typical signals of hydrocarbons due to the degradation products of polystyrene. The degradation occurred by both end chains and random cleavage and gave only aromatic compounds such as styrene monomer and oligomers, benzene, and toluene. The spectrum shows the typical frequencies of aromatic compounds, such as the stretching of the C-H bond at 3000 cm⁻¹, the stretching of the aromatic double bond at 1600–1450 cm⁻¹, and the signals between 900 and 700 cm⁻¹ of the aromatic C-C backbone.

The sample was also subjected to DSC analysis, using three thermal ramps in the temperature range from -10 to 200° C, alternating heating-cooling-heating, in an inert atmosphere. The DSC analysis (**Figure 13**) shows the presence of a peak at about

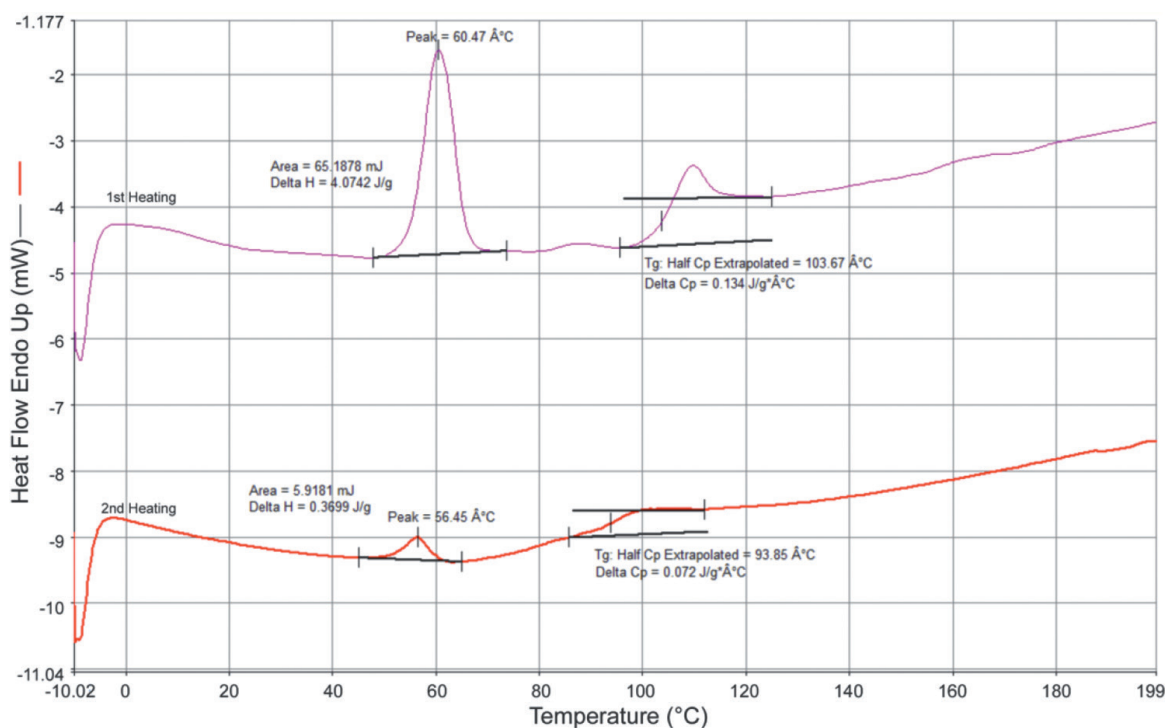


Figure 13.
DSC analysis of EPS.

60°C, which almost completely disappears in the second heating, probably due to the memory effect or to the presence of traces of volatile compounds in the sample, not visible in the TGA analysis. Furthermore, the sample shows a temperature glass transition at about 94°C, which agrees with the classical T_g of polystyrene. The TGA and DSC analyses show that the sample is essentially polystyrene with probable traces of volatile substances and a small percentage of inorganic impurities.

3.1.2 Acrylonitrile-butadiene-styrene rubber (ABS)

The sample was analyzed without any pretreatment. Two thermal ramps were adopted for the TGA analysis, the first at a rising temperature of 20°C/min in an inert atmosphere followed by an isotherm in an oxygen atmosphere. As can be seen from the thermogram (**Figure 14**), the following weight losses were recorded:

- at about 330°C, weight loss of 8.2 wt%;
- between 400 and 530°C, weight loss of 78.3 wt%, associated with the degradation of the polymeric component;
- at 700°C, weight loss of 2.5 wt% associated with the degradation of inorganic compounds;
- at 800°C after the switch in the atmosphere of O₂ weight loss of 3.3 wt%.

At the end of the analysis, a final residue of 7.7 wt% of the sample was present and associated with inorganic compounds that do not degrade up to this temperature.

The FTIR spectrum of the gas released by the sample during TGA analysis is reported in **Figure 15**. In the FTIR spectrum of the gas released at 330°C (black line) is present only the emission of CO₂, probably due to the degradation with the temperature of inorganic compounds present in ABS. At 440°C, the FTIR spectrum shows signals associated with degradation products of a carbonate containing ABS.

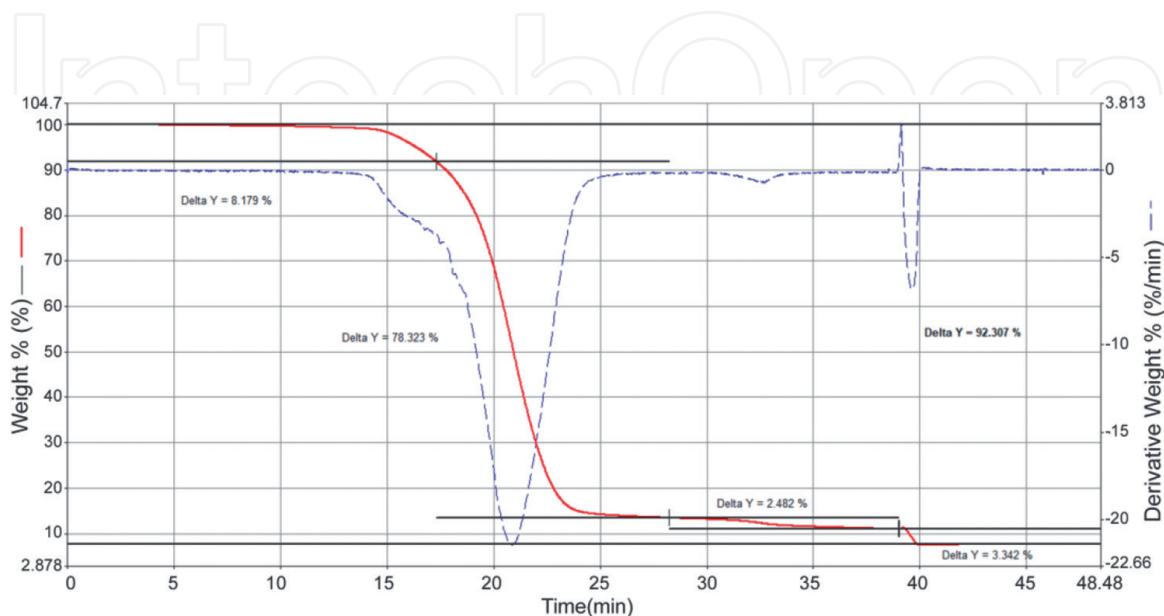


Figure 14.
TGA analysis of ABS.

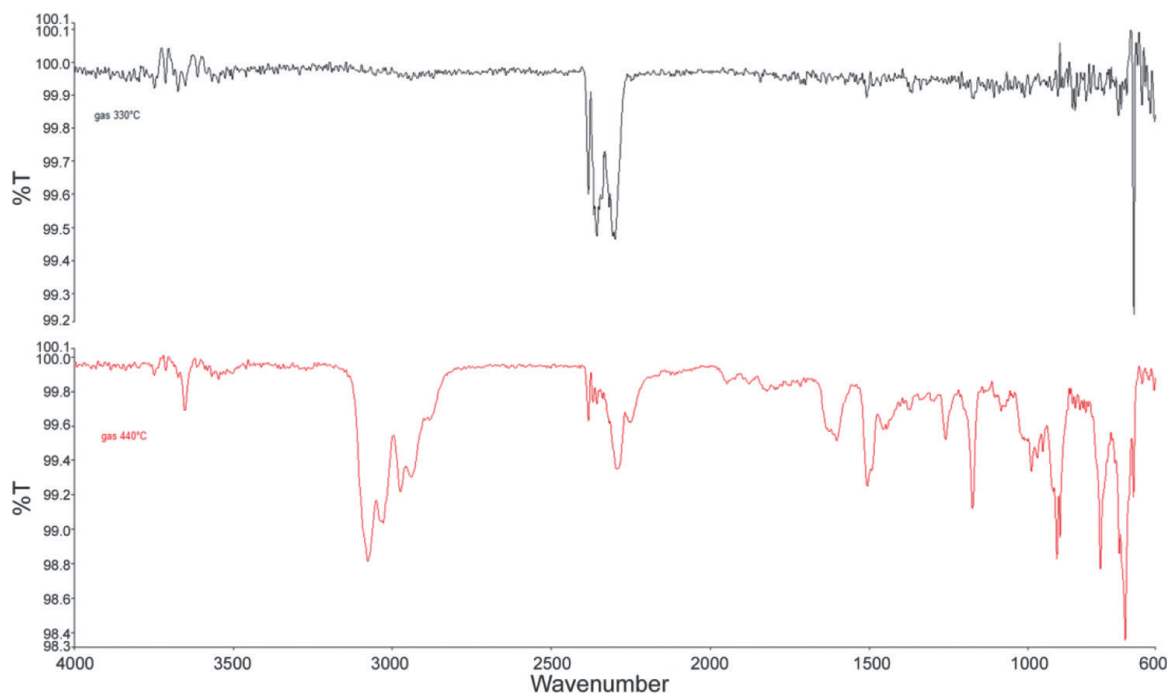


Figure 15.
FT-IR spectra of gases released at 330°C (black) and 440°C (red) during the TGA analysis of ABS.

As reported in the literature, the thermal degradation of ABS polymer begins at 340°C with the formation of the butadiene monomer. The aromatic compounds begin to be noticed at 350°C, a temperature at which the degradation of polybutadiene units is still evident. As the temperature increases, the formation of styrene becomes more important, and at 420°C, the intensities of the C-H bands of butadiene and styrene are approximately equal. At higher temperatures, the presence of aromatics decreases in intensity while that of butadiene is very strong. The evolution of acrylonitrile begins at about 400°C and ends at 450°C [27].

According to the above description, the spectrum of gas released at 440°C (Figure 15, red line) shows the stretching of aromatic C-H at 3100 cm^{-1} , and aliphatic C-H stretches at 2900 cm^{-1} and the stretching of the nitrile group at approx. 2200 cm^{-1} . Another sample of ABS was crushed and subsequently subjected to DSC analysis, running three thermal ramps in the temperature range from 25 to 300°C, alternating heating-cooling-heating, in an inert atmosphere. DSC analysis shows a glass transition at $T = 108.25^\circ\text{C}$ (Figure 16, red curve) associated with the styrenic portion typical of acrylic copolymers such as acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), or acrylonitrile-styrene-acrylate (ASA), a glass transition at $T = 124.08^\circ\text{C}$ associated with polycarbonate present and a glass transition at $T = 162.42^\circ\text{C}$ associated with ABS.

From the DSC and TGA/FTIR analyses, the sample is a polycarbonate containing ABS (78.3%) with small quantities of polypropylene.

3.1.3 Polypropylene (PP)

Propylene experiments were carried out using single-use masks as a sample of PP. The single-use masks were cut to separate the non-woven polypropylene from the elastic bands, and the two samples were analyzed separately by DSC. For each sample, three thermal ramps were performed in the temperature range from -10 to 300°C , alternating heating-cooling-heating, in an inert atmosphere. Measurement of the glass transition temperature, (T_g), of polypropylene is generally considered difficult

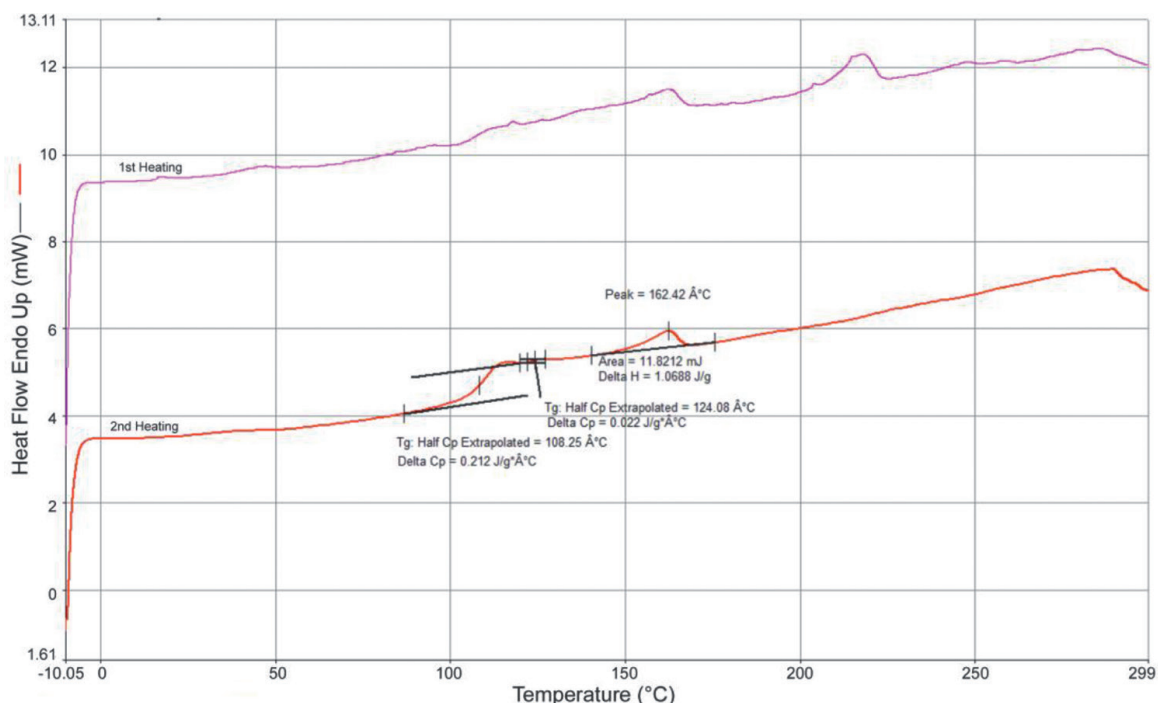


Figure 16.
DSC analysis of ABS.

to detect with DSC analysis because the transition is weak. The graph (**Figure 17**) instead shows a peak at 167°C corresponding to the melting temperature of polypropylene (green curve) and a peak at 221°C typical of the nylon used to realize the elastic bands of single-use masks (purple curve).

3.2 Pyrolysis products

The products formed in the MAP process of these plastic materials were liquid, gas, and char. In all cases, the liquid was the most important fraction both in quantity and commercial value. The characterization of this fraction for the most significant tests is reported below; the chemical–physical properties are shown in **Table 5**. Physical characteristics of liquids from MAP of PS were not affected by the variation of the MW power. The density recorded in all samples was almost the same and in a very narrow range among 0.92–0.95 g/cm³. Furthermore, close values of ultimate analyses and the molar C/H ratios suggested that all the liquid samples had a similar composition, even if different process parameters have been employed. The C/H molar ratio in a range between 0.94 and 1.0 wt% confirmed the prevailing presence of the aryl compounds in liquids from PS pyrolysis.

The lower calorific value (LHV) of the liquids from MAP of PS also showed the same trend as the C/H molar ratio, with values close to styrene, benzene, and ethylbenzene (LHV of 39.6, 40.0, and 39.1 MJ/kg, respectively for PS1, PS2, and PS5). As foreseen from the literature and in agreement with the tests carried out both in the laboratory and on the pre-industrial prototype, the main products of PS pyrolysis are aromatic hydrocarbons such as benzene, toluene, ethylbenzene, styrene, and α -methylstyrene (**Table 6**).

Styrene is always the predominant compound in each liquid sample. From the analysis of data reported in **Table 7** it is possible to show how the amount of styrene (evaluated by chromatographic area of the GC/MS spectra) is correlated with the

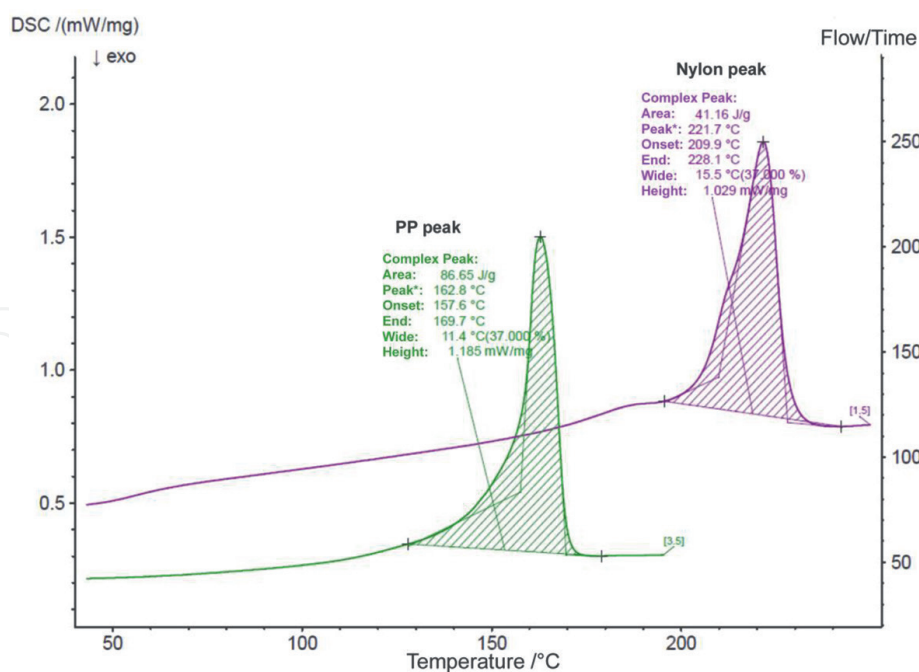


Figure 17.
 TGA analysis of single-use mask.

Entry	Density (g/cm ³)	LHV (MJ/kg)	Elemental analysis (wt %)			C/H molar ratio
			C	H	N	
PS1	0.94	39.6	82.8	7.35	<0.50	0.94
PS2	0.95	40.0	89.2	7.60	<0.50	0.98
PS5	0.92	39.1	85.2	7.07	<0.50	1.00
ABS1	1.02	34.4	79.8	7.8	2.9	0.85
PP2	0.75	34.3	84.3	14.3	0.0	0.49

Table 5.
 Physical characteristics of liquids obtained from MAP of plastics.

microwave power used. The highest amount of styrene was present in PS2 and PS4 (respectively 52.8 and 56.9%), corresponding to experiments where a higher microwave power was used. In contrast, using a lower microwave power (PS1, **Table 7**), the amount of styrene was drastically reduced. Also, as reported above for PS, the MAP of ABS gives a liquid fraction with a density between 0.97 and 1.02 g/cm³ and C/H molar ratio of 0.85 wt% indicative of the prevailing presence of aromatic compounds. The liquid fraction was analyzed by GC-MS, a complete list of compounds identified through the NIST library is reported in **Table 8**. Aryl compounds, especially styrene, are present in large amounts in the liquid from MAP of ABS. In the presence of acrylonitrile, nitrile compounds such as 2-methylenpropionitrile were formed in a significant amount. MAP of PP gave a low-density liquid (0.746–0.760 g/cm³) and a C/H molar ratio of 0.5 wt%, confirming the prevailing presence of aliphatic compounds in this liquid. The main compounds identified in the liquid from MAP of PP are reported in **Table 9**, they were branched saturated and unsaturated hydrocarbons, which were formed through C-C bond cleavage of the PP backbone. In particular, there was

Compounds	Area (%)
Toluene	3.4
Ethylbenzene	7.9
Styrene	56.9
Cumene	1.2
α -Methylstyrene	8.0
1,3-Diphenylpropane	4.0
Bis(1,1'-(1-methyl-1,3-propanedyl))benzene	1.6
Stilbene	0.7
1,2-Diphenylcyclopropane	2.2
Bis(1,1'-(3-methyl-1-propenylidene))benzene	1.4
Others	12.7

Table 6.
Main compounds identified in liquid from MAP of PS₄, by GC-MS.

Entry	Power (kW)	Styrene (wt%)
PS1	6;12	37.4
PS2	12	52.8
PS4	18	56.9

Table 7.
Correlation between styrene in liquid and MW power in the MAP of PS.

Compounds	Area (%)
2-Methyl-2-propenenitrile	12.5
Toluene	4.4
Ethylbenzene	8.8
Styrene	20.8
Cumene	3.8
α -Methylstyrene	12.5
6,7-dihydro-5-methyl-5H-cyclopentapyrazine	7.9
1,3-Diphenylpropane	7.2
Others	22.1

Table 8.
Main compounds identified in liquids from MAP of ABS, by GC-MS.

a prevalence of C₉-C₁₂ hydrocarbons, and among these, the 2,4-dimethyl-1-heptene was found as the main compound, in agreement with previous results [8]. Many other compounds were present in very low amounts and reported as others. The presence of aromatic hydrocarbons was attributed to cyclization and aromatization reactions of unsaturated compounds formed during the MAP process as reported.

Compounds	Area (%)
5-Methylhex-1-ene	0.8
2,4-Dimethyl heptane	12.5
1,4-Dimethylbenzene	1.2
1,3,5-Trimethylbenzene	0.5
1,2,4,5-Tetramethylbenzene	0.2
2,4,6,8-Tetramethylundec-1-ene	3.5
2,4,6,8-Tetramethylundecane	2.3
2,4,6,8,10-Pentamethyltridec-3-ene	0.6
Others	78.4

Table 9.
Compounds identified in liquids from MAP of PP, by GC-MS.

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.

4. Conclusions

The quality and quantity of end-of-life plastics are continuously improved while the amount of recycled material is always too low. Several firms such as AmSty and Agylix [28], ReVital Polymers, Pyrowave, and INEOS Styrolution [29], BASF, Quantafuel, and REMONDIS [30], Neste [31], and so on are involved in recycling plastic materials using thermochemical processes [1] using, mainly, classic heating method. This review shows the MAP process developed by Techwave as an industrial novelty proposed for the friendly and economical disposal of waste/contaminated plastics. In this way, valuable products, useful as a source of secondary raw material, close the cycle of a circular economy because plastic waste is converted in a feedstock for the production of new plastics.

MAP is a very interesting way to dispose of end life plastics because it does not produce waste from chemical recycling of plastics but three classes of products: a char, an oil, and a gas, 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 Techwave proposal offers an industrial plant designed to obtain secondary raw materials from plastic wastes, thus closing the cycle for a circular economy and giving a strong advantage in terms of environmental protection and expansion of the recycled material market in a green and sustainable way.

Finally, the plant was realized as planned, so it is possible to introduce in two standard containers for its shipping. Furthermore, a plant of this dimension may be installed in a municipal collecting and selecting center of waste plastic where it may be employed to pyrolyze the mixed plastic present, avoiding the transport of this waste for disposal. The plant may be useful also for a large hospital to dispose of the waste/contaminated plastic present, taking into account that the pyrolysis products do not contain biological contamination because they are destroyed in the course of

the process as reported in the literature [24, 25] while the products formed may be sold on the market. The dimension of the plant lets its installation on one small ship where the waste plastic materials present in the sea may be collected and immediately disposed. The products formed may be employed to produce the energy required for all operations, while the excess may be sold on the market.

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References

- [1] Frediani P, Frediani M. Mixed or contaminated waste plastic recycling through microwave: Assisted pyrolysis. In: Ibrahim HAH, editor. *Recent Perspectives in Pyrolysis Research*. London: IntechOpen; 2021. p. 100179. 2021, DOI: 10.5772
- [2] PlasticsEurope. Plastic-the fact 2019 An analysis of European plastics production, demand and waste data. Available from: <https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts-2020> [Accessed June 25, 2021]
- [3] Frediani P, Rosi L, Frediani M, Undri A, Occhialini S. Production of hydrocarbons from copyrolysis of plastic and tire material with microwave heating. WO2012110990, 2012, PCT/IB2012/050747
- [4] OCSE. *Global Plastic Outlook: Economic Drivers, Environmental Impacts and Policy Options* OECD, 2022. DOI: 10.1787/de747aef.en
- [5] Do O, Pelucchi M, Van de Vijver R, Van Steenberge PHM, Dooze DR, Cuoci A, et al. The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. *Progress in Energy Combustion Science*. 2021;84:1009001. DOI: 10.1016/J.PECS.2020.100901
- [6] Kaminsky W. *Feedstock Recycling and Pyrolysis of Waste Plastics*. New York: John Wiley & Sons; 2006, ISBN:9780470021521
- [7] Undri A, Rosi L, Frediani M, Frediani P. Efficient disposal of waste polyolefins through microwave assisted pyrolysis. *Fuel*. 2014;116:662-671. DOI: 10.1016/j.fuel.2013.08.037
- [8] Undri A, Frediani M, Rosi L, Frediani P. Reverse polymerization of waste polystyrene through microwave assisted pyrolysis. *Journal of Analytical and Applied Pyrolysis*. 2014;105:35-42. DOI: 10.1016/j.jaap.2013.10.00110
- [9] Frediani P, Undri A, Rosi L, Frediani M. Waste/contaminated polystyrene recycling through reverse polymerization. In: Lynwood C, editor. *Polystyrene Synthesis, Characteristics and Applications*. New York: Novapublisher; 2004, ISBN 978-1-63321-356-2
- [10] Bartoli M, Rosi L, Frediani M, Undri A, Frediani P. Depolymerization of polystyrene at reduced pressure through a microwave assisted pyrolysis, *Journal of Analytical and Applied Pyrolysis*. 2015;113:281-287. DOI: 10.1016/j.jaap.2015.01.026
- [11] Undri A, Rosi L, Frediani M, Frediani P. Microwave pyrolysis of polymeric materials. In: Chandra U, editor. *Microwave Heating*. London: InTech; 2011. pp. 207-226
- [12] Williams PT, Williams EA. Interaction of plastics in mixed-plastics pyrolysis. *Energy Fuels*. 1999;13:188-196. DOI: 10.1021/ef980163x
- [13] Undri A, Rosi L, Frediani M, Frediani P. Conversion of poly(lactic acid) to lactide via microwave assisted pyrolysis. *Journal of Analytical and Applied Pyrology*. 2014;110:55-65. DOI: 10.1016/j.jaap.2014.08.003
- [14] Frediani P, Rosi L, Frediani M, Undri A, Occhialini S, Meini S. Production of hydrocarbons from pyrolysis of tyres. WO2012110991, 2012, PCT/IB2012/050748
- [15] Undri A, Meini S, Rosi L, Frediani M, Frediani P. Microwave

- pyrolysis of polymeric materials: waste tires treatment and characterization of the value-added products. *Journal of Analytical and Applied Pyrolysis*. 2013;**103**:149-158. DOI: 10.1016/j.jaap.2012.11.011
- [16] Undri A, Rosi L, Frediani M, Frediani P. Upgraded fuel from microwave assisted pyrolysis of waste tire. *Fuel*. 2014;**115**:600-608. DOI: 10.1016/j.fuel.2013.07.058
- [17] Undri A, Sacchi B, Cantisani E, Toccafondi N, Rosi L, Frediani M, et al. Carbon from microwave assisted pyrolysis of waste tires. *Journal of Analytical and Applied Pyrolysis*. 2013;**104**:396-404. DOI: 10.1016/j.jaap.2013.06.006
- [18] Rosi L, Bartoli M, Frediani M. Microwave assisted pyrolysis of halogenated plastics recovered from waste computers. *Waste Management*. 2018;**73**:511-522. DOI: 10.1016/j.wasman.2017.04.037
- [19] Undri A, Rosi L, Frediani M, Frediani P. Fuel from microwave assisted pyrolysis of waste multilayer packaging beverage. *Fuel*. 2014;**133**:7-16. DOI: 10.1016/j.fuel.2014.04.092
- [20] Undri A, Rosi L, Frediani M, Frediani P. Microwave assisted pyrolysis of corn derived plastic bags. *Journal of Analytical and Applied Pyrolysis*. 2014;**2014**(108):86-97. DOI: 10.1016/j.jaap.2014.05.013
- [21] Frediani P, Rosi P, Frediani M, Undri M, Occhialini S. Produzione di idrocarburi da Co-Pirolisi di Materiali Plastici e Pneumatici con riscaldamento a Microonde” CAF scarl, Italian patent N. 1404131B1 (2011); Patent request N. FI2011A000029
- [22] Undri A. Produzione di idrocarburi da pirolisi di gomme, Master thesis, University of Florence (Italy), 2010
- [23] Available from: <https://www.dw.com/en/plastic-pollution-in-oceans-growing-dramatically-wwf-warns/a-60692503#:~:text=WWF%20warned%20that%20plastic%20content,plastic%20waste%20in%20the%20ocean> [Accessed February 26, 2022]
- [24] Techwave private communication
- [25] Available from: <https://www.fraunhofer.de/en/press/research-news/2021/june-2021/closed-loop-recycling-pilot-project-for-single-use-face-masks.html> [Accessed February 26, 2022]
- [26] Bartoli M, Frediani M, Briens C, Berruti F, Rosi L. An overview of temperature issues in microwave-assisted pyrolysis. *Processes*. 2019;**7**:658. DOI: 10.3390/pr7100658
- [27] Suzuki M, Wilkie CA. The thermal degradation of acrylonitrile-butadiene-styrene terpolymer as studied by TGA/FTIR. *Polymer Degradation Stability*. 1995;**47**:217-221. DOI: 10.1016/0141-3910(94)00122-O
- [28] Available from: <https://amsty.com/news/amsty-agilyx-announce-collaboration-to-build-advanced-recycling-facility> [Accessed: February 25, 2022]
- [29] Available from: <https://www.ineos-styrolution.com/news/revital-polymers-pyrowave-and-ineos-styrolution-partner-to-launch-closed-loop-north-american-polystyrene-recycling-consortium> [Accessed: February 25, 2022]
- [30] Available from: <https://www.basf.com/global/en/who-we-are/sustainability/whats-new/sustainability-news/2021/basf-quantafuel-and-remondis-want->

to-cooperate-on-chemical-recycling-of-plastic-waste.html [Accessed February 25, 2022]

[31] Available from: <https://www.neste.com/releases-and-news/plastics/neste-successfully-completed-its-first-industrial-scale-processing-run-liquefied-waste-plastic> [Accessed February 25, 2022]

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