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6.2.2 – Report: Results of the Pyrolysis tests on 250 kg marine litter treatment. Results on the characterisation of the input feedstock and of the pyrolysis products (elemental analysis, carbon content, heating value and pollutants content)

WP6 – Action 6.2

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PROJECT MARLESS

Work Package:	**WP6 - Pilot Actions to prevent, recover, process marine litter, including Stakeholders Toolbox**
Activity:	**6.2 - Pyrolysis micro plant in Ravenna: test what we do**
WP Leader:	**Alma Mater Studiorum Università di Bologna**
Deliverable:	**6.2.2 – Report: Results of the Pyrolysis tests on 250 kg marine litter treatment. Results on the characterization of the input feedstock and of the pyrolysis products (elemental analysis, carbon content, heating value and pollutants content)**

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ABSTRACT AND SCOPE

WP6 focused on demonstrating the feasibility of different new technologies in the field of prevention, recovery and treatment of marine litter, through different pilot actions.

UNIBO was involved in the coordination and monitoring of the WP activities, including the technologies adopted.

Among the various pilot actions adopted in WP6, the Environment, Energy and Sea Research Center of Marina di Ravenna was involved in experimenting the valorisation of plastic collected with a pyrolytic technology.

The activities of the "Pyrolysis testing on Plastic Marine Litter" included the receipt of plastic samples collected by the Partners (thanks to the collection methods tested in the other pilot projects), the analysis and the separation of the different types of plastics (polyamides, polycarbonate, polyester, etc.), the shipment to Fraunhofer UMSICHT, Sulzbach-Rosenberg Branch, for the pyrolysis and for characterization of the pyrolysis products (oil, char and syngas) in terms of elemental analysis, carbon content, calorific value and content of pollutants (sulphur, halogens).

The result was a procedure for the treatment of Plastic Marine Litters, adapted to the different types of plastic collected.

1. INTRODUCTION

To improve the quality of the environmental conditions of the coastal area and the Adriatic Sea, the MARLESS project proposed some innovative and experimental techniques which allow the treatment of the collected plastic waste. Pyrolysis was the pilot action experimented at the Research Center of Marina di Ravenna, which allows energy and chemical recovery of plastic components.

Pyrolysis is a thermochemical process which carries out the thermal decomposition of materials by applying heat in the absence of oxygen, at temperatures between 300 and 600°C.

For the MARLESS project, a pilot plant for pyrolysis was used, designed by the Fraunhofer research institute in Germany.
The main idea behind the MARLESS project is to have boats with the sole purpose of collecting plastics dispersed in the sea, pyrolysing them and to use the pyrolysis products as a source of energy for self-sustainability of the boats, without the need to return to port for refuelling. However, the possibility to pyrolyse plastics collected in the sea and treated inland has been explored, as a less ambitious but feasible objective.

2. CHARACTERISATION OF THE INPUT

The Cetacea Foundation was supposed to collected marine litter during their boat trips, but due to the pandemic, trips were postponed until 2022.
The first load arrived in the Research Center on Environment, Energy and the Sea in June 2022, with about 83 kilograms of marine litter, collected on the seabed.
Other loads arrived between November 2022 and February 2023, for a total of about 230 kilograms of marine waste, also with the contribution of the Arpa Veneto partners. These loads included also floating and beached plastics.

2.1. Sorting

A manual sorting was carried out: the plastic wastes were first separated from the non-plastic one, then the plastic wastes were separated according to the polymer type.
The wastes collected from the seabed were wet and dirty with mud and full of organic material, later identified as gastropod eggs. To separate plastics into the different polymers, common applications of each class of polymer were considered: bottles are generally made of polyethylene terephthalate, plastic plates are made of polystyrene, bottle caps are made of polyethylene, etc…

Of all the marine litter collected on the seabed, 71% was plastic litter, with the following fractions:

- polyethylene: 10.5%
- polystyrene: 0.3%
- polypropylene: 56.5%
- polyethylene terephthalate: 3.5%
- polyvinyl chloride: 0.3%

Floating plastics, on the other hand, were almost clean and dry; in addition to considering the application sectors of the polymers, the identification symbol of the polymer used was still visible on many of them, which was used to separate plastics.

A part of the floating plastics was fragmented, so it was not possible to identify the starting object; an attempt was made to determine the polymer to which it belongs by means of a density test. In a cylinder with a predefined volume of water, fragments of an unknown plastic were added, until the volume of the cylinder increased by 1 ml; also considering the increase in mass during the process, it was possible to calculate the density of the analyzed plastic, and therefore identify the polymer to which it belongs. However, plastic surfaces are hydrophobic, and air bubbles show a high affinity for these surfaces. Furthermore, foam materials have a micro-porosity, which further increases the ability to retain air bubbles on their surfaces.
The presence of air bubbles alters the mass values recorded in the density test; therefore, this test was not applicable for expanded polystyrene, expanded polyurethanes, films, and very small objects having a low thickness.
Finally, this test was not useful because the plastics were dirty with organic material, wet, and also full of sand, all factors that altered the test results.

Of all floating and beached marine litters, between 15% and 54% were plastic litters, with the following plastic fractions, in percentual (minimum-maximum value):

- polyethylene: 1.4-11.9%
- polystyrene: 0.7-4.9%
- polypropylene: 2.8-19.2%
- polyethylene terephthalate: 3.4-18.9%
- polyvinyl chloride: 0-0.6%
- polyurethane: 0.1-0.5%
- mixed plastics: 5.9-15.1%, they were all plastics for which it was not possible to define the polymer they belonged to.

Overall, many plastic objects were collected, all different from each other, gathered in groups of the same polymer, according to the sector of application of the typical polymer, and the polymer's identification symbol. Following these operational choices, some plastics may be placed in the wrong polymer fraction, considering the great variety of objects collected; however, it was possible to make two groups of the same object and the same polymer: BAGS in polyethylene and NETS in polypropylene. These two groups were treated as two distinct samples, from the sorting phase up to pyrolysis.

2.2. Drying

To be pyrolyzed, plastics need to have less than 15% residual humidity, to avoid losing energy in the thermochemical process, due to the evaporation of the water contained in the plastics.
For this reason, all plastics collected from the seabed, were dried in a stove; for the smaller fractions, such as PS (polystyrene) and PVC (polyvinyl chloride), a period of 48 hours at 40 °C was sufficient, while for the larger fractions, such as PE (polyethylene) and PP (polypropylene), 72 hours at 50°C were necessary. The PET (polyethylene terephthalate) was first dried at 40°C for 48 hours, then for 24 hours at 50°C.

Between separation and drying, there was a weight loss of approximately 50% by mass, corresponding to the dried organic material, which detached after drying.

For the floating plastics, on the other hand, no drying process was necessary, as the quantity of water with which they came into contact with was extremely small. Only the PET had a residual humidity of around 15%: many of the bottles collected were closed with the cap and water or damp sand remained inside them; for this fraction, drying was required.

2.3. Calculation of humidity

To verify that the residual humidity of each group of plastics was within the established parameters, a representative sample of about 30 grams was taken from each plastic fraction, which was placed in an oven at 105 °C for 24 hours and the residual moisture fraction was calculated. All samples resulted with less than 10% moisture present.
As already mentioned before, of the floating plastics, only PET had a higher residual humidity between 15 and 17%.

2.4. Shredding

For pyrolysis, the plastic needed to have a particle size of less than 2cm. Plastic is a very flexible and malleable material, and this can lead to problems: in a counter-rotating roller shredder, the plastic does not cut cleanly, as would happen with metal or aluminium, but when cut it deforms and gets stuck between the blades, blocking the gears.

To avoid this problem, the possibility of cooling the plastic with liquid nitrogen was evaluated, to make it much more fragile, and therefore easily shredded. However, the idea was scrapped because handling liquid nitrogen was deemed too risky.

An external company was identified which had a shredding system suitable for even the most flexible plastics, such as polypropylene nets; all the collected plastic samples were sent to them, and these were not only shredded to a particle size even smaller than that required, but the process itself did not cause any damage to the entire system.

3. PYROLYSIS

At the beginning of the project, the use of the iCycle® plant was foreseen, with a flow rate of 70 kg/h of raw material. With the lower quantity available, it was decided that similar but smaller plants could be used:

- Pyrolysis of individual plastic fractions, sorted by polymer, in a lab-scale plant (approximately 20-50 g of feedstock), providing sufficient product mass for analysis;
- Pyrolysis of a mixed material sample, in a larger scale plant, with a flow rate of approx. 10kg/hour.

3.1. Technical characteristics of thermo-chemical conversion of marine litter and conditions of pyrolysis

Two types of experiments were conducted: the pyrolysis with the lab-scale plant of several plastic samples (one sample for each polymer) and a batch-scale experiment of a single mixed plastic sample.
Nine different plastic wastes were treated in a laboratory-scale pyrolysis plant. The reactor was always filled to its maximum capacity, based on the bulk density of the sample.

Plastic samples were:

- PP: Polypropylene
- NETS: Polypropylene nets for mussels
- PET: Polyethylene terephthalate + Polyethylene + Polypropylene (plastic bottles + PET items)
- PS: Polystyrene
- MIX: Mixed polymers (unsorted plastics)
- PVC: Polyvinyl chloride
- PU-PS: Internal walls in polyurethane and polystyrene
- PE: Polyethylene
- BAGS: Polyethylene

Subsequently, all samples were mixed and processed in a batch larger scale plant. The mixed raw material (25kg) contained all 9 different materials, represented proportionally to the effective presence in the collected samples.

The composition of the mixed raw material (called MIXED FRACTION) was:

- PP: 3.2%
- NETS: 45.6%
- PET: 10.6%
- PS: 4.6%
- MIX: 14.4%
- PVC: 0.9%
- PU-PS: 0.6%

- PE: 12.7%
- BAGS: 7.2%

3.1.1. Lab-scale pyrolysis

The test setup shown in Figure 3.1.1 was used to conduct all thermochemical conversion tests of pure fractions in this project. For each pyrolysis test, the respective material (~15-50g) was prepared in the reactor inlay (1) which was inside the reactor tube (2) and sealed by the closure head (3), a gasket (4), and a fixing (5). The closure head led to the distillation bridge (6) with a conical flask (7) attached to it. The conical flask was cooled by an ice water bath (8) to enhance the condensation of the evolving gaseous pyrolysis products. Before each conversion run, the described system (1-7) was purged with nitrogen to at least three times the reactor volume. The nitrogen flow was introduced through the lance of the locking head (3).
For each run, the reactor (1-3) was placed in a high temperature oven which was pre-heated to the desired temperature for the respective run. Gases, which were not condensed in the conical flask (7), were carried to the intensive cooler and to the subsequent gas scrubbing system (9). The nitrogen flow rate for all experiments was set to 50 mL/min.
All experiments were conducted at a temperature of 600 °C for at least 30 minutes with a nitrogen flow of 50 mL/min to ensure comparability and complete conversion of organic compounds.

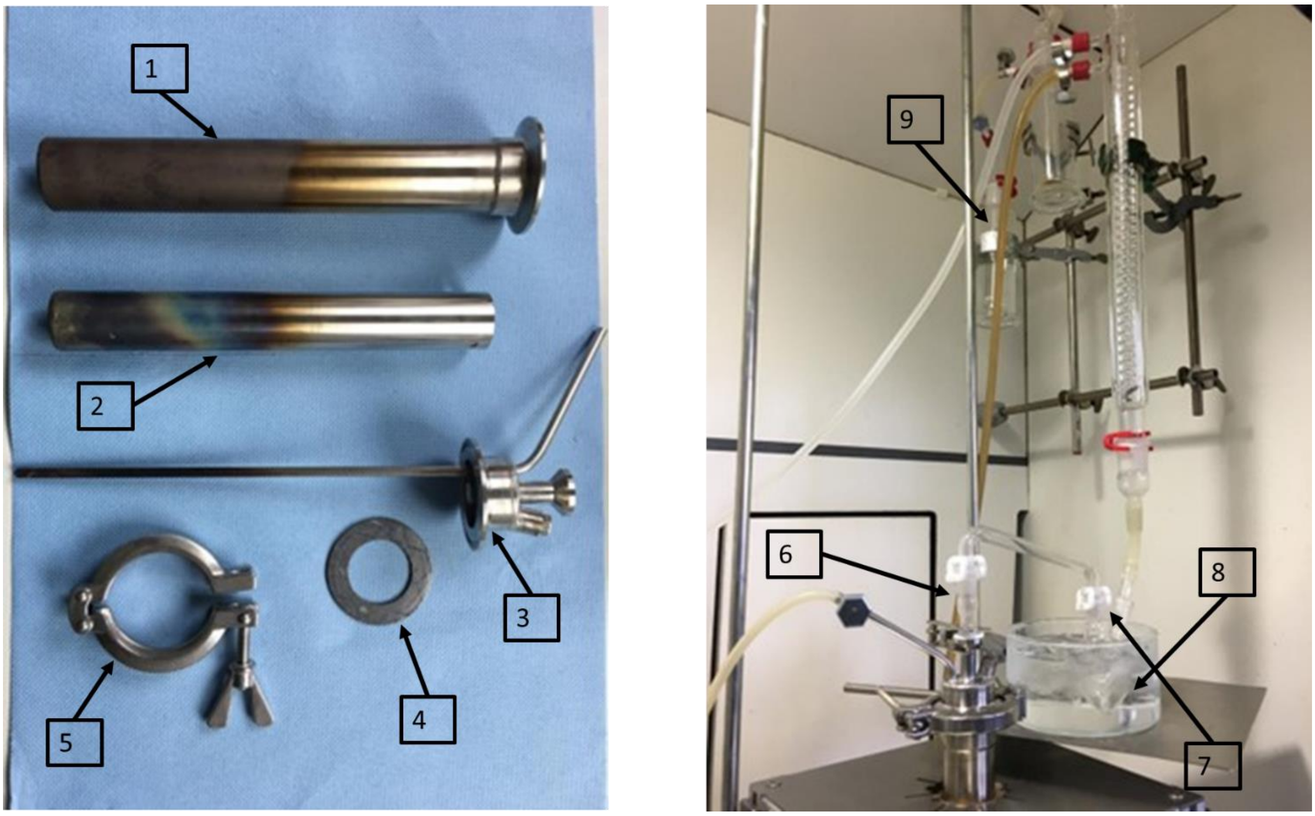

Figure 3.1.1 Lab-scale setup for thermo-chemical conversion, © Fraunhofer UMSICHT

3.1.2. Batch-scale pyrolysis

The rotary kiln shown in Figure 3.1.2 was used for the pyrolysis process of the mixed fraction containing all nine different raw materials.

Before the start of the experiment, the reactor was filled with the raw material and subsequently purged with nitrogen to create an inert atmosphere. The reaction chamber (drum) was rotated about the horizontal axis at a rotational speed of approx. 5 rounds per minute. This ensures that the material remains in motion during the treatment and is heated evenly from all sides. The reaction chamber was heated to the target temperature of 600°C using an electric heating jacket. Reaching the set temperature took approx. 15 minutes. Upon reaching the target temperature, the 30-minute treatment period began. The emerging gases and vapours flowed from the reaction chamber into a condensing unit (shell and tube heat exchanger), where vapours were condensed into the liquid product. After the condensing unit, a gas extraction station was installed using a bypass. At this point, the composition of the gas was determined in the experiment. The remaining gas was released into the environment after passing through an activated carbon filter. After the treatment period expired, the heater was turned off while the reaction chamber continued to rotate. As soon as the temperature in the reaction fell below 200°C, the rotation was also stopped.

The experiment was carried out at a temperature of 600°C with a retention time of 30 min with a nitrogen flow of 1 L/min, at ambient pressure.

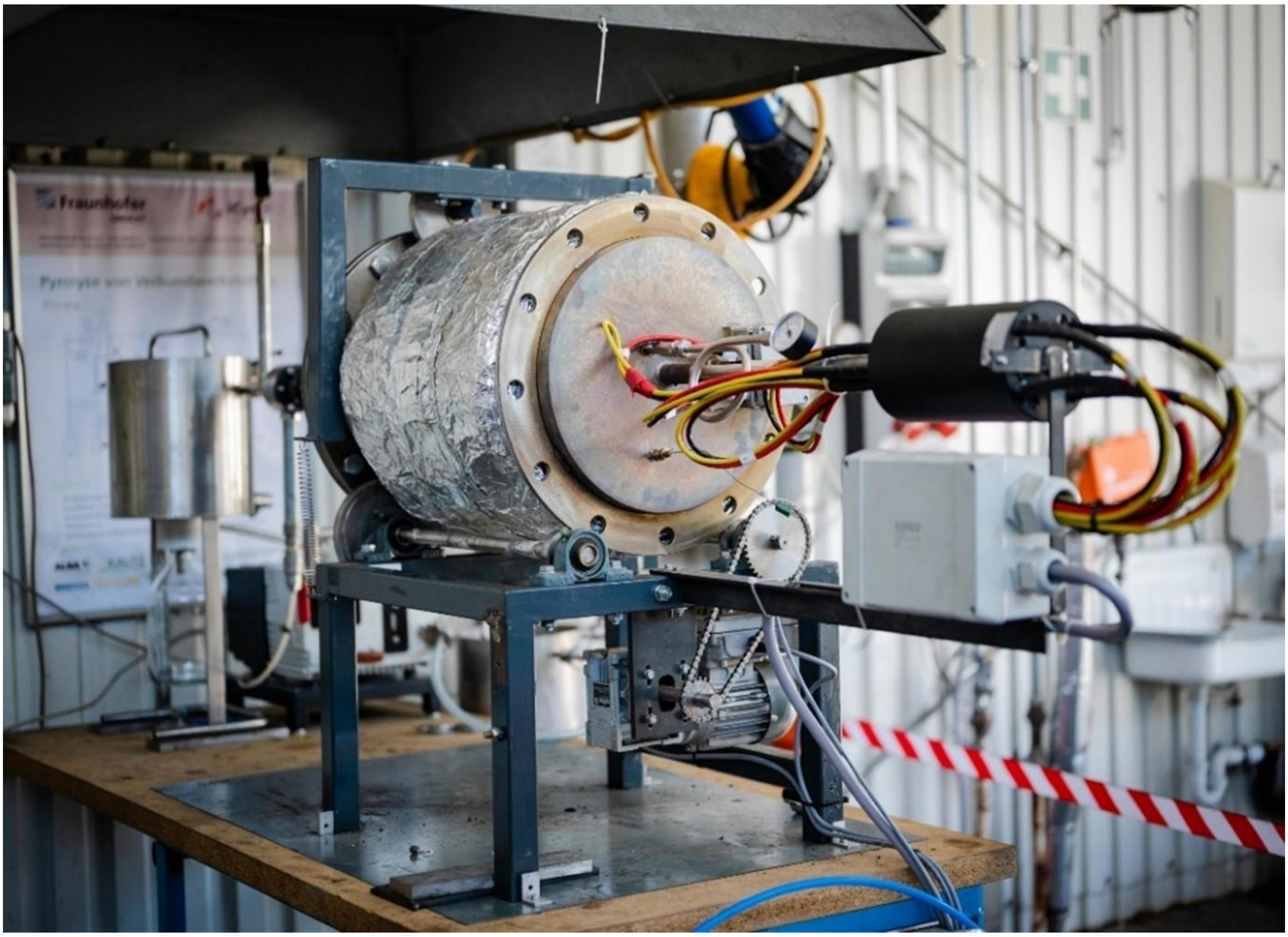

Figure 3.1.2 Batch-scale plant for the thermo-chemical conversion, © Fraunhofer UMSICHT

The plant cooled down overnight and was opened the next day to collect and weigh all products. The following products were collected:

- SOLID PRODUCT, which was present in the reaction chamber after the experiment;
- OIL PRODUCT, which was present in the condensing unit and the collection container mounted on it after the experiment;
- GASEOUS PRODUCT, which was not collected and weighed. The mass of gaseous product was determined as the difference between the mass of treated material and the masses of solid and liquid products and losses;
- LOSSES, which were the small quantities of products that could not be transferred to the collection containers and weighed. LOSSES were estimated at 2% by weight of the input material. Without this estimate, real LOSSES would be erroneously attributed to the gaseous product.

After harvesting and weighing the products, plant components were cleaned, and the plant was prepared for the next experiment.

3.1.3. Mass Balances

Figure 3.1.3a shows percent yields of pyrolysis products, solid, liquid, and gaseous, of all lab-scale pyrolysis samples, and of the MIXED FRACTION of the batch-scale experiment.

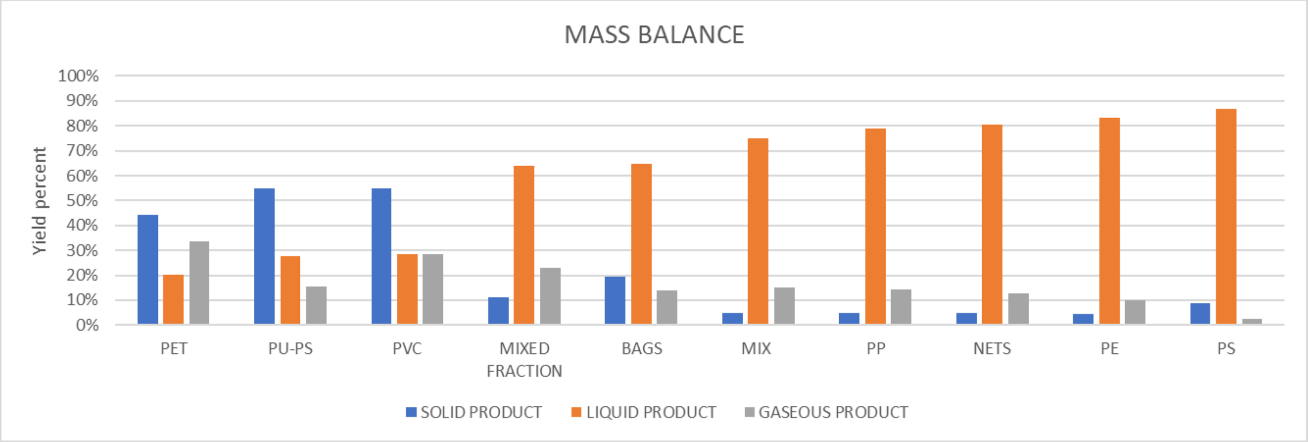

Figure 3.1.3a Percentage value of product yields

Significant differences in product yields could be observed with the lab-scale pyrolysis experiments. The highest oil yield was obtained for PS, the lowest for PET.
The lighter coloured oils, as seen in figure 3.1.3b (e.g. NETS, BAGS, PE) have a high viscosity at room temperature. Oils made from PVC, PS or PU-PS are characterized by their low viscosity.

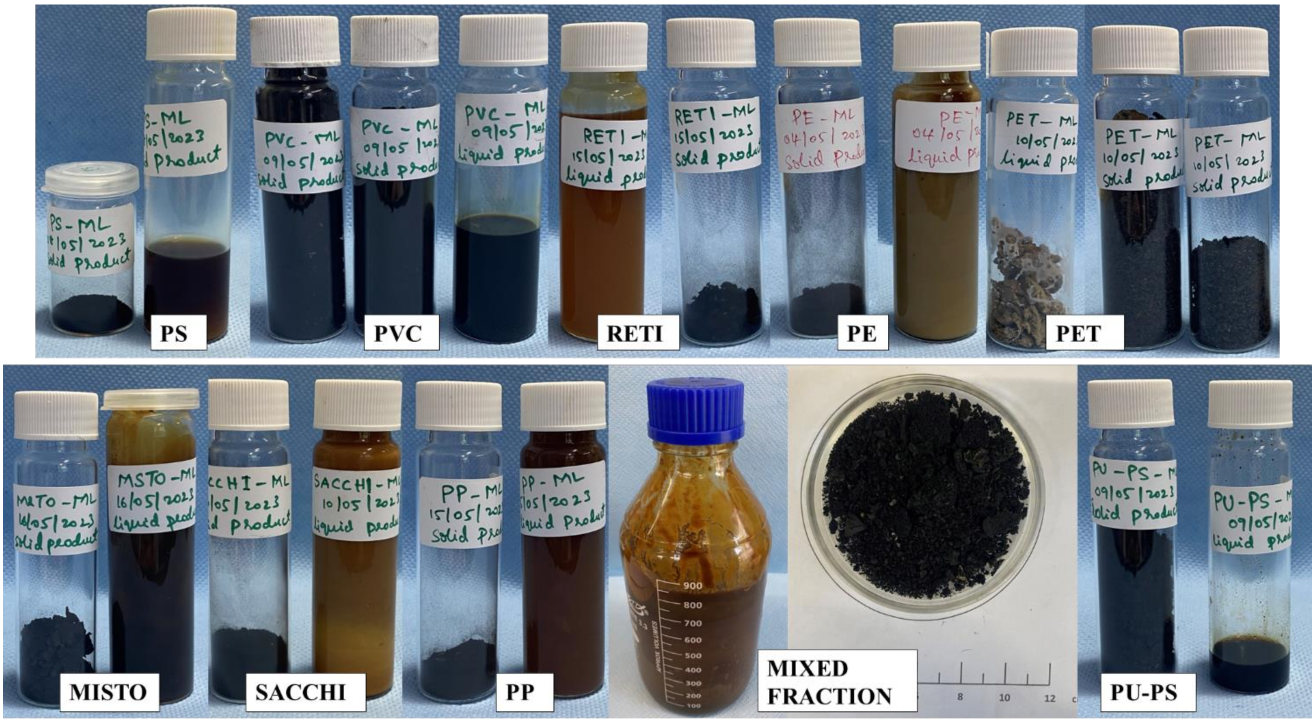

Figure 3.1.3b Pictures of the pyrolysis products, © Fraunhofer UMSICHT

3.2. Analytic results

After the pyrolysis processes, all pyrolysis products were analysed using the following analytical methods:

- Determination of dry matter and loss on ignition;
- Determination of the calorific value;
- Elemental analysis (CHNS);
- Gas chromatography combined with mass spectroscopy (GC/MS);
- Analysis of X-ray fluorescence (XRF).

Due to the different bulk density, of the different raw materials and the various product yields during lab-scale experiments, only the pyrolysis oil produced from each sample could be analysed.

3.2.1. Calorific value determination

Figure 3.2.1 shows results of the calorific value of all the oils produced from the laboratory scale pyrolysis and from the MIXED FRACTION, SOLID PRODUCT and OIL PRODUCT from the batch scale experiment.

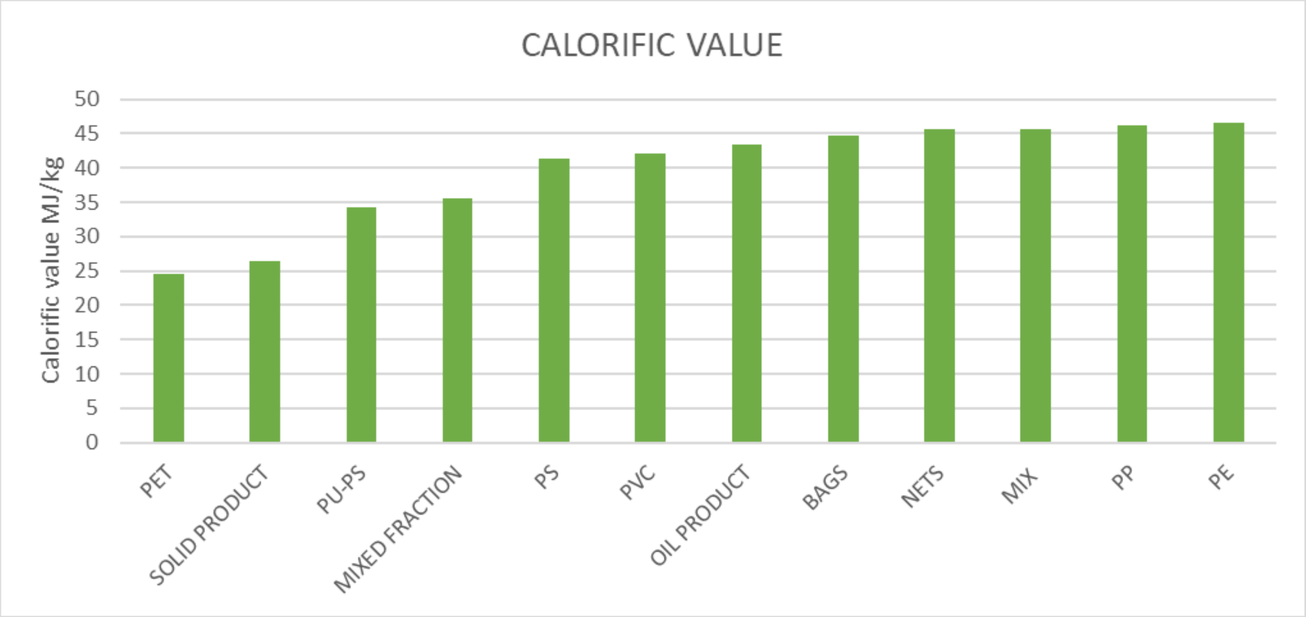

Figure 3.2.1 Calorific value of all sample

Excluding the PET, PU-PS, SOLID PRODUCT and MIXED FRACTION samples, all samples have a calorific value between 40 and 47 MJ/kg.

3.2.2. Elemental analysis C, H, N, S

Figures 3.2.2a and 3.2.2b show the results of the CHNS analysis of all the oils produced from the laboratory scale pyrolysis and from the MIXED FRACTION, SOLID PRODUCT and OIL PRODUCT of the batch scale experiment.

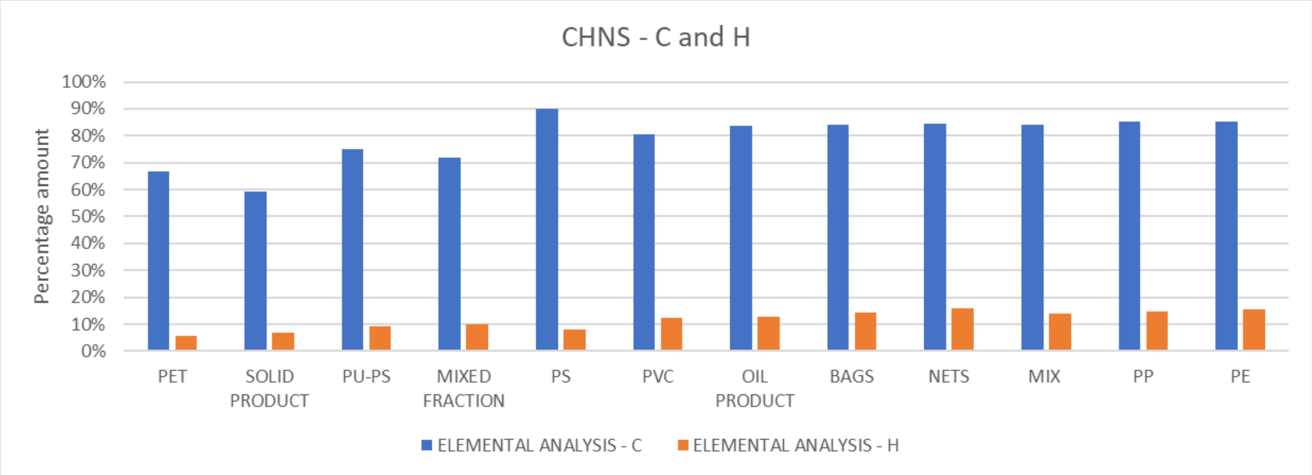

Figure 3.2.2.a Percentage value of C and H, for each sample, relative to the CHNS analysis

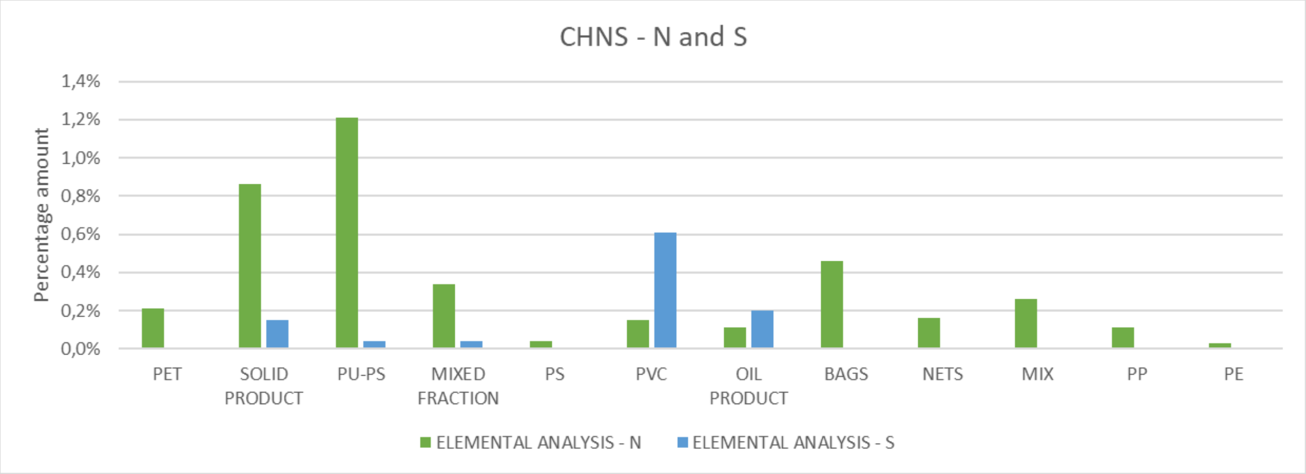

Figure 3.2.2.b Percentage value of N and S, for each sample, from the CHNS analysis

For the BAGS and PU-PS samples, significantly higher nitrogen concentrations could be observed. The PVC sample was the only lab-scale pyrolysis sample that consisted of parts of sulphur. The lowest concentration of hydrogen was identified for PET.
An enrichment of nitrogen and sulphur was highlighted, and a decrease of carbon and hydrogen, from the MIXED FRACTION to the SOLID PRODUCT.

3.2.3. Water content, Loss on ignition and Acid value

Figures 3.2.3a and 3.2.3b show the water content and loss of ignition for MIXED FRACTION and SOLID PRODUCT. The SOLID PRODUCT has a higher water content, but the MIXED FRACTION almost completely loses its weight during the ignition loss analysis.
Loss on ignition is the process of measuring the change in weight of a sample after it has been heated to a high temperature causing some of its contents to burn or volatilize.

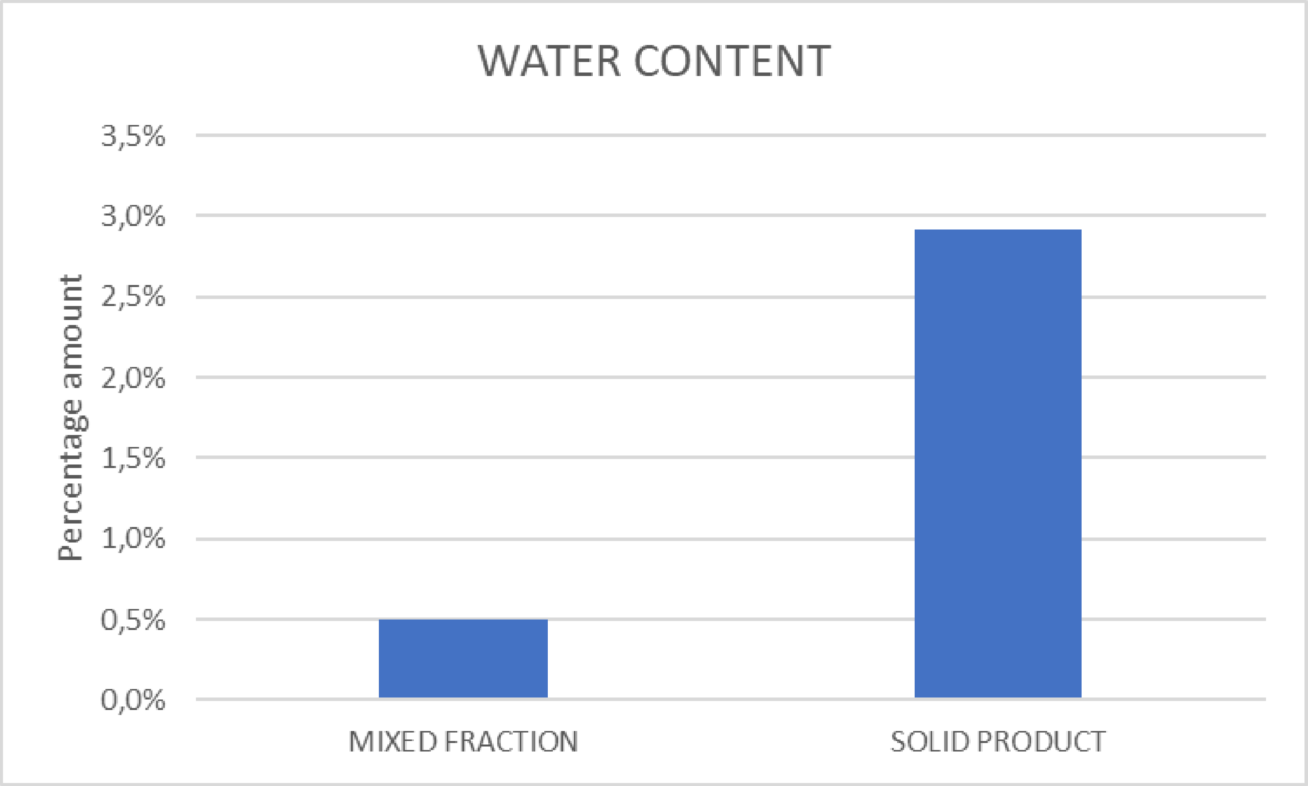

Figure 3.2.3a Water content, in percent, of MIXED FRACTION and of SOLID PRODUCT

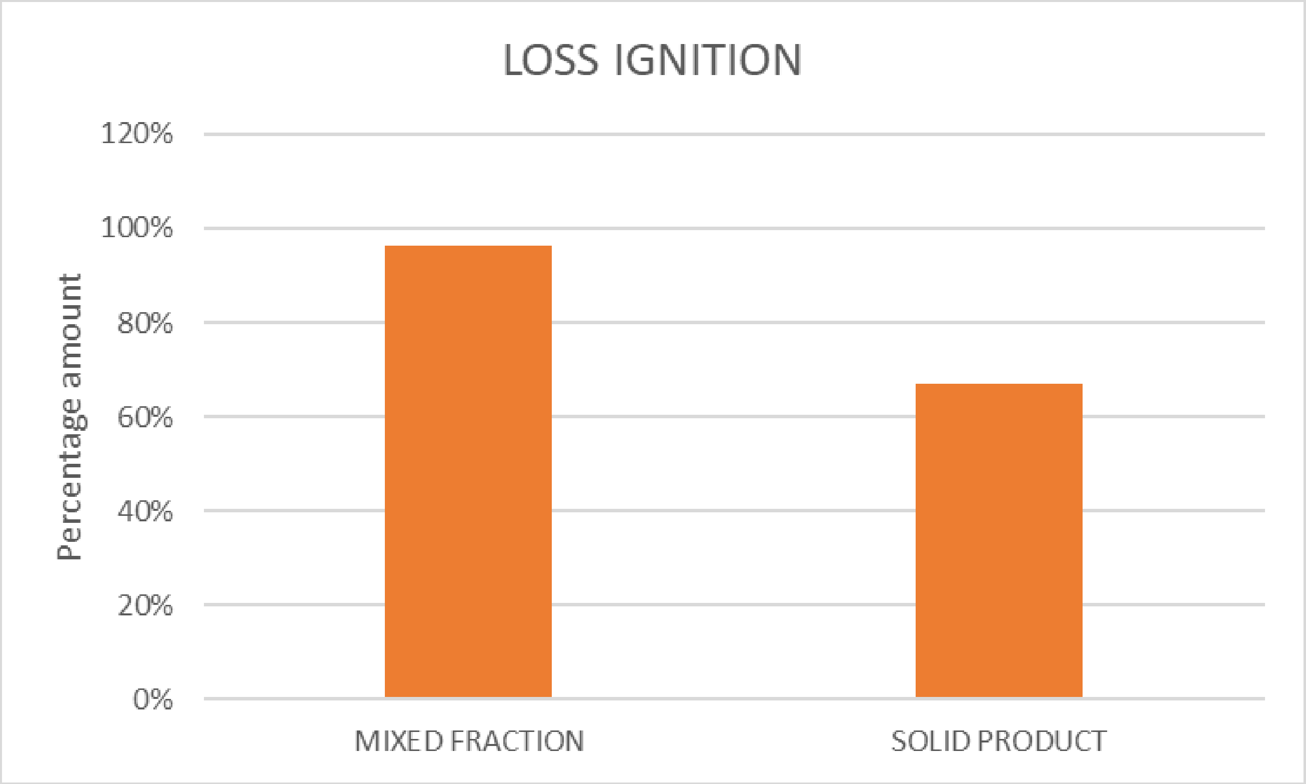

Figure 3.2.3b Loss of ignition, in percentual, of MIXED FRACTION and of SOLID PRODUCT

The TAN (Total Acid Number) and the water content (H2O) were not conducted due to the high viscosity of the oil, because these two analytical operations only work with liquid oils.

3.2.4. GC-MS analysis

The GC-MS analysis of all the oils produced from the laboratory scale pyrolysis and the OIL PRODUCT from the batch scale experiment, gave the following results:

- MIX oil consists almost entirely of aliphatic compounds and styrene is the only aromatic compound detected with a percentage of 4.17%;
- Prevalence of aliphatic compounds in BAGS, NETS, PP and PE oil;
- PU-PS oil consists entirely of aromatic compounds, is very rich in BTEX-aromatics and styrene;
- PVC oil is a mixture of aliphatic and aromatic compounds, with a predominance of aliphatic compounds;
- Styrene is 78.60% of PS oil;
- PET oil contains mainly acidic compounds; benzoic acid with over 75% represents the main component of the oil;
- In the OIL PRODUCT, the main components are 2,4-dimethyl-1-heptene (33.66 %) and styrene (18.62 %). The other components are various aliphatic compounds having carbon numbers between C8 and C24. Also, some other aromatic compounds could be identified.

3.2.5. Elemental determination by XRF

XRF analysis was performed only for solid material (MIXED FRACTION and SOLID PRODUCT of batch scale experiment) and OIL PRODUCT of batch scale experiment. The results were:

- Solid materials: various quantities of inorganic and metallic elements were identified, such as Ca and Si, as well as Cl, S, P and Br;
- OIL PRODUCT: The S and Cl content was ~0.5 and 0.3%. There are also inorganic elements with concentrations below 0.1%, such as Si and P.

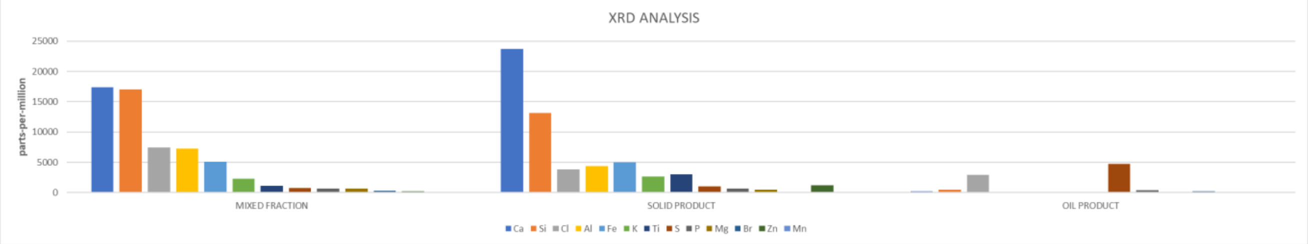

Figure 3.2.5 XRF analysis results, in ppm (ratio of measured quantities of one million to one), of MIXED FRACTION, SOLID PRODUCT and LIQUID PRODUCT

3.2.6. Analytic results of the gaseous product

The gas analysis unit, installed between the cooling unit and the activated carbon filter, measured the GASEOUS PRODUCT during the experiments. Gases CO, CO_2, CH_4, C_nH_m, H_2, O_2 and N_2 were measured on-line during the experiment, every 20 seconds. The gas stream consists mainly of nitrogen (49%), the gas used during pyrolysis to create an inert atmosphere.

The average values, in percent, of the other gases measured are:

- CO: 7.55%
- CO_2: 7.75%
- CH_4: 13.30%
- C_nH_m: 14.99%
- H_2: 1.16%
- O_2: 6.21%

The lower calorific value (LHV) of the gas was calculated at approximately 19.51 MJ/m^3.

3.3. Discussion of results

The liquid products of laboratory-scale pyrolysis experiments led to different results. The calorific value of the oils was mostly around 45 MJ/kg. Only PET and PU-PS oils produced lower calorific values. PET, as seen in the GC-MS results, consists mainly of acids, which reduce its calorific value to about 25 MJ/kg. The liquid phase of PU-PS contains components with a high calorific value, but also a water content that lower the calorific value.

The GC-MS results for PP, NETS and MIX are very similar. All consist of the main component 2,4-dimethyl-1-heptene and aliphatic compounds with different carbon values. Furthermore, the GC-MS results of PE and BAGS oils are comparable and mainly consist of same aliphatics.

Very high concentrations of a specific compound were recorded in PET and PS oils. PET contained almost 77% benzoic acid and PS almost 79% styrene. Both chemical compounds are monomers which are basic components in the chemical structure of plastics.
The oil produced from PU-PS contained many valuable aromatics. A lot of toluene (~15%), ethylbenzene (~29%) and styrene (~36%) was determined in the oil. All these chemicals are raw materials in chemical industry to produce different chemicals or plastics.

The OIL PRODUCT of the batch-scale pyrolysis experiment mainly contained two components, 2,4-dimethyl-1-heptene with approx. 34 % and styrene with approx. 19%. Other chemical compounds were mainly aliphatic with a number of carbon atoms of at least 8. Some aromatics were also identified in the oil, in addition to styrene (about 6 %). The presence of chlorine and sulphur in the oil indicates that further refining is needed (such as through hydration to remove those atoms). The chlorine content in the oil is due to the PVC present in the raw material.

The SOLID PRODUCT of the batch-scale pyrolysis experiment serves as an alternative fuel to provide heat for the pyrolysis plant. Due to very low quantity of hazardous/toxic elements in the coke flue gas, cleaning after incineration is not complicated. Same as for the oil, a prior separation of PVC will remove chlorine from the coke. With its calorific value of 26,4 MJ/kg it is comparable to hard coal and provides an ideal feedstock for thermal utilization.

The GASEOUS PRODUCT of the batch-scale pyrolysis experiment contained high amounts of short-chain hydrocarbons such as methane, ethane, and ethene. As a result of this, a high calorific value of the gas was measured. Due to its low hydrogen content (~1%) further use as a syngas or to separate hydrogen is not worthwhile. Its ideal use is to supply process heat for the pyrolysis plant.

4. CONCLUSIONS

As part of the project, many marine plastic wastes, both from the seabed and stranded, was collected, and subjected to various treatments: sorting by polymer, drying, shredding. Subsequently, plastic fractions were split into nine different plastic samples, which were pyrolysed as individual polymer fractions in laboratory-scale applications.
The oils produced from each polymer fraction, except for PET and PU-PS, have a calorific value of 45 MJ/kg, while PET oil is rich in acids and PU-PS is rich in toluene, ethylbenzene and styrene, important compounds for the chemical industry.

Additionally, a mixed sample, containing all nine different types of waste, was treated in a batch-scale rotary kiln. Pyrolysis experiments in both plants were conducted without problems. From the results of the analyses carried out on the pyrolysis products of the mixed sample, it can be said:

- The gaseous product can be used to supply process heat to the plant, as it has a high calorific value;
- The solid product can be used as an alternative fuel to coal or to supply process heat to the pyrolysis plant;
- The liquid product, after further refinement, can be used as a raw material for steam crackers, to produce new plastics or to be used as a raw material for the chemical industry.