Thermogravimetric analysis and kinetic study of marine plastic litter

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ABSTRACT

This paper deals with marine plastic debris and its collection and recycling methods as one possible answer to the rising amount of plastic in marine environments. A novel approach is to use energy recovery, for example pyrolysis of marine plastic debris into high-energy products. Compared to other thermal processes, pyrolysis requires less technical effort and the end products can be stored or directly reused. In order to design such an onboard pyrolysis reactor, it is necessary to know more facts about the feedstock, especially the thermochemical behaviour and kinetic parameters. Therefore, a thermogravimetric analysis was carried out for three selected plastic sizes with a temperature range of 34–1000 °C. The results obtained from TGA showed the same curve shape for all samples: single stage degradation in the temperature region of 700–780 K with most of the total weight loss (95%). Small microplastics had an average activation energy of 320–325 kJ/mol.

1. Introduction

Marine plastic litter in the ocean is not a recently found phenomena but has already been known for decades. From the first report on marine litter in the 1970s (Venrick et al., 1972) to today, the number of items of litter found as well as the number of studies reporting it has increased intensely. The focus of those studies is on the growing amount of synthetic materials within the marine litter samples. Plastic represents 83% of the litter found and the remaining 17% is mainly textiles, paper, metal, and wood (UNEP, 2009). This vast amount of plastic causes not only aesthetic problems. The damaging impact of plastic litter is well documented and ranges from the release of toxic compounds (Mato et al., 2001), entanglement and ingestion through marine fauna (UNEP, 2009; Barnes et al., 2009), to economical damage (Galgani et al., 2010). Every year, approximately 8 million tons of plastic enters the ocean (Jambeck et al., 2015) and then either sinks to the seabed, washes up on shores (Thompson, 2015; Barnes et al., 2009), or ends up as floating litter in large gyres at the ocean surface (Lebreton et al., 2012). Global ocean circulation models demonstrate accumulation zones in all five subtropical oceans (Lebreton et al., 2012). Although the plastic litter undergoes degradation and fragmentation triggered by UV-light and wave action (Andrady, 2011), it persists for hundreds to thousands of years (Barnes et al., 2009). These stable and durable plastic fragments are buoyant, which allows them to be transported even to remote areas by currents and wind (Barnes et al., 2009). Removing this harmful litter is a goal for many foundations and organizations around the world. Examples are the International Coastal Cleanup, which engages volunteers to conduct cleanup events (Sheavly and Register, 2007), or the Ocean Cleanup Foundation, which presents a passive removal approach with U-shaped floating barriers. The Cleanup Foundation is still in the test phase, but the idea is to buffer the collected litter until a ship can transport it to land (Ocean Cleanup, 2017).

A more active approach is the method which will be presented in this article. Since the litter consists largely of synthetic materials, the conversion into high-energy products is evident (thermal recycling). Also, material recycling could be a possibility, but because it is more labour intensive due to the separation step required prior to the recycling step (Kukreja, 2009), the focus is on energy recovery. The thermochemical processes to transform the feedstock into a secondary energy carrier are varied (Goyal et al., 2008), but several aspects indicate pyrolysis. During pyrolysis the plastic, which consists of long-chain polymer molecules, degrades through heat and the absence of oxygen (Sharuddin et al., 2016) into end products in liquid, gaseous, and solid state. The end products are adjustable by controlling the parameters (Sharuddin et al., 2016). Hence the conditions of high temperature and a long residence time can lead to a large gaseous output, whereas the opposite conditions are required for liquid production (Basu, 2010). It is understandable that the most frequently produced types of plastics are also the ones most likely to be found in the marine environment, and therefore polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinylchloride (PVC) (Andrady, 2011; Hidalgo-Ruz et al., 2012). The pyrolysis of plastic feedstock produces mainly liquid oil, namely up

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Table 1
Densities of marine plastic litter in different regions used for reference.

Mean mass ρ	Sampling area	Mesh size	Reference
5114 g/km^2 (64–30,169 g/km^2)	Surface of North Pacific central gyre, surface	333 μm net	(Moore et al., 2001)
281–639 g/km^2	Subtropical ocean gyres	–	(Cózar et al., 2015, p. 5)
423 g/km^2	Mediterranean surface waters	0,2 mm	(Cózar et al., 2015, p. 5)
3000 g/km^2	Southern California shore	333 μm net	(Lattin et al., 2004)
2000 g/km^2	Southern California shore	333 μm net	(Moore et al., 2002)
60,000–400,000 g/km^2	Mediterranean 1387–3000 m depth	20 mm/40 mm	(Pham et al., 2014)
1–10,000 g/km^2	Global model	0,33 mm	(Eriksen et al., 2014)
46–1210 g/km^2	North Pacific Garbage Patch	–	(Liubartseva et al., 2016)
0–153,000 g/km^2 Mean: 3600 g/km^2	Western North Pacific Ocean	330 μm	(Yamashita and Tanimura, 2007)
71 g/km^2 (mean)	North Pacific Garbage Patch	–	(Liubartseva et al., 2016)
16,7 g/km^2	Northern South China Sea	< 2,5 ≤ 10 cm	(Zhou et al., 2011)

to 80 wt% (Fakhrhoseini and Dastanian, 2013), whereby LDPE produces the highest amount (93.1 wt%) followed by HDPE (84.7 wt%) and PP (82.12 wt%) (Sharuddin et al., 2016). According to Sharuddin et al. (2016), the liquid oil produced from HDPE, PP and LDPE has a calorific value similar to those of commercial diesel and gasoline. PET and PVC, on the other hand, produce a large amount of gaseous product (Fakhrhoseini and Dastanian, 2013), whose main components are hydrogen, methane, ethane, ethane, propane, propene, butane, and butane (Encinar and Gonzalez, 2007). As pyrolysis involves complicated chemical and physical processes (Gai et al., 2013), understanding them, especially in the case of new up growing feedstocks like marine litter, creates important data for designing and optimizing operation conditions and for the application of gasification (White et al., 2011).

2. Densities of marine plastic litter

The number of works in the literature about microplastics in the marine environment is increasing, but there are still huge differences in sampling techniques, and studies that give a plastic density in grams per square kilometre are very rare. Nevertheless, the results in Table 1 show that an important mass of plastic waste can be observed in different regions.

Therefore, a thermo-chemical upgrade directly on board a marine litter collection system could transform waste into valuable products (Fig. 1).

The new idea is to transform and use as well as store the end products directly on board of a ship. The liquid oil can be used in applications like furnaces and turbines (Sharuddin et al., 2016) and the gaseous output can be used to compensate the energy requirement of the pyrolysis plant (Abnisa and Daud, 2014). In order to design a pyrolysis reactor, it is necessary to gain knowledge of the kinetics reaction of the marine plastic (Saha and Ghosha, 2005). In the literature, the pyrolysis of plastic is well examined (Encinar and Gonzalez, 2007; Sharuddin et al., 2016) but no study has yet been conducted on a marine plastic litter sample. This study aims to investigate the characteristics and kinetics that describe the thermal decomposition process of marine plastic litter.

3. Experimental method

3.1. Sample preparation

The marine litter sample used in this study was collected on a sandy beach on the Greek island of Rhodos in summer 2015. The Mediterranean Sea has densely populated coasts and 30% of the world's marine traffic (UNEP, 2009) and therefore represented a good sample location. A member of the Institute of Chemical and Energy Engineering at the University of Natural Resources and Life Sciences, Vienna collected several kilos of marine litter. The plastic litter sample used in the study was prepared before analysis.

In order to identify the types of polymer, the densities of the particles in the sample were analyzed by using batches with different ethanol water mixtures. As the particle density correlates with the type of polymer, the measured average mass distribution on five different samples were: PP 91,8%, PE-LD 3,9%, PE-HD 3,9%, PVC 0,3%, PET 0,1%.

The sample was air-dried and then sieved with vibrating plate sieves into three selected size classes as described in the following.

At the moment, there is no globally coherent nomenclature for the ever-decreasing plastic particles within the oceans, which would be helpful for monitoring and assessment (Galgani et al., 2015). In general, scientists agree that microplastics are particles smaller than 5 mm in length (Andrady, 2011). In this study, the sample was divided into four selected size classes. Plastic particles smaller than 1 mm are called small
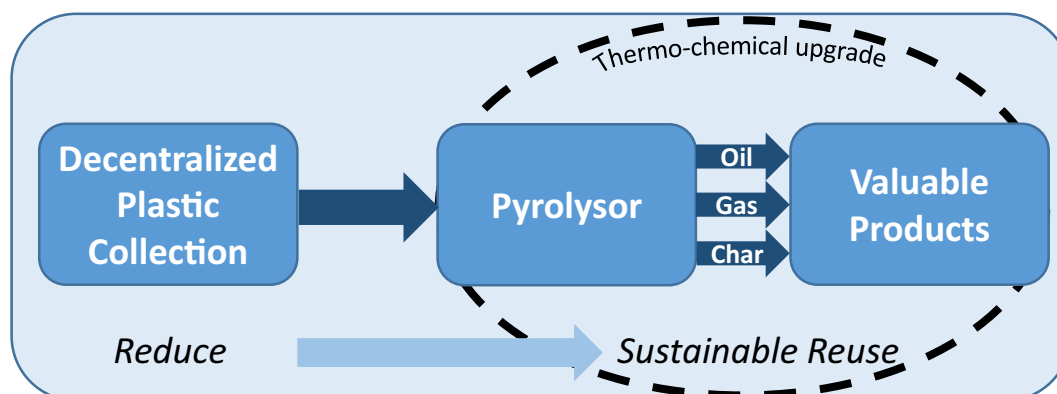

Fig. 1. Process description.