

2014 - 2020 Interreg V-A Italy - Croatia CBC Programme Call for proposal 2019 Strategic

MARLESS (MARine Litter cross-border awarenESS and innovation actions)

Priority Axis: Environment and cultural heritage; Specific objective: 3.3 - Improve the environmental quality conditions of the sea and coastal area by use of sustainable and innovative technologies and approaches

6.7.2 – Toolbox on plastic treatment in Pyrolytic small plants

AT 6.7

WP6

Version: FINAL Distribution: PUBLIC Date: 28/06/2023



PROJECT MARLESS

Work Package:	WP6 - Pilot Actions to prevent, recover, process marine litter,		
	including Stakeholders Toolbox		
Activity:	AT 6.7 Toobox		
WP Leader:	Alma Mater Studiorum Università di Bologna		
Deliverable:	6.7.2 – Toolbox on plastic treatment in Pyrolytic small plants		

Version:	Final 1.0	Date:	28/06/2023	
Туре:	Report			
Availability:	Public			
Responsible Partner:	Alma Mater Studiorum Università di Bologna			
Involved Partner				
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CONTENT:

ToolBox: Pilot Actions to prevent, recover, process marine litter -Activity 6.7-

WP6 aims to demonstrate the feasibility of several new technologies in the field of prevention, recovery and treatment of marine litter. The activity in question will produce Tool boxes for stakeholders aimed at boosting the transferability of WP main outputs. Please, complete with the following information requested:



1.1 Brief description of the performed activity

A lot of marine waste was collected by MARLESS' partners and brought to the Research Center of Marina di Ravenna, where it was separated into plastic waste and non-plastic waste. The plastic waste was sorted by polymeric class (polyethylene, polystyrene, polyvinyl chloride, etc.), dried in an oven and shredded into small fragments.

Subsequent activities took place in the Fraunhofer laboratories in Germany. Two pyrolysis experiments were conducted:

- Separate pyrolysis of plastics fractions in a lab scale plant (approx. 20-50g of feedstock), which provides enough product mass for the analytical analyzation of pyrolysis products;
- Pyrolysis of mixed materials in a larger scale plant, which has a throughput of approx. 10kg/h.

Analytical analysis, such as gas chromatography, calculation of calorific value and water content, were performed on the pyrolysis products, and the composition of the pyrolysis gas was measured.

1.2 Goals achieved

The basic idea of the MARLESS project was to put boats into the sea with the sole purpose of collecting the plastics dispersed at sea, pyrolysing them and using the pyrolysis products as a source of energy for self-sustainability, without the need to return to port for refueling. The pyrolysis of some plastics, such as PVC (polyvinyl chloride) and PET (polyethylene terephthalate), leads to the formation of some gaseous pollutants and corrosive products for the pyrolysis system; these problems did not occur in the pyrolysis process used for the MARLESS project.

Each plastic has been pyrolysed, without the use of catalysts (necessary for some processes) or additives (used to prevent damage to the pyrolysis system).

From the results obtained, it was observed that the pyrolysis of the individual plastics and that of the mixed sample, produces oils whose calorific values are comparable to those of fuels (except for PVC and PET, whose values were lower).

One of the advantages of the pyrolysis process is that all the products have commercial value: the gas can be recycled to feed the process heat, the oil can be refined, if necessary, to produce chemicals and fuel, and the solid product can have many applications. The solid product of the MARLESS project is comparable to hard coal and provides an ideal feedstock for thermal utilization.



The availability of an efficient pyrolysis process, which does not require the use of additional chemical compounds, and the production of pyrolysis oils with a good calorific value, makes the pyrolysis of plastic waste, collected at sea, feasible.



2. **DELIVERABLE METHODOLOGY**: (first briefly describe what was done, then some tips for the replication of the action – suggestions are reported below)

The collected marine litter was divided into plastic and non-plastic waste. Then, the plastic waste was sorted by polymer type, using two identification methods:

- symbol of the polymer used, if still visible;
- class of the polymer: bottles are generally made of poly-ethylene terephthalate, plastic plates are made of polystyrene, bottle caps are made of polyethylene, etc...

Subsequently, all the plastics were dried in an oven and shredded into small fragments. Finally, the plastics were pyrolysed, either as separate polymers or as a mixed sample. The pyrolysis products were subjected to analytical analysis.

The separation of the plastics by polymer was manual, and following visual criteria: the results, obtained from the analyses on the pyrolysis products, showed that the sorting used was accurate, and therefore can be repeated, for this type of activity.

For shredding plastics, a shredder designed for shredding waste is essential, capable of shredding even long and elastic materials such as fishing or mussel nets.

For pyrolysis, the experimental plant used by Fraunhofer was able to prevent the problems linked to the pyrolysis of plastics (HCl formation, corrosion, etc...), therefore it is the most suitable of the plants present on the market now, for the thermochemical recycling of plastics.

Both the gas and the solid produced by pyrolysis can provide process heat for the pyrolysis plant, but it is necessary to remove the chlorine from the pyrolysis solid. To do this, the PVC must be removed from the feedstock during manual sorting.

In addition, some pyrolysis oils were characterized by high viscosity and contained chlorine, so after pyrolysis, a refining process must be added, to improve the chemical and physical characteristics of the pyrolysis products.

2.1 WHERE: Deliverable location description (the location can affect the effectiveness of the action? What about the seasonality?)

Location and seasonality are factors that influence the amount of plastic collected at sea, due to currents and weather conditions; thus, they affect the amount of feedstock which can be pyrolysed.

2.2 WHO: Experts Involved (Which background do you need to perform well the action? What's the minimum team?)

At least one experienced technician is required for the operation of the pyrolysis system and one for the pyrolysis oil refining process.

The sorting and shredding phases do not require specific qualifications, just knowing how the shredder works, and having a suitable table for the manual sorting of plastics (a table created by collecting information on the internet, cross-referencing data taken from various sites).



2.3 HOW: Description of the activity realized (specific technology are needed? And the timing needed?)

For sorting, no tools are needed and about 15-25 kg of marine litter can be processed at a time.

For drying, a Falc stove was used, mainly for drying the plastics collected from the seabed. In the absence of an air recirculation system, inside the stove, about 1-3 kg of plastic were dried at a time, at 40-50 °C for 48-72 hours.

An ideal procedure for drying would be a ventilated structure with jets of hot air, which heat and, at the same time, remove the evaporated humidity.

For the shredding, the Tiger Shark S100 shredder of the company Fulltech Instruments srl was used, for 2 working days, for shredding about 54-55 kg of plastic.

The pyrolysis experiments at the laboratory plant took about 2 weeks, including evaluation and analysis.

The execution of the rotary kiln experiments, including analysis and feedstock preparation, took approx. 1,5 weeks.

The time specifications for the different experiments were:

- Lab scale pyrolysis:
 - Heating phase: 10-12 min
 - Dwell time of feedstock: 30 min
 - Cooling phase after experiment: 2-3h
- Batch scale pyrolysis:
 - Heating phase: 15-20 min
 - Dwell time of feedstock: 30 min
 - Cooling phase after experiment: 8-10h

2.4 Outputs achieved vs Outputs expected

From the analyses carried out by Fraunhofer it was observed that the pyrolysis oils, produced both by lab scale pyrolysis and by batch scale pyrolysis, have a calorific value equal to that of normal fuels.

However, further studies are necessary, as their properties, such as density, viscosity, sulfur content, etc., must fall within a given range of values, to meet all engine requirements in compliance with the limits in force.

The gas and solid produced by pyrolysis can also be used:

• to provide process heat for the pyrolysis plant itself, without any cleaning treatment;



• given that the calorific value of the solid product is comparable to that of coal, it is an excellent raw material for thermal use. But chlorine must be removed, to avoid the formation of HCl.

Furthermore, the need to remove PVC from feedstock before pyrolysis shows that the sorting phase is necessary both to separate plastic waste from non-plastic waste, and to remove polymers unsuitable for this pyrolysis process. Future studies can also focus on how much the variation of the polymer composition influences the properties of the pyrolysis products.

2.5 SWOT ANALYSIS

Describe, with the support of the SWOT analysis scheme, how the performed action can be improved

	Helpful	Harmful
Internal Origin	STRENGHT:	WEAKNESS:
internal origin	Sorting can be manual, without	For certain plastics, is not
	the use of specific equipment.	possible to remove the pollutants
	The pyrolysis technology used	from the oil and from the solid
	avoids the dispersion of gaseous	during the pyrolysis process;
	pollutants in the air.	post-pyrolysis treatments are
	It is possible to recycle a large	necessary, also to reduce the
	quantity of different plastics,	viscosity of the oil.
	collected directly from the sea,	The presence of chlorine in the
	even in a single mixed sample.	fuel leads to the formation of
	This process can be done both on	gaseous pollutants. Chlorine
	land and at sea on a boat.	comes from the pyrolysis of PVC,
		which therefore cannot be
		pyrolysed with other plastics.
Fxternal Oriain	OPPORTUNITIES:	THREATS:
	The pyrolysis of plastic materials	Barriers from regulations can
	for chemical recycle is a very	prevent the diffusion of the
	active field, so there are	technology.
	expectations for improved plants	
	with even easier operating	
	conditions and better products.	



main achievement of the pilot action (after this pilot, can be set a new baseline for new studies? What can be done to continue this pilot actions?)

Analytical analyses carried out on pyrolysis oils, in particular the calculation of their calorific value, demonstrate that they could be used as fuel.

Other analyses on the oils must be carried out, in particular on the physical and chemical characteristics required by the fuel regulations, for example the ISO 8217 standard. Further studies must focus on how to vary the pyrolysis parameters, so that the products fall within the ranges of the regulatory parameters; it is necessary to understand whether it is necessary to modify the composition of the plastic feedstock, whether to vary the parameters of the pyrolysis process, or whether a specific refining treatment is necessary after pyrolysis.



4. **TRANSFERABILITY**: please describe how the experience gained in these pilot actions will allow to define a set of procedures / best-practices for the usage of the selected technologies in the context of the Adriatic sea

Thanks to the experience gained in these pilot actions, it was possible to define a series of best practices for the use of the pyrolysis plant on the ship.

The main problem was the drying of plastic collected by seabed; a system was devised, at a theoretical level, with which to dry the plastics, directly on the boat, starting from the same sorting.

Figure 4.1 summarizes all the actions to be taken for plastic recycling, while figure 4.2 shows, more clearly, the process from the drying phase to the post-pyrolysis phase.

After the collection of marine litter (Figure 4.1) in the sea by diving action, by trawling and by use of robot:

- While the plastics are removed from the nets (and separated from non-plastic waste), they are sorted, placing each polymer in each container, on the bottom of which there is a grate on which the plastics will rest. As the quantity of a given polymer increases, the underlying plastics are crushed, and lose the excess surface water, which will accumulate on the bottom of the container, under the grate;
- After a few hours, the plastics are shredded and dried; as shows in Figure 4.2, thanks to a heat exchanger (1), which draws heat from the engine exhaust fumes line. Once the fumes are sufficiently cooled, they are conveyed to the pyrolyzer (2);
- The dried plastics are then sent to the pyrolyzer (3);
- All pyrolysis products can have an energic use, but the oil must be refined.

If plastics is collected on the beach, the dry's phase isn't necessary, and all plastics can be pyrolysis, with the same process show on Figure 4.2.



Figure 4.1 Best-practices for the usage of the selected technologies in the context of the Adriatic Sea.



Figure 4.2 Ideal closed-circuit system for the self-sustainability of ships dedicated to the collection of plastics at sea.



If available please add photos and link of videos

Phase of sorting



Figure 5.1 Plastic litters, before and after the sorting

Phase of shredding



Figure 5.2 Plastic net, before and after the shredding





Figure 5.3 Plastic litters in the stove





Figure 5.4 Batch-scale plant and lab scale set-up for the thermo-chemical conversion, © Fraunhofer UMSICHT



Figure 5.5 Oil and solid product of pyrolysis, © Fraunhofer UMSICHT