



Thermogravimetric analysis and kinetic study of marine plastic litter

Gregor Tondl*, Leonora Bonell, Christoph Pfeifer

Institute for Chemical and Energy Engineering, Department of Material Science and Process Engineering, University of Natural Resources and Life Sciences Vienna, 1180 Vienna, Austria

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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

* Corresponding author.

E-mail address: gregor.tondl@boku.ac.at (G. Tondl).

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 μ m 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 μ m net	(Lattin et al., 2004)
2000 g/km ²	Southern California shore	333 μ m 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	Western North Pacific Ocean	330 μ m	(Yamashita and Tanimura, 2007)
Mean: 3600 g/km ²			
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, 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

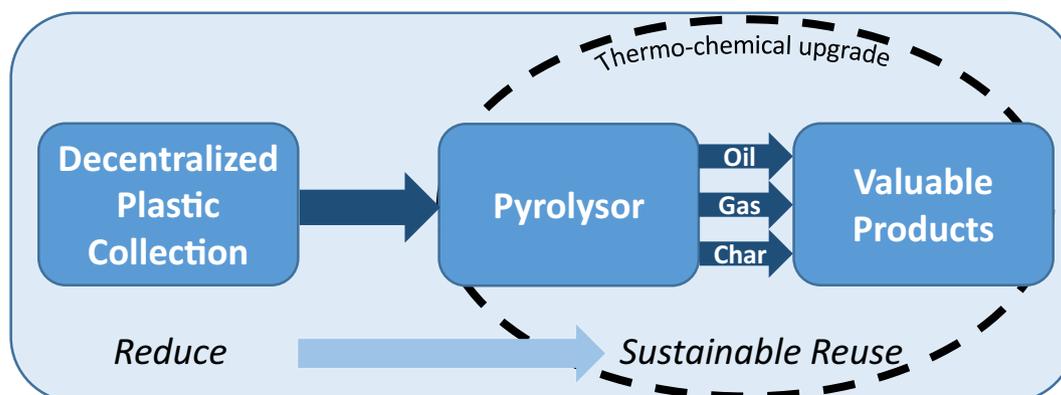


Fig. 1. Process description.

microplastics, those between 1 and 4 mm are called large microplastics, and those between 4 and 25 mm are called mesoplastics. The selected size classes for particles bigger than 25 mm are called macroplastics, but this category was omitted because none of the particles fulfilled this criterion.

The sieved particle fractions were then visually sorted, with the plastic particles being separated from other materials (Hidalgo-Ruz et al., 2012). The synthetic material was then mechanically processed to obtain a homogenous feedstock for the thermogravimetric analysis. The three classes were milled separately with a disc vibrating mill (Retsch RS1, 700 turns/min) and a centrifugal mill (Retsch ZM 1000, 10,000 turns/min and a 0.5 mm sieve).

3.2. Experimental techniques

The experiments were carried out in a Netzsch STA 409 CD thermogravimetric analyzer to measure and record the change in sample mass with temperature over the course of the pyrolysis reaction. For each of the three selected size classes, 16 mg ($\pm 1\%$ variation) of sample was weighed into a separate aluminium oxide (Al_2O_3) crucible. The samples were treated with the same temperature programme starting from 34 °C and rising to 1000 °C and were run through a start-standby (34 °C with a heating rate of 1 K/min for 10 min) to better compare the different tests.

Several kinetic curves are required to perform isoconversional analysis methods (Khawam, 2007) and therefore the samples were heated at four different heating rates, namely 5, 10, 15, and 20 K/min. For each heating rate, a separate blank curve was carried out for baseline correction by using an empty crucible. Between all the pyrolysis tests the furnace needed an oxidative process (1000 °C; argon: 40 ml/min; oxygen: 10 ml/min) to remove all possible remaining from the sample in the furnace. Argon gas was used as an inert purge gas at a flow rate of 50 ml/min to displace air in the pyrolysis zone. The results were used in the kinetic analysis.

3.3. Theory

The global kinetics of the pyrolysis reaction (Gai et al., 2013) are the solid-state reaction, which can be described as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the fraction of conversion, $f(\alpha)$ is the function of conversion, T is the absolute temperature (K), and $k(T)$ is the rate constant described by the Arrhenius equation. The conversion (α) is calculated through the total weight loss (Vyazovkin et al., 2011), $\alpha = (m_i - m_t)/(m_i - m_f)$, where m_i is the initial mass, m_t represents the weight at time t , and m_f represents the final mass after the reaction (Vyazovkin et al., 2011).

$$k(T) = Ae^{\frac{-E}{RT}} \quad (2)$$

The Arrhenius equation describes the temperature dependence of the rate constant $k(T)$, where A is the pre-exponential factor (min^{-1}), E is the apparent activation energy (kJ/mol), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K).

Combining Eqs. (1) and (2) and adding the linear heating rate β ($\beta = dT/dt$), the final equation for the dynamic analysis of the non-isothermal data is as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = \frac{A}{\beta} e^{\frac{-E\alpha}{RT}} f(\alpha) \quad (3)$$

Various methods of kinetic analysis of decomposition processes exist; they are generally classified as “model-fitting kinetics” and “model-free kinetics” methods (Khawam, 2007). The model-fitting method follows the approach of choosing the model with the best statistical fit after forceful fitting of the kinetic parameters to the equation.

The result is an ambiguous interpretation and the Arrhenius parameters vary drastically (Vyazovkin and Wight, 1999). The model-free method does not need any assumption of specific reaction models (α) and yields kinetic parameters as a function of either conversion (isoconversional analysis) or temperature (non-parametric analysis) (Vyazovkin, 2000). The advantage in choosing the model-free analysis is the simplicity and avoidance of errors. For thermochemical conversion research, the isoconversion methods are reliable methods for determining the activation energy and are more frequently adopted (Aboyade et al., 2012) and are therefore applied in this research.

Isoconversional analysis methods are based on the isoconversional principle, which states that at a constant extent of conversion, the reaction rate is a function only of the temperature (Vyazovkin and Sbirrazzuoli, 2006). This constant extent of conversion may be defined as the stage at which a fixed amount is transformed (Starink, 2003), so it represents an equivalent stage of the reaction for different heating rates. Based on the basic equation used, these isoconversion methods can be divided into two classes, namely differential (Starink, 2003) and integral analysis methods (Mishra and Bhaskar, 2014). Because of its unreliability and variability in the measured values (Starink, 2003), the differential method was not applied in this study.

The integral methods are based on the integral form of Eq. (3) (Mishra and Bhaskar, 2014).

$$\int \frac{d\alpha}{f(\alpha)} = G(\alpha) = \left(\frac{A}{\beta}\right) \exp \int \left(\frac{-E}{RT}\right) dT = \left(\frac{A}{\beta}\right) p(x) \quad (4)$$

The temperature integral, the term $p(x)$ in Eq. (4), has no exact analytical solution but there exist various approximations made by various researchers (Gai et al., 2013). The best-known methods are the Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa methods (FWO), which use different empirical approximations (Gai et al., 2013), and based on the KAS method there is a deviation by Starink, called the Starink method. All of the integral analysis methods can be described using a general formula as follows (Gai et al., 2013):

$$\ln\left(\frac{\beta}{T^s}\right) = C_s - \frac{BE}{RT} \quad (5)$$

where for the KAS method $s = 2$, $B = 1$, and $C = \ln(AR/(E_\alpha g(\alpha)))$; for the FWO method $s = 0$, $B = 1.052$, and $C = \ln(AE/Rg(\alpha)) - 5.331$; and for the Starink method $s = 1.8$, $B = 1.0037$ and $C = \ln(AR/(E_\alpha g(\alpha)))$.

The activation energy is obtained by plotting the left hand side of Eq. (5) versus $1/T$, which yields a straight line whose slope gives the value (BE_α/R) and the intercept gives the value of C from Eq. (5) (Slopieca et al., 2011).

For the pyrolysis of plastic, the first-order reaction is presumed to be the best fitting reaction model based on the results obtained by different researchers (Ceamanos et al., 2002; Encinar and Gonzalez, 2007) and the risk that the reaction order could change during the pyrolysis process due to the complicated physical and chemical processes (Gai et al., 2013). For the first-order reaction model, the function for the expression $g(\alpha)$ for solid state reactions in the integral form is $g(\alpha) = -\ln(1 - \alpha)$ (Mishra and Bhaskar, 2014).

4. Results and discussion

4.1. Thermogravimetric analysis (TGA)

The mass loss thermograms (TGs) of thermal decomposition of marine plastic litter pyrolysis of the selected size class “large microplastics” at four heating rates of 5, 10, 15, and 20 K/min under an argon atmosphere are shown in Fig. 1. The TG curve shows the loss of mass with temperature at different heating rates, where all three selected size classes showed similar temperature behaviour. Therefore only the selected size class of large microplastics is shown in Fig. 1, as the shapes of the decomposition curves for the other two size classes are nearly

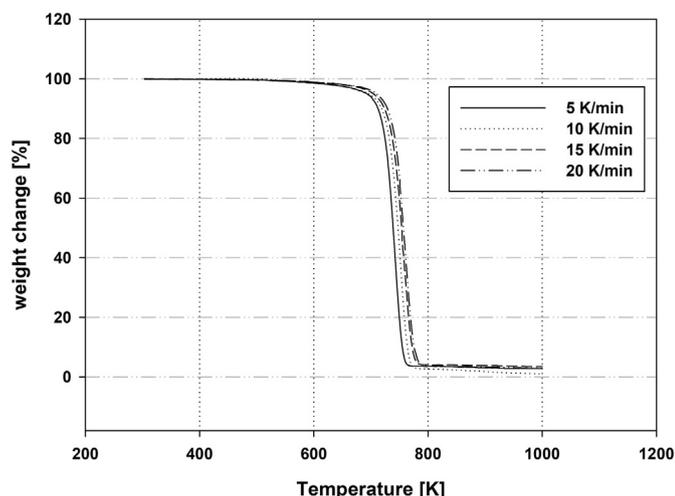


Fig. 2. TG of weight loss curves of large microplastic at four heating rates.

identical. As can be seen from the plot (Fig. 1), there is no great variation in the first 600 K, because there is a lack of inherent water. The degradation process begins at about 700 K and proceeds rapidly until 780 K. After 790 K there is no variation to observe. After the entire structural breakdown, there is almost no solid residue (around 2–5%).

The DTG curve is the first derivation of the TG curve and thus demonstrates the mass change per time during the temperature programme.

Fig. 2 shows the DTG curve for the selected size class of large microplastics. It shows a single stage degradation with a single peak. The main pyrolysis process starts at approximately 700 K and ends at 760 K for low heating rates and at 800 K for high heating rates. As mentioned above, the different selected size classes demonstrated no great variation of the TG curve, whereas only the results for the largest selected fraction are displayed.

It is important to define the value of conversion and thus an equivalent stage of the reaction for different heating rates, as the activation energy is calculated for each conversion point (Khawam, 2007). Also, the other three heating rates showed the same trend, and the selected values for alpha within this study are 0.05–0.95 for all tests.

4.2. Kinetic analysis results

The activation energy and pre-exponential factor (A) were obtained using isoconversional analysis methods based on the integral approach,

namely the KAS method, Starink method, and FWO method. The apparent activation factors were obtained from the slope and the pre-exponential factors from the intercept of the regression line. The regression lines for the KAS methods and thus the plot of $\ln(\beta / T^2)$ versus $1000 / T$ at different values of conversion for the selected size class of large microplastics are shown in Fig. 3.

The similar regression lines of the two other methods, that is, the Starink method, which plots $\ln(\beta / T^{1.8})$ versus $1000 / T$, and the FWO method, which plots $\ln(\beta)$ versus $1000 / T$, at different values of conversion, are shown in Figs. 4 and 5, respectively. As can be seen, the results for the three applied methods are very close to each other, which indicates the proper selection of the methods as well as reliable results for the further utilization of the figures for the process design.

The same approach was used for the two other selected size-glass groups, namely small microplastics and mesoplastics. The obtained values for the activation energy, pre-exponential factor, and correlation coefficient for the average of all class sizes are presented in the Table 2.

All three size classes showed similar trends, on average. The values generated by the FWO method had the lowest apparent activation energy. The curves for KAS and Starink are almost overlapping with similar trends, but the apparent activation energy obtained by Starink was slightly higher. The small microplastics had average activation energy values of 320–325 kJ/mol, the large microplastics had values of 329–334 kJ/mol, and the mesoplastics had values of 338–344 kJ/mol. Hence the values generated by the three different methods for each category differed only slightly. Therefore, the average of every plastic size class in Table 1 is significant for the investigated marine plastic litter.

With the increase of conversion from 0.05 to 0.95, the activation energy varied considerably. Different energy levels for different points of conversion mean that pyrolysis proceeds with varied reaction mechanisms and speed. It is therefore a complex multistep mechanism and the whole decomposition process and activation energy are dependent on conversion (Slopieca et al., 2011).

Arrhenius parameters for synthetic polymers found in the literature were calculated by different methods and under different conditions. Aboukasa et al. (2010) examined individual plastics and calculated the activation energy after a pyrolysis process with the model-free kinetic methods according to KAS and FWO. For LDP, they reported values of 215 kJ/mol when using KAS and 218 kJ/mol when using FWO; for HDPE, the corresponding values were 238 and 243 kJ/mol; and for PP, the corresponding values were 179 and 183 kJ/mol. Cai et al. (2007) found an activation energy of 457 kJ/mol and pre-exponential factor of $3.5 \times 10^{30} \text{ min}^{-1}$ for HDPE; 300 kJ/mol and $2.2 \times 10^{20} \text{ min}^{-1}$ for LDPE; and 319 kJ/mol and $5.9 \times 10^{20} \text{ min}^{-1}$ for PP. Encinar and

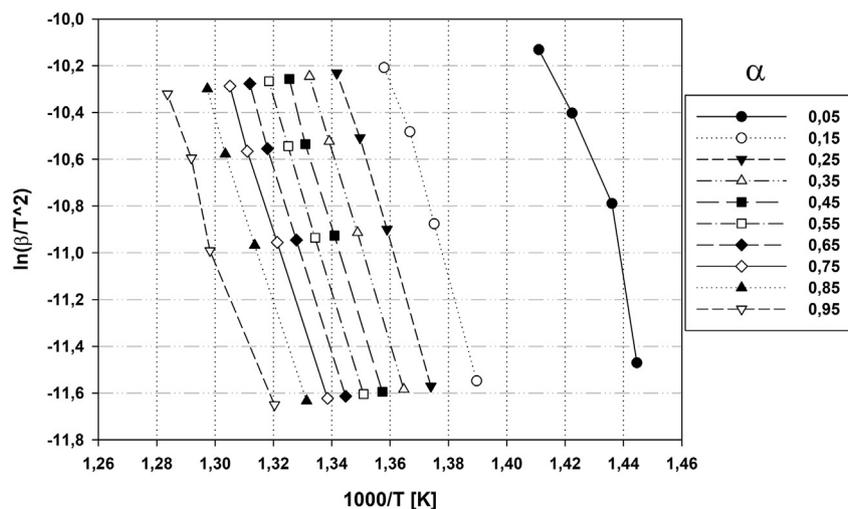


Fig. 3. KAS plot of large microplastic for different values of conversion.

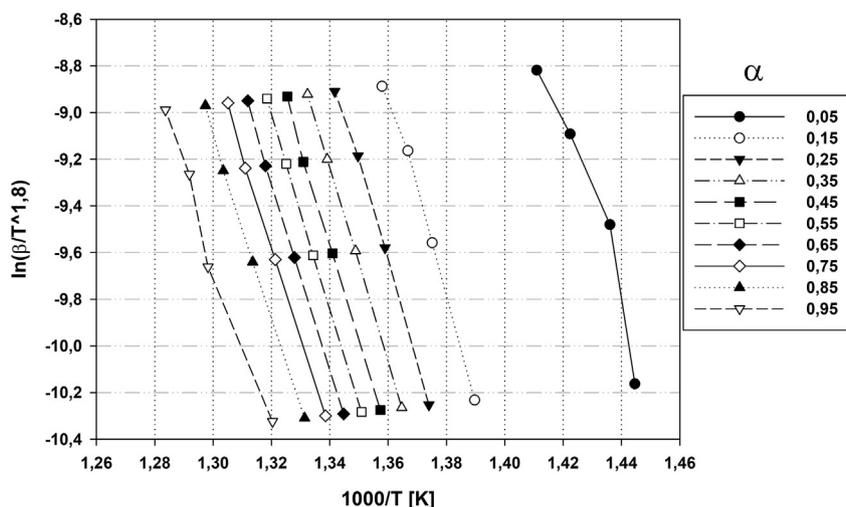


Fig. 4. Starink plot of large microplastic for different values of conversion.

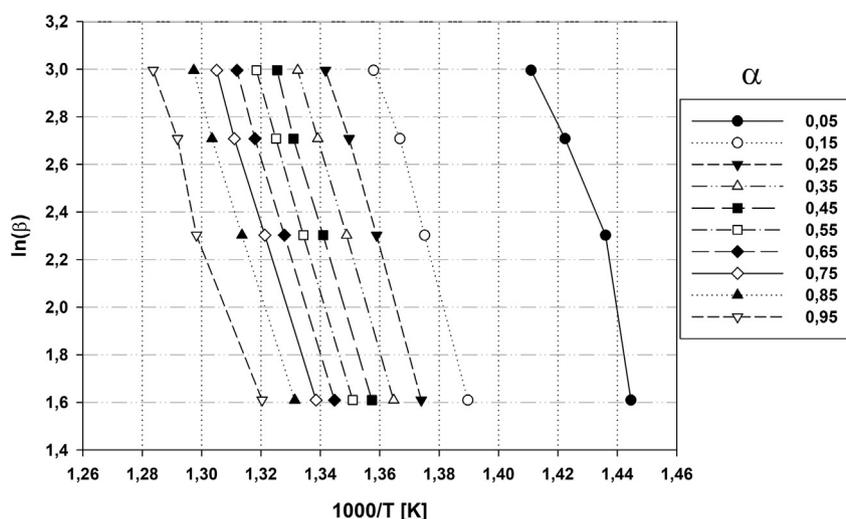


Fig. 5. FWO plot of large microplastics for different values of conversion.

Table 2

Activation energy and pre-exponential factor for micro-, meso-, and large plastics as averages.

α	KAS		Starink		FWO	
	E (kJ/mol)	A (min ⁻¹)	E (kJ/mol)	A (min ⁻¹)	E (kJ/mol)	A (min ⁻¹)
005	232	327 × 10 ²¹	234	149 × 10 ²²	256	807 × 10 ¹⁸
015	331	190 × 10 ²⁴	333	888 × 10 ²⁴	360	399 × 10 ²¹
025	339	95 × 10 ²³	341	435 × 10 ²⁴	369	208 × 10 ²¹
035	343	291 × 10 ²⁴	345	134 × 10 ²⁵	373	612 × 10 ²¹
045	348	115 × 10 ²⁵	351	528 × 10 ²⁵	379	232 × 10 ²²
055	355	208 × 10 ²⁵	358	957 × 10 ²⁵	387	417 × 10 ²²
065	355	278 × 10 ²⁵	357	128 × 10 ²⁶	386	557 × 10 ²²
075	353	350 × 10 ²⁵	355	161 × 10 ²⁶	384	701 × 10 ²²
085	347	305 × 10 ²⁵	350	141 × 10 ²⁶	379	618 × 10 ²²
095	339	505 × 10 ²⁶	342	233 × 10 ²⁷	370	946 × 10 ²³
Av.	334	636 × 10 ²⁵	337	294 × 10 ²⁶	364	121 × 10 ²³

Gonzalez (2007) pyrolysed individual and recycled plastics at different heating rates; at the heating rate of 20 K/min, they obtained a value of 175 kJ/mol for the activation energy and 4.61 × 10¹³ min⁻¹ as the pre-exponential factor for polystyrene; the corresponding values were 224 kJ/mol and 2.34 × 10¹⁷ min⁻¹ for PET, 219 kJ/mol and 3.09 × 10¹⁶ min⁻¹ for PP, and 234 kJ/mol and 1.38 × 10¹⁷ min⁻¹ for

recycled plastic.

The differences in kinetic parameters derive from the diverse chemical composition of the plastic feedstock. Moreover, the different experimental conditions and calculations may lead to different kinetic parameter values (Slopieca et al., 2011) as well.

5. Conclusion

Many scientists, companies, and other organizations are trying to find a solution to manage existing as well as future plastic debris in a sustainable way. Collecting marine debris can help to tackle the problems of marine plastic debris but cannot be the only priority in order to be effective. The overall goal in dealing with marine plastic debris should be to use a mixture of different instruments targeting waste generation and management on- and offshore. Instruments such as international conventions, economic instruments, and command and control instruments can help address the problem. When using collection to approach the problem of marine plastic offshore, the concept proposed needs basic investigations in terms of new feedstocks (marine litter) for pyrolysis. The first step in approaching such a project is to investigate the thermal behaviour and kinetic parameters in order to know the required temperature as well as the residence time of the feedstock. The marine litter in the oceans contains > 80% plastic and the most frequently found types of plastic are PE, PP, PS, PET, and PVC.

The collected sample certainly comprised those components too but cannot be compared with individual original plastic because it was set under different conditions such as wave action or UV-light exposure. The results obtained from TGA showed the same shape of curve for all samples, indicating single-stage degradation in the temperature region of 427–507 °C (700–780 K) with most of the total weight loss (95%). The DTG curve revealed a single peak, which shifted with the heating rate. The Arrhenius parameters, activation energy, and pre-exponential factor were obtained by the KAS, Starink, and FWO model-free methods. The values generated by those three methods for the three selected size classes differed only slightly. The FWO method had the lowest activation energy values and the Starink method had slightly higher ones than the KAS method. All three selected size classes of plastic showed the same trend of the average values: for small microplastics, the average activation energy was 320–325 kJ/mol; for large microplastics, it was 329–334 kJ/mol; and for mesoplastics, 338–344 kJ/mol.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2018.05.048>.

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