Comparative Analysis of the Behaviour of Marine Litter in Thermochemical Waste Treatment Processes

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Abstract: Plastic in the ocean, especially plastic on the ocean surface is not only researched intensively but also photos and reports raise awareness of the challenge in the general public. While research is concerned with the fate of marine litter in the environment, recycling of these materials after collection is rarely addressed, mainly because there is neither considerable data on composition nor a suggested process to do so. This study is the first to analyse and evaluate chemical recycling (pyrolysis, gasification) and energy recovery (incineration) of marine litter. Two heterogeneous marine litter samples from Sylt and Norderney, North Sea, Germany, were analysed, consisting of six different material groups. Agricultural mulch foil was used as reference material. The thermochemical treatment processes were reproduced by thermogravimetric analysis. Furthermore, pyrolysis trials on a semi-technical scale were conducted and the residues were analysed by proximate, ultimate and X-ray fluorescence analysis. The results indicate that heterogeneous and weathered material mixtures can be treated by thermochemical processes. Finally, the pyrolysis condensates are discussed as substrate for biotechnological upcycling. In summary, we present a comprehensive approach from the material characterisation of marine litter to the analysis of three different thermochemical treatment processes and the possibility to use the generated pyrolysis condensate for subsequent upcycling. The data collected form the basis for the evaluation and application of possible treatment options for the collected marine litter.

Keywords: marine litter; waste treatment; plastic waste; pyrolysis; gasification; incineration; thermogravimetric analysis; biotechnological upcycling; plastics recycling

1. Introduction

Plastics are a versatilely and controversially discussed topic. Due to the many advantages of the various materials concerning durability, low-costs in production, light weight and the possibility to fulfil numerous requirements (formability, heat resistance, insulation, etc.) it is ubiquitous [1]. Historic production is estimated at 8300 million metric tons (Mt) of virgin plastics with a waste generated of 6300 Mt [2].

While the materials themselves have a high added value, the problem of their material characteristics arises when getting into the environment. Here, there are different ways of entry which can be divided into land-based including river transport and ocean-based including oil and gas platforms [3]. Causes are littering, industries, natural storm events, wear and tear and defective waste management. The plastic leakage of land-based, mismanaged waste which is entering the oceans from coastlines is calculated to an annual
amount of 4.8 to 12.7 Mt taking into account solid waste, economic status, population density and coastal access [4]. After entering the environment, plastics are transported mainly in riverine systems, temporarily accumulate on sediments, in soils and on water surfaces and eventually deposit on the sea floor as a final sink [3].

Based on an oceanographic model which was additionally calibrated with data from numerous expeditions, Eriksen et al. [5] estimated the total count of plastic pieces and its weight floating in the oceans worldwide (Table 1). Thereby, the results showed a total count of $525.0 \times 10^{10}$ plastic particles with a total weight of $2689.4 \times 10^2$ tons. The results do not consider the plastics that sank to the ground.

|          | NP    | NA    | SP    | SA    | IO    | MED   | Total  |
|----------|-------|-------|-------|-------|-------|-------|--------|
| Count    | 199.0 | 93.0  | 49.1  | 29.7  | 130.0 | 24.7  | 525.0  |
| Weight   | 964.0 | 564.7 | 210.2 | 127.8 | 591.3 | 231.5 | 2689.4 |

Research on plastic in the environment started in 1972 [6]. Since then, many terms and definitions have been used describing this contamination focusing different aspects, such as size (nano-, micro-, meso- and macroplastic, macro litter), shape (plastic debris) or origin (anthropogenic litter, marine litter, marine plastic, plastic litter) [3]. These different terms make it particularly difficult to compare results of already published studies and thus to derive further prevention and waste treatment strategies.

A frequently used term also applied on a political level (United Nations, European Commission, Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection) is ‘marine litter’ [7–9]. According to the United Nations Environment Programme marine litter is defined as ‘any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment’ and thus includes not only plastics but also other possible waste fractions and emphasises the heterogeneity of the material [7].

The ocean surface can be seen as temporary sink within the life cycle of marine litter, as there are already different technical solutions to collect these waste items: extraction by vacuum, skimmer, air barrier, sand filters, drones and robots, waterway litter traps, detection aids, boats and wheels, river booms, large-scale booms and miscellaneous capture [10]. After the collection of marine litter, a further application in terms of recycling is required. In general, there are different treatment possibilities for waste plastics (Figure 1).

Although these methods are proven as treatment processes for plastics, especially the recycling routes are mainly restricted to pre-processed, sorted and separated polymer fractions. Considering marine litter in particular, additional points of conflict occur since the material is not only very heterogenous but also strongly weathered by various environmental influences. These external influences include mechanical degradation based on wave movement and sandy shores as well as degradation due to UV radiation, oxidation and the general process of biofouling [11]. Leaching of chemical additives (e.g., plasticisers) within the plastic fraction due to external influences additionally changes the material properties [12].

There are no standardised treatment processes for marine litter to date caused by missing recovery and recycling strategies. Furthermore, research on the applicability of treatment and recycling processes for marine litter is still lacking. This study is the first to analyse thermochemical waste treatment processes in application for marine litter comparing the methods of pyrolysis, gasification and incineration on a laboratory scale (Figure 1).
2. Materials and Methods

The material used in this study consists of three batches. The batches one and two were procured by Pacific Garbage Screening and originate from the North Sea where it was collected on Sylt and Norderney (Table 2). The sampling sites are shown in Figure 2. The materials were washed up on the beach and due to their location, origin and appearance the materials meet categorisation criteria for marine litter (ML). Manual collection was carried out randomly. Therefore, the material cannot be considered representative for the total waste load of the respective beach. The third batch used as reference material was commercial mulch foil for agricultural usage purchased from a hardware store.

Table 2. Material characteristics of the two batches of marine litter and mulch foil.

| Characteristics                  | ML Sylt                                                                 | ML Norderney                                      | Mulch Foil                        |
|----------------------------------|-------------------------------------------------------------------------|---------------------------------------------------|-----------------------------------|
| Marine litter washed up on the   | Marine litter washed up on the beach.                                    | Virgin grade LD-PE mulch foil (black)              |                                   |
| beach and mostly collected after |                                                                        |                                                   |                                   |
| high tide                        |                                                                        |                                                   |                                   |
| North Sea Germany, Sylt, Wadden  | North Sea Germany, Norderney, Wadden Sea National Park Norderney,       |                                                   |                                   |
| Sea National Park Sylt, West     | Norderney East                                                         |                                                   |                                   |
| Beach and East Beach             |                                                                        |                                                   |                                   |
| Coordinates                      | 55.014167° N 8.370444° E                                               | 53.715902° N 7.283360° E                           | -                                 |
| Weight                           | 5478 g                                                                 | 4522 g                                            | 975 g                             |
| Volume                           | 0.08 m³                                                                | 0.162 m³                                          | -                                 |
| Date of collection               | 22 April–15 May 2020                                                   | 17 April 2020                                     | -                                 |
2.1. Material Composition According to Material Group Catalogue

The sorting of the samples revealed a mixture of various types of material. They were sorted by hand according to a material group catalogue consisting of the following: 3D plastics, films, metals, nets, rubber, foamed plastics and others (e.g., glass and unidentifiable items). After sorting, the fractions were weighed to determine gravimetric composition (Table 3). Subsequently, the type of plastic of the individual materials was determined using a laboratory scale near-infrared spectroscopy (NIR) analyser.

Table 3. Composition of the marine litter (ML) samples used in this study [wt%].

| Material Group          | ML Norderney | ML Sylt |
|-------------------------|--------------|---------|
| 3D plastics             | 88 wt%       | 15 wt%  |
| Films                   | 10 wt%       | 6 wt%   |
| Metals                  | 1 wt%        | 2 wt%   |
| Nets                    | -            | 55 wt%  |
| Rubber & Elastomers     | -            | 8 wt%   |
| Foamed plastics         | <<1 wt%      | 5 wt%   |
| Others                  | 1 wt%        | 9 wt%   |
2.2. ML Sylt

In the ML Sylt sample, the nets fraction made up the highest proportion with 55 wt% (Table 3). As shown in Figure 3D, the nets consisted of different types of plastic such as polypropylene (PP) and high-density polyethylene (HDPE). 3D plastics made up 15 wt% of the total weight. In contrast to ML Norderney, there were no bottles within the sampled material. This fraction mostly comprised fragments of boxes, caps and canisters made of polystyrene (PS), PP, polyvinyl chloride (PVC), HDPE and acrylonitrile butadiene styrene (ABS) (Figure 3A). 8 wt% were rubber and elastomers, like the glove shown in Figure 3E and 6 wt% films consisting of PP, PVC, PA, HDPE and PS. Foamed plastics made up 5 wt% of the total weight including polyethylene terephthalate (PET), PS, HDPE and polyurethane (PUR) foams. Non-polymer materials of the sample made up 9 wt% and consisted of glass, textiles, bones or feathers. Metals, like the spray can shown in Figure 3C, represented 2 wt% of the sample.

Figure 3. ML fractions Sylt: (A) 3D Plastics; (B) Films; (C) Metals; (D) Nets; (E) Rubbers & Elastomers; (F) Foamed Plastics and (G) Others. The scale amounts to 1 cm per section (Picture: Jacqueline Plaster, Johann Hee).

2.3. ML Norderney

For the ML Norderney sample, the 3D fraction made up the highest proportion with 88 wt%, comprised of plastic bottles (Table 3 and Figure 4A). The materials from this fraction consist mainly of PET, PP and HPDE but also PS and PUR. Films made up 10 wt% of the total quantity including PVC, HDPE, PS, PP, ABS (Figure 4). The remaining portion (1 wt%) consisted of metals, others (1 wt%) and foamed plastics with less than 1 wt% in relation to the total weight. In contrast to the material from Sylt, no nets were found.
2.4. Selection of A Comparative Material

For the thermochemical conversion experiments investigating the behaviour of ML in thermal waste treatment processes, mulch foil was chosen as a reference material for the two ML fractions. Mulch foil is often used in agriculture for vegetable production to enhance the soil temperature and to protect crops from unfavourable growing conditions, such as weed growth, evaporation of soil moisture and the spread of soil-borne diseases. The material usually consists of PE from fossil resources which is hardly biodegradable. Due to its benefits and leading to a higher harvest yield the use of mulch foil increased rapidly over the last decades. At seasons end the material requires collection and disposal. Instead, because of wear and tear, photodegradation, lack of waste collection at seasons end and its durability the material continuously accumulates in the environment and thus becomes an increasing contamination [13,14].

Recent developments in recycling processes focus on the biotechnological degradation of PE and subsequent enzymatical conversion of decomposition products into precursor chemicals. The most promising results in precursor yields are currently observed at microbial fermentation experiments on pyrolysis condensate from PE. [15] A possible aim for future so called biotechnological upcycling is to include a pyrolytic pre-treatment to provide access to a suitable carbon source. Consequently, the mulch foils are a suitable reference material for evaluating the behaviour of a homogeneous fraction in thermal waste treatment processes in comparison to heterogenous ML.
2.5. Chemical Composition of Material Samples

For the analytical determination of their chemical composition and thermogravimetric analysis (TGA) trials the respective material fractions were mixed again, shredded and sampled in accordance with LAGA PN 98 [13]. After separation of metallic fractions, the samples were milled to <1 mm grain size.

Table 4 depicts the results of laboratory analyses of the raw materials used in thermochemical conversion trials. The two types of marine litter ML Sylt and ML Norderney show similar results both in proximate and elemental composition. Apart from the ash contents of 13.52 and 10.55 wt%, they mainly consist of volatile matter of 84.6 and 91.0 wt% respectively. Both present a similar relation of carbon and hydrogen while the ML Sylt sample additionally shows significant amounts of nitrogen, sulphur and chlorine as potential pollutant precursors. Comparatively the virgin nature of the mulch foil reference sample becomes apparent, containing no detectable pollutant precursors and negligible amounts of ash. Subsequently it delivers the highest values for C, H and energy content.

Table 4. Characteristics of ML fractions and mulch foils (as received) (* n = 2; ** n = 3).

|                      | ML Sylt | ML Nordenery | Mulch Foil |
|----------------------|---------|--------------|------------|
| **Proximate analysis** (wt%) |         |              |            |
| Moisture             | <0.2    | <0.2         | <0.2       |
| Ash (550 °C)         | 13.52   | 10.55        | 0.83       |
| Volatile matter      | 84.6    | 91.0         | 96.8       |
| **Ultimate analysis** (wt%) |         |              |            |
| C                    | 68.2    | 66.8         | 85.6       |
| H                    | 9.2     | 9.5          | 13.6       |
| N                    | 0.7     | <0.1         | <0.1       |
| S                    | 0.6     | <0.1         | <0.1       |
| Cl                   | 1.3     | 0.5          | <0.1       |
| **Calorific value** (kJ/kg) | 33,430  | 35,970       | 42,920     |

2.6. Experimental Setup

The thermochemical experiments were conducted in a Linseis STA PT1600 thermobalance. The furnace chamber can be purged with different gases and thus different processing atmospheres can be set. The sample material was placed in a crucible, which rested on a thermocouple measuring the sample temperature through the ceramic bottom. All experiments were conducted with a heating rate of 30 °C/min up to 850 °C sample temperature. To establish the atmospheric conditions of pyrolysis, gasification and incineration a mass-flow-controller for nitrogen and synthetic air was used. During the experiments, the weighing system of the thermobalance was protected by nitrogen as purge gas flow at 75 mL/min, not interfering with the conversion process. The sample gas, which determines the thermochemical process, was injected separately and flushed the sample at 50 mL/min. Pyrolysis was performed in nitrogen atmosphere while synthetic air was used for incineration. For gasification, an air ratio of 0.3 was calculated based on data from fuel analysis and synthetic air flow set accordingly.

The sample materials created for laboratory analysis were also used as sample material in the TGA. The sample weight was 100 mg per trial and at least three repetitions (n) were carried out.

Pyrolysis trials were repeated for all three materials in a retort furnace with an increased sample size of 0.5 kg. As shown in Figure 5, the setup consisted of a modified Thermconcept KM 70/13 chamber furnace containing a stainless steel retort as fixed-bed reactor.
To ensure oxygen exclusion and thus pyrolytic conditions, the retort was continuously flushed with nitrogen. The furnace was heated up at a rate of ca. 8–10 K/min. To minimise the risk of sudden pressure rises the heating program involved a 30 min plateau at 250 °C before heating up to the target temperature of 700 °C and holding for another 30 min. The pyrolysis gas produced in the retort was led through steel containers tempered to −20 °C to collect all condensable components. In case of blockage this condenser can be bypassed through a bursting disc which was not necessary in the presented trials. The remaining permanent gas fraction was burned in a post-combustion chamber to minimise harmful gas emissions. After each trial, char and condensable product fractions were collected from the retort and the condenser respectively and analysed for proximate and elemental composition. As mentioned above, the condensate was additionally used for pre-trials in biotechnological processing. On this basis, an outlook is given for its potential to produce precursors for chemical industries.

2.7. Biotechnological Upcycling

Microorganisms can colonise various habitats by metabolising a variety of molecules. In biotechnology, this potential is applied by converting inexpensive substrates into economically interesting molecules. For this purpose, microbes are isolated from diverse habitats. Hydrocarbon-degrading microbes can be found for example in soils and sediments and even enriched in the event of an oil-spill [16]. Lignolytic microbes often have the properties to degrade polycyclic aromatic hydrocarbons [17]. The idea of biotechnological upcycling is to use those abilities to metabolize pyrolysis condensate components and convert them into molecules that can be further used in the sense of a circular economy [18].

The approach to utilise pyrolysis condensate as feedstock has already been demonstrated for pure fractions. Ward et al. [19] were able to produce the biodegradable plastic polyhydroxyalkanoate (PHA) by feeding *Pseudomonas putida* CA-3 with pyrolysis oil from polystyrene (PS). For the pure fraction of polyethylene (PE), a pyrolysis condensate consisting of 99% alkanes and alkenes was also converted to PHA with *Pseudomonas aeruginosa* PAO-1 [20]. Pure polyethylene terephthalate (PET) pyrolysis condensate, which mainly consisted of oligomers of terephthalic acid, was added to a sodium hydroxide solution, resulting in 97% terephthalic acid of the solid fraction. Kenny et al. [21] were able to isolate several bacteria, also of the genus *Pseudomonas*, which metabolise terephthalic acid and thus also capable produce PHA from the PET pyrolysis condensate.

These studies each used a pure plastic fraction as starting material. In the case of mixed polymer fractions, the composition of the pyrolysis condensate can differ considerably from the pyrolysate of the pure fraction. It can consist of a mixture of all the substrates described above and additional molecules. The organism growing on this mixture must be able to ideally convert a wide range of substrates and tolerate the presence of potentially toxic
substances. Furthermore, the following requirements apply when using mixed-fraction pyrolysis condensate as a substrate:

1. The hydrophobic condensate must be introduced into the microbial liquid culture in such a way that the microbes are able to access and use it as carbon source. Some microbes naturally produce biosurfactants to gain access to hydrophobic substrates. To improve substrate uptake, bioavailability can be increased by the targeted application of biosurfactants such as rhamnolipids [20]. With increased organic phase surface, the mass transfer into the water phase or directly to microbes increases, allowing increased conversion rates.

2. In the next step, the microbe must be able to transfer the molecule into the cell, while the cell wall normally serves as a barrier for hydrophobic compounds. Therefore, the microbe must possess transporters supporting this transfer such as an alkL pore in the outer cell membrane of some alkane-degrading Pseudomonas [22].

3. After uptake of the hydrophobic molecules into the cell, the microbe must be equipped with biochemical pathways for their degradation. Here, the metabolic funnel of microbes allows ideally the co-consumption of alternative carbon and energy sources [23], while the use of synthetic microbial mixed-cultures are discussed, in which microbial members take-up individual degradation tasks, converting the mixed substrate source to a single product [24].

3. Results and Discussion

3.1. Thermogravimetric Analysis

In total 39 marine litter trials were conducted with TGA to simulate pyrolysis (n = 14), gasification (n = 11) and incineration (n = 14).

The curves of the TGA (Figure 6A, Figure 7A, Figure 8A) and first derivative of TG (DTG) (Figure 6B, Figure 7B, Figure 8B) show similar trends for pyrolysis, gasification and incineration. As expected, the curves for the homogeneous reference material mulch foils are significantly smoother in all trials. However, the curves for the individual materials differ in relation to the respective thermochemical process. Pyrolysis mass losses were determined for ML Sylt at 79 wt%, Norderney at 88 wt% and mulch foils at 91 wt%. For all materials, the TGA and DTG signal show gradual progress of further mass loss above 500 °C until the end of the programme, which indicates a migration of fixed carbon to volatile phase.

For ML Sylt, mass loss for gasification (Figure 6) increases (compared to pyrolysis) insignificantly up to 80 wt%. The increase in mass loss of the other two materials is larger and an indication that the char remaining after pyrolysis is gasified. In the case of incineration, the analysis results of the ash content listed in Table 4 differ from those of the TGA for ML. As shown in Figure 7, the ash content can be determined for ML Sylt at 14 wt%, ML Norderney at 5 wt% and mulch foil at 0.1 wt%. Reason for this difference is the heterogeneity of the collected sample or the calcination of contained carbonates at temperatures above 550 °C in TGA.

TGA measurements can vary greatly depending on the sampling. Figure 9 shows a comparison of determined sample mass constancy of all conducted TGA trials. In order to evaluate the significance of the TGA trials independently of the heterogeneity of the sample, the deviation from the reference material mulch foil can be considered. The complexity of the investigated thermochemical processes pyrolysis (A), gasification (B) and incineration (C) are clearly visible. Further oxidation decreases deviation in total.
Figure 6. (A) shows the thermogravimetric analysis (TGA) mean value of pyrolysis. (B) shows the standardised derivative of TG (DTG) signal. (ML Sylt n = 5, ML Norderney n = 5, Mulch foil n = 4).

Figure 7. (A) shows the TGA mean value of gasification. (B) shows the standardised DTG signal. (ML Sylt n = 4, ML Norderney n = 4, Mulch foil n = 3).

Figure 8. (A) shows the TGA mean value of incineration. (B) shows the standardised DTG signal. (ML Sylt n = 5, ML Norderney n = 5, Mulch foil n = 4).
Table 5 shows the measured reaction temperatures and calculated standard deviation, respectively. $T_i$ indicates the initial temperature when 1 wt% mass loss is quantified while $T_p$ marks the temperature of the highest relative mass loss as calculated by the derivation of the TGA signal. Although no moisture could be quantified in the sample of ML Sylt, initial mass loss can be observed at temperatures below 150 °C. The temperature of the reaction peak ranges from 438–467 °C. $T_p$ differs slightly between the ML fractions, while $T_p$ for mulch foil is very constant. Based on $T_c$, it can be observed that devolatilization of ML during pyrolysis is significantly slower and occurs up to high temperatures. The reaction with oxygen during incineration is completed earlier that is, at lower temperatures. In conclusion, it can be stated that the standard deviation for the results of the ML fractions is consistently higher than for the mulch foils.

3.2. Retort Furnace

The pyrolysis trials in the retort furnace allow separate capture of char and condensate products and subsequent analysis of samples. The results are presented in Table 6. The trials resulted in char yields ranging from 9.3–18.2 wt% and condensate yields of 21.5–
32.3 wt%. As suggested by raw material analysis the char fractions from marine litter educts contain higher amounts of ash and thus lower carbon. Elementary composition in general reflects the results of ultimate analyses as shown in Table 4 with heteroatoms of hydrocarbons concentrating in the char fractions up to 2.0 wt% of sulphur and 4.4 wt% of chlorine. Ultimate analysis shows high contents of carbon and hydrogen for marine litter condensates likely deriving form organic hydrocarbons while mulch foil condensate leaves a significant gap in the balance of detectable elements. This does not match its comparatively high calorific value suggesting an impression in elementary analysis. For all educts calorific values of condensate exceed their respective char fractions, demonstrating the release of energy-rich compounds in the pyrolysis process. These results appear plausible considering the raw materials consisting mainly of ash and volatile matter.

| Table 6. Characteristics of pyrolysis products derived from different plastic wastes (as received) (* n = 2; ** n = 3). |
|---------------------------------------------------------------|
| Product fraction (wt%) | Sylt Char | Norderney Char | Mulch Foil Char | Sylt Condensate | Norderney Condensate | Mulch Foil Condensate |
|-----------------------|-----------|---------------|----------------|----------------|---------------------|-----------------------|
| Proximate analysis *  |
| Moisture              | <0.2      | <0.2          | <0.2           |                |                     |                       |
| Ash (550 °C)          | 84.89     | 52.75         | 27.57          |                |                     |                       |
| Volatile matter       | 7.3       | 4.1           | 4.3            |                |                     |                       |
| Ultimate analysis **  |
| C                     | 20.3      | 49.7          | 72.2           | 77.0           | 72.7                | 56.6                  |
| H                     | 0.2       | 1.0           | 0.3            | 11.0           | 10.3                | 8.8                   |
| N                     | 0.7       | 0.3           | <0.1           | 0.4            | <0.1                | <0.1                  |
| S                     | 2.0       | 0.2           | 0.3            | 0.1            | <0.1                | <0.1                  |
| Cl                    | 4.4       | 3.0           | <0.1           | 0.2            | 0.9                 | <0.1                  |
| Calorific value *(kJ/kg) | 8590   | 18,440        | 25,080         | 41,500         | 37,210              | 42,170                |

For further elemental analysis of the pyrolysis products an X-ray fluorescence (XRF) analysis was performed and the detected elements with the highest mass fractions were plotted as shown in Figures 10A, 11A and 12A. Furthermore, the content of heavy metals mentioned in the German ordinance for waste incineration (17. BImSchV) was determined in the samples and plotted on the right side (B). Due to the methodical detection limits of the XRF analyser, sodium (Na) and magnesium (Ma) were not included for condensate products. The XRF analysis of the ML raw materials shows significantly increased contents of sodium, silicon and calcium compared to the reference material (Figure 10A). These elements are used in plastics manufacturing as additives with the function of, for example, filler and reinforcing material [25]. However, the cause of the increased concentration in ML could be explained by the origin from sand and soil before collection. As shown in Figure 12 almost all elements are concentrated in the pyrolysis char. Amounts of potential harmful substances were found in low quantities in all the samples, peaking at 0.015 wt% lead for ML Sylt raw material and 0.35 wt% in the char, which had been expected higher for material containing fishing gear. The lead is partly built into the ropes as a weighting for the nets to improve sinking in the water. Previous studies showed lead contents of up to 0.75 wt% in the raw material and 2.25 wt% in the char of ML [26]. Norderney condensate and mulch foil char evince unexpected measurements, as contents of iron, chromium and nickel show the same ratio, which indicates cross-contamination with stainless steel in the sample pre-treatment.
Combining the results of pyrolysis product analysis with those of gas measurements allows examining the distribution of selected elements. Carbon and hydrogen were balanced according to their recovery rate in the product fractions, results are presented in Figure 13. Comparing elementary content in raw material with the accumulated content in pyrolysis products shows minor deviations in relation to the methodically inevitable imprecisions especially in pyrolytic processes. Carbon distributes across all three product fractions while hydrogen almost completely releases from the solid phase. In both elemental balances the gas fraction represents by far the highest fraction, due to slow cooling rates and thus high residence time in the gas phase allowing further cracking of condensable components into permanent gases. The distribution of elements across the product fractions is similar in all trials conducted.
Figure 12. Mass fraction of selected elements in pyrolysis char determined by XRF (n = 2). (A) shows detected elements with the highest mass fractions. (B) shows heavy metals mentioned in the German ordinance for waste incineration (17. BImSchV).

Figure 13. Elementary balances of pyrolysis products compared to analysed content in raw material. (A) carbon distribution across product fractions in wt%. (B) hydrogen distribution across product fractions in wt%.

To rank the transferability of results from the different experimental setups the distribution of pyrolysis products from the retort furnace is compared to the residual mass from the TGA setup. The latter one represents the char fraction while the mass loss is ascribed to the volatile compounds as a sum parameter consisting of condensate and gas as they correspond to the retort furnace. As presented in Figure 14 the char yields of the materials show very similar results in retort furnace and TGA setup. Both experiments used low heating rates of 8–10 °C/min and 30 °C/min thus returning virtually equal amounts of char. Target temperature (700 °C for retort furnace, 850 °C for TGA) appears to have an insignificant influence. Overall results validate both experimental setups used, suiting them for general material characterisation.
The three pyrolysis condensates of this study are unexpectedly of wax-like consistency. Previous studies on ML pyrolysis in the same retort furnace produced liquid condensates of honey-like consistency for the temperature investigated [26]. The current focus of the upcycling-efforts therefore is on requirement 1 (Section 2.7) how to make the condensate bioavailable by introduction into the liquid culture. Solvents and biosurfactants are tested for the ability to dissolve the condensate and their biocompatibility. As shown in Figure 15C,D, simply supplementing the liquid medium with the condensate and rhamnolipids, as in the study of Guzik et al. [28], will not be sufficient with the condensates of this study. One promising solvent is ethyldecanoate (Figure 15A), which has recently been shown to not affect the growth of Pseudomonas putida KT2440 but to be suitable for biotechnological application [27].

Biocompatibility is tested with several strains of Pseudomonas but also other metabolic versatile organisms with affinity towards hydrocarbons as Rhodococcus opacus who harbours...
genes for the AlkB monooxygenase [28] and known alkane-degrader Alcanivorax borkumensis [29] fulfilling requirements (2) and (3) (Section 2.7). In the following step, potential growth of microbes on pyrolysis condensate will be monitored via CO$_2$-development. When bacterial growth on the mixed-plastic pyrolysis condensate can be confirmed, the production of valuable compounds will be investigated.

4. Conclusions

The investigations performed and results presented refer to the collected material of the ML Norderney and ML Sylt. Since the collection was carried out randomly and without standardized conditions, it cannot be considered representative of all the waste washed up on the beach on Norderney and Sylt or other locations. The ML presented in this study rather shows the randomness of the composition of waste samples.

The results presented in this study demonstrate the principal possibility of thermochemical treatment of ML. The determined fluctuations in reaction temperatures, ash content or pollutants do not pose any problems for thermal treatment plants with state of the art process and emission control systems. Process selection depends on legislative incentives and possible cascaded recycling of intermediate and end products.

Conclusively, the necessity of tackling the pollution of the World Ocean with ML becomes obvious. Pyrolysis as part of a chemical recycling process needs extensive pre-treatment to remove impurities, for example, by crushing and sorting. The obtained condensable fractions present a valuable product for material recovery. Combustion of pyrolysis gases supplies the necessary process heat. The pyrolysis char is contaminated with pollutants such as heavy metals and must be post-processed safely in waste incineration plants for energy recovery and discharge of pollutants.

The use of condensable fractions for biotechnological upcycling presents an innovative approach to access the material potential of plastics unsuitable for mechanical recycling sustainably. Biotechnological use of pyrolysis condensate poses many challenges but versatile microbes as Pseudomonas might be able to meet them. They offer opportunities to produce valuable molecules for further industrial applications, thus reintegrating plastic waste fractions into a circular economy.

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