

## Plastics in the ocean - A thermochemical solution

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**Abstract:** Plastic under the most diverse forms, whether as insulators, toys or even as other materials' constituents, they're everywhere in our everyday life. Bags and packages represent the largest end-use markets for these polymers; however, the resulting residues have been experiencing an exponential growth worldwide, that have been contributing to a never seen before pollution, especially in the oceans. In this dissertation several thermal degradations studied were carried to one of the most used polymers in the world, the polyethylene, or more specifically the High-Density PolyEthylene (HDPE), with and without sea's actions, in order to understand if it's possible to create a circular economy for these residues. To this end, the thermal pyrolysis of this compound was studied, coming from plastic bags of the fruit, using a thermogravimetric scanning differential calorimetry device (TGA-DSC). A controlled environment was created at the Oeiras's dock, where several samples were deposited, which were analyzed and later compared to other virgin samples, also analyzed in the laboratory. The results showed that, despite certain differences between the samples, the plastics retain their integrity after being collected from the sea and can be recovered for other purposes. A kinetic study, where the activation energy and the rate constant were calculated from certain experiments, however the model used was too simple regarding this reaction's complexity. The products of the degradation reaction after using the reactor were subjected to a chromatography process to identify the resulting components. It was concluded that in the gaseous products there were hydrocarbons from C2 to C5, while in the liquid products the compounds were heavier, from C6 to C12. In short, to reuse these materials, they must be subjected to recycling processes like those used for the reprocessing of materials with the same polymer, making it possible to build a circular economy for these wastes.

**Keywords:** Plastic, thermal degradation, Polyethylene, kinetic study, circular economy

## 1. Introduction

With no shadow of doubt, plastic has been one of the most useful inventions in the last decades. Due to its thermal isolation, decreasing substantially energy trades, or to its durability, since it's a material that doesn't suffer either corrosion or oxidation and that requires little maintenance compared to the main part of the other products, these polymers are very often used in the chemical industry and in everyday life<sup>[1]</sup>, whether on packaging or in the agriculture, etc. (Figure 1).

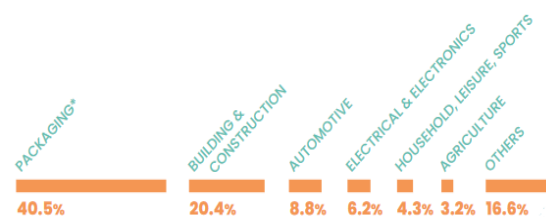


Figure 1 – Plastic's applications. Adapted from [2]

Among the most important polymers, polyethylene emerges as one of the most used, contributing to about 17,4% of the total plastic consumed (Figure 2). This material, specifically High-Density

PolyEthylene (HDPE), will be studied in this work.

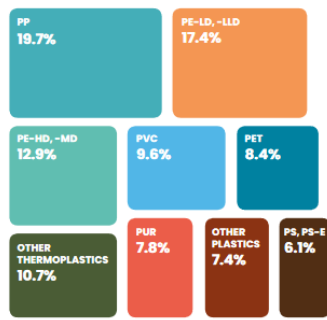


Figure 1 - Europe's plastic distribution in 2020. Adapted from [2]

Although these materials are very versatile and have been substituting a lot of others, they've been contributing to an exponential increase in litter accumulation worldwide, especially in the oceans[3].

This work aims to study if it's possible to develop a circular economy for these residues. For this matter, some HDPE fruit bags were deposited in a controlled marine environment, near Oeiras's dock, simulating plastic adrift at sea. These samples were analyzed after a period and compared to other virgin samples, or in other words, bags that didn't suffer these external actions from the sea, the sun or even the animals.

## 2. Overview of plastics

### 2.1 Definition of plastics

According to the *American Chemistry Council*, plastic is a synthetic polymer, made from complex organic compounds, forming long chains of little monomers. These materials are extremely moldable, enabling its formation in different sizes and shapes. The characteristics and properties of the final products are largely due to the monomers that constitute them. For this purpose, each material is unique and elaborated taking into account its function[4].

### 2.1.1 Types of plastics

There are two types of plastic, the thermoplastics and the thermosets.

The thermoplastics, when heated, they soften and become moldable, hardening again when the temperature lowers. HDPE is included in this group. The biggest contrast between these and the thermosets is the fact that the thermosets maintain their form and stay solid when heated. This happens because there are a lot more bonds amidst chains in this group of plastics, called crosslinks, that don't break and keep the chains static[5].

### 2.2 Circular economy

Tied with the exponential growth of the production and globalization of these materials, it's also notorious the growing accumulation of residues in the oceans. It is estimated that, since the beginning of its commercialization until 2015, only 2500 Mton of the plastic ever produced is still in use, while 6300 Mton have become waste. From these, just 800 Mton were incinerated (12%) and 600 Mton (9%) recycled, leaving us with 4900 Mton that ended up in sanitary landfills or in the environment[6][7].

Nowadays, overall, most of the raw materials come directly from Nature. The products are then created from these and eventually end up as wasted residues, following a linear process. Some sectors of work have been working on an alternative to fight this wasting spree, through a circular economy. This is a production and consumption model that reutilizes, repairs, shares, etc., the existent products as far as possible until the end of its lifetime. After this, the constituent materials can be reutilized in the formation of new products[8][9].



Figure 3 - Circular economy's representation. Adapted from [10]

In this work, HDPE samples that were deposited in a controlled marine environment will be analyzed and compared with other HDPE virgin samples, in order to study a possible process of circular economy able to carry out in marine plastic litter. For this matter, the pyrolysis method will take place, as it's a simple and effective way to conduct a recycling process, more particularly a tertiary recycling process.

### 2.2.1 Pyrolysis

This technique consists of the thermal degradation of a solid or an organic liquid into smaller volatile molecules, in an oxygen free atmosphere. This chemical process is heavily influenced by the type substrate and by the heating rate, from which result two main products, coke, that is used as industrial fuel, and charcoal<sup>[11][12]</sup>. This method can serve an important purpose in a future plastic's circular economy, especially when exposed to natural elements. These materials end up suffering a faster deterioration, altering their properties and turning them not suitable to other recycling types. Simultaneously, there's the degradation of pathogenic and toxic agents, due to the high temperatures, the amount of water needed is very reduced when compared to other methods and there's also a big decrease in external fuel supply on account of the produced gas recovery<sup>[13]</sup>.

## 3. Materials and methods

### 3.1 Samples

The samples used in this work were taken from HDPE bags used to takeaway fruit (Figure 4).



Figure 4 - Samples used in the pyrolysis tests with the melting pot

### 3.2 TGA-DSC equipment

To carry out the ThermoGravimetry-Differential Calorimetry analysis, the Perkin-Elmer STA 6000 equipment was used (figure 5).

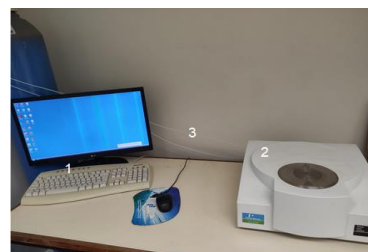


Figure 5 - TGA-DSC Equipment. 1 - Computer to collect data; 2 - Perkin-Elmer STA 6000; 3 - N<sub>2</sub> Flow

### 3.3 Reactor

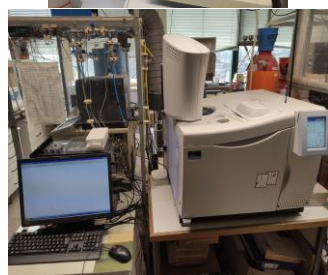
Some pyrolysis tests were carried out in the reactor (Figure 6) to collect the liquid and gaseous products for posterior analysis through gaseous chromatography.



Figure 6 - Reactor assembly: 1 - Oven; 2 - Reactor; 3 - Adaptor; 4 - Collector; 5 - Condenser; 6 - Volumetric balloon; 7 - thermoregulator; 8 - Thermocouple; 9 - Temperature's display: 9.1 - SetPoint Temperature; 9.2 - Reactor's temperature; 9.3 - Programming buttons; 10 - Oven's temperature

### 3.4 Gaseous chromatography

Two chromatographs were used: The one for the liquid samples (figure 7) and another for the gaseous samples (figure 8).



Figures 7 and 8 - Gas chromatographs for the gaseous (up) and the liquid (down) samples

## 4. Results and discussion

### 4.1 TGA-DSC

All tests were carried out in a temperature range between 40 and 800 °C. After obtaining the DTG curves by derivation of the TG curves, the  $T_{Max}$ , which corresponds to the curve minimum, is obtained. This temperature reflects the maximum temperature of degradation. From the DSC curves, the  $T_{onset}$ , or temperature at which the degradation starts, is obtained, as shown in the figure 9. The intensity of the degradation peak is calculated through the trapezoidal rule. The activation energies were acquired from the fitting of the equation 1 into the TGA curves, where the  $k_0$  stands for the pre-exponential factor,  $W$  the sample's weight and  $n$  the reaction order.

$$-\left(\frac{dW}{dt}\right) = k_0 e^{\frac{-E_a,ap}{RT}} W^n \quad 1$$

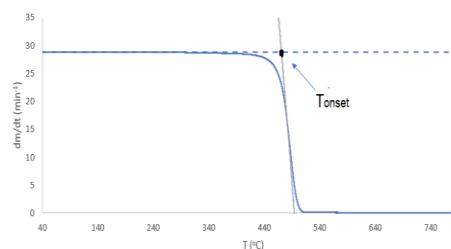


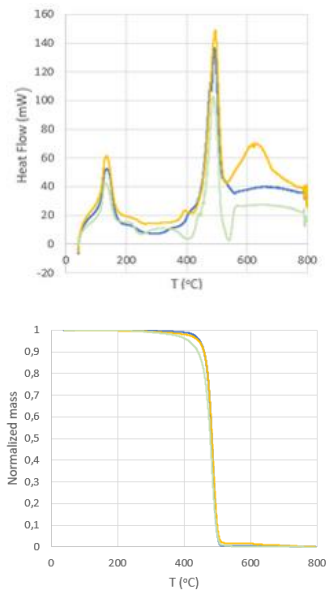
Figure 9 - How  $T_{onset}$  is obtained

#### 4.1.1 Different bag zones

Firstly, all three sections of the bag were analyzed to see if there were significant differences, at 20 °C/min. In the figure 10 these zones are shown. The figures 11 and 12 show the DSC and TGA curves for all the three tests, respectively, while the table 1 displays the temperatures values.



Figure 10 - Bag sections: 1 - Pressed area; 2 - Colored zone; 3 - Normal zone



Figures 11 and 12 - DSC (up) and TGA (down) curves for the different bag zones. The blue line represents the normal zone, the yellow one the colored zone and the green line the pressed zone.

Table 1 - Most important values from the tests

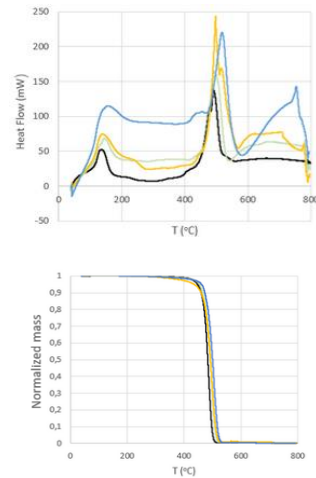
Test	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	Area (mW/g)	E <sub>a</sub> (kJ/mol)
1 - Normal zone	470,9	481,7	1,7 x 10 <sup>5</sup>	376,9
2 - Colored zone	472,0	482,1	1,4 x 10 <sup>5</sup>	344,2
3 - Pressed zone	462,6	484,8	2,2 x 10 <sup>5</sup>	270,1

The pressed zone had a slightly earlier degradation's start, that could have been caused due to the weakening of the material's bonds, since the pressing was probably carried out through a heat treatment. The bump in the yellow curve

doesn't represent a mass loss, wherefore it might have been caused by an interference or an equipment's miscalculation. The third test's activation energy is the lowest, supporting the weakening theory.

#### 4.1.2 Different heat rates

In order to study the heat rate's effect on the curves, 3 tests were conducted at different heat rates, them being 40 °C/min, 50 °C/min and 100 °C/min. In the figures 13 and 14 and at the table 2 are shown the results.



Figures 13 and 14 - DSC (up) and TGA (down) curves at different heat rates. Black line - 20 °C/min; Green - 40 °C/min; Yellow - 50 °C/min; Blue - 100 °C/min

Table 2 - Most important values from the tests

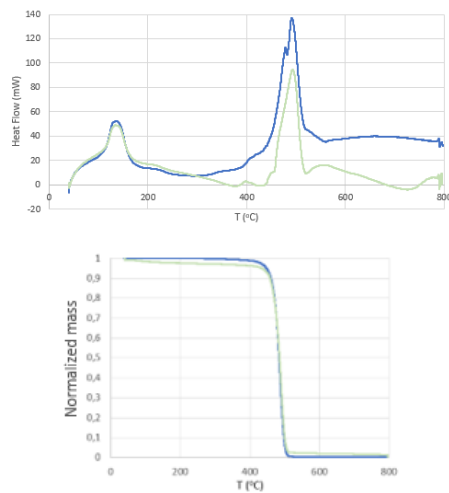
Test	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	Area (mW/g)	E <sub>a</sub> (kJ/mol)
1 - 20 °C/min	470,9	481,7	1,7 x 10 <sup>5</sup>	376,9
4 - 40 °C/min	475,3	491,1	2,5 x 10 <sup>5</sup>	343,6
5 - 50 °C/min	473,7	497,3	4,0 x 10 <sup>5</sup>	-
6 - 100 °C/min	482,9	502,9	3,8 x 10 <sup>5</sup>	310,0

As expected, the Heat Flow curves, as the heat rate increases, the power provided also increases, since the amount of energy is the same, but it's consumed in shorter time, also influencing the peak's intensities. There are also horizontal shifts to the right, that are mainly due to kinetic facts. This is visible in the table 2, as the temperatures and the peak's intensities rise with the

increase of heat rate. The higher the heat rate, shorter the time, therefore there's less time to break the polymer's bonds, so these are broken at higher temperatures. The activation energies decrease as the heat rates increase, whereby they're very far from reality (From a lot of literature values, there's 197,35 kJ/mol for the degradation's reaction<sup>[14]</sup>).

#### 4.1.3 Sea's samples

On June 13th, the samples were placed in the sea. The first samples collected were taken on 22nd June, 9 days later. These samples suffered a manual washing and drying treatment before being analyzed, in order to take out marine residues and salty water. In the figures 15 and 16 and in the table 3, there's a comparison between this sample and a virgin one, both at 20 °C/min.



Figures 15 and 16 - DSC (up) and TGA (down) of the virgin and 22-06 samples. Blue - Virgin sample; Green - Sea's sample

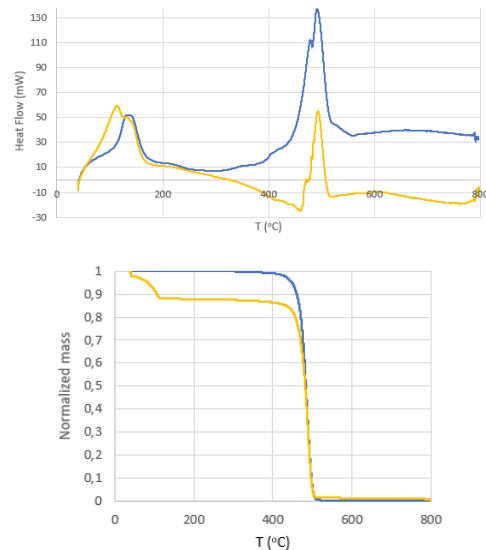
Table 3 - Most important values from the tests

Test	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	Area (mW/g)	E <sub>a</sub> (kJ/mol)
1 - Virgin	470,9	481,7	1,7 x 10 <sup>5</sup>	376,9
7 - Not virgin (22-06)	469,0	490,7	1,1 x 10 <sup>5</sup>	261,1

From the DSC results, it's quite clear that the virgin tests require a higher power during the trial. Firstly, this might mean that the sample has lost some of its characteristics, resulting in weaker bonds.

Comparing the peak's areas, there's a 65% difference that supports this theory. Another plausible reason comes from the fact that the sample could still have some water residues after the treatment, since there's a mass loss before the degradation, observable in the TGA curve.

On 9th July, the second samples were retrieved. Sadly, there were the last samples taken, because on 9th August, the date for the retrieval of the third samples, they were gone. This might have been caused due to the sea's strength or to human action, for at low tides the samples could be visible. In the figures 17 and 18 and at table 4 the tests 8 and 1 are compared.



Figures 17 and 18 - DSC (up) and TGA (down) of the virgin and 09-07 samples. Blue - Virgin sample; Yellow - Sea's sample

Table 4 - Most important values from the tests

Test	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	Area (mW/g)	E <sub>a</sub> (kJ/mol)
1 - Virgin	470,9	481,7	1,7 x 10 <sup>5</sup>	376,9
8 - Not virgin (09-07)	466,6	483,1	3,5 x 10 <sup>4</sup>	261,7

The fusion's process for the sea's test took place significantly earlier when compared to the homologous virgin test. This happened because of the the mass loss of about 10%, visible in the TGA curve at around 110 °C, on account of the water

residues still present after a faulty washing/drying process. Following the trend, there was also a decrease in power supplied, especially in the peak, which may indicate the loss of some of the material's characteristics. However, both curves follow a similar behavior. The activation energy has also decreased meaningfully, supporting what was said earlier, however this also may have been due to the bad fitting of the model, which was too simple for complexity of the process.

## 4.2 Pyrolysis on the reactor

Some tests were carried out in the reactor to study the components of the liquid and the gaseous products. Firstly, it was conducted a blank test to obtain the  $MC_p$ , the UA and the L (Thermal loss coefficient) from the equation 2. The values are presented in table 5.

$$M_{Empty\ reactor} C_{p, Empty\ reactor} \frac{dT_{Reactor}}{dt} = UA(T_{Oven} - T_{Reactor}) - L(T_{Reactor} - T_{Room}) \quad 2$$

Table 5 - Parameters obtained from the equation 2

$MC_p$ (kJ/K)	UA (kW/K)	L (kJ/(K min))
$7,5 \times 10^{-2}$	$1,0 \times 10^{-2}$	$1,8 \times 10^{-5}$

After obtaining the parameters, the reactor tests were carried out. For the purpose of getting the Heat Flow curves, the equation 3 was used to fit in the test's results.

$$Heat\ Flow = UA(T_{Oven, sample} - T_{Reactor, sample}) - L(T_{Reactor, sample} - T_{Room}) - MC_{p, Empty\ reactor} \frac{dT_{Reactor, sample}}{dt} \quad 3$$

In the figure 19, it's presented the fitting for the virgin sample.

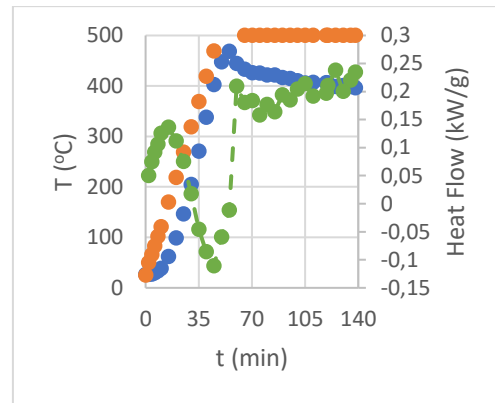


Figure 19 - Heat supplied during the test of the virgin sample. The blue line indicates the reactor's temperature, the orange one the oven's temperature and green represents the Heat Flow

The first peak represents the material's fusion. The degradation's process is very endothermic, as can be seen by the positive Heat Flow values and by the reactor's temperature decrease, because this heat is being consumed to break the polymer's bonds. The various peaks in the degradation phase may have been caused due to experimental noise.

Thereafter, the 22-06 sample was analyzed. The results are shown in the figure 20.

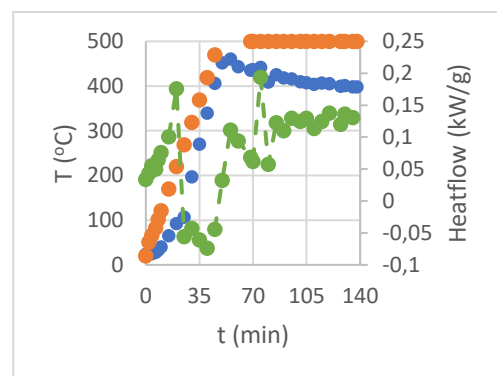


Figure 20 - Heat supplied during the test of the 22-06 sample. The blue line indicates the reactor's temperature, the orange one the oven's temperature and green represents the Heat Flow

There's a meaningful difference in the Heat flow at the fusion phase because this sample, since it went through the washing/drying treatment, it may have gone to the reactor with some water residues

attached. At the degradation process, there was a similar behavior when compared to the last test, although there was a bigger peak, that may have happened due to marine remnants still present in the sample, or the material may have suffered some changes when in the sea, losing some components.

Lastly, the 09-07 sample was analyzed. The results are shown in the figure 21.

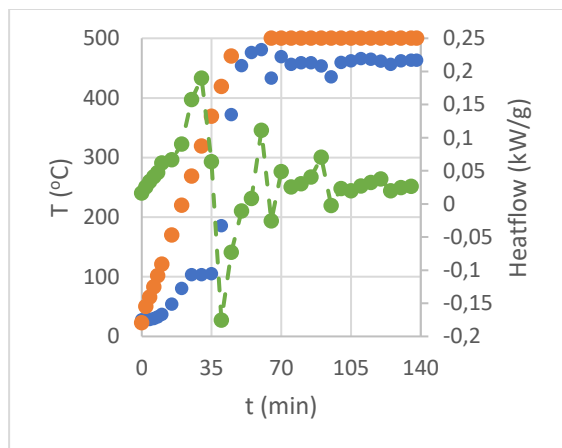


Figure 21 - Heat supplied during the test of the 09-07 sample. The blue line indicates the reactor's temperature, the orange one the oven's temperature and green represents the Heat Flow

The fusion values rose even more, there must have been a higher water content in the sample, since this treatment process was humanely executed the efficiency isn't the same from test to test. However, the degradation phase stays relatively constant in the 450 °C, in contrast to the other two tests. The reaction became less endothermic, requires less heat throughout the time. About 1 month after the deposition of the samples, the material lost some resistance to the heat.

### 4.3 Gas chromatography

One gas chromatography test was carried out for each of the liquid and the gaseous products, to study its components. It's expected to find the heavier products on the liquid sample.

#### 4.3.1 To the gaseous product

After collecting the gas from the reactor, 2  $\mu$ l of gas were injected through the injection membrane. The resulting chromatogram is presented in the figure 22, along with the identification of the components in table 6.

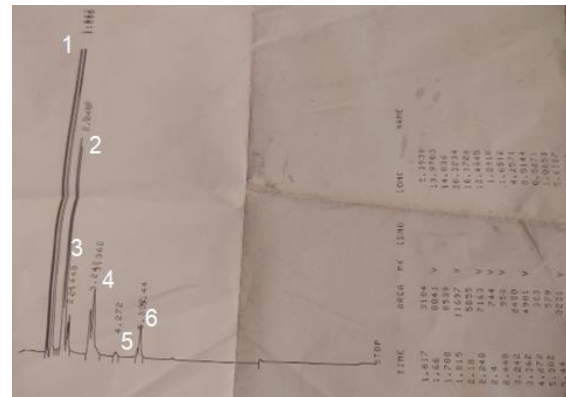


Figure 22 - Gas chromatogram

Table 6 - Gas sample's components

Peak	Tempo (min)	Area ( $\mu$ V.s)	Compound	Compo-sition (%)
1.1	1,617	3104	Ethane	5,40
1.2	1,660	8041	Ethylene	13,97
1.3	1,788	8539	Propane	14,84
1.4	1,815	11697	Propylene	20,32
2.1	2,180	5855	Isobutane	10,17
2.2	2,248	7163	n-butane	12,44
3.1	2,400	744	Butene	1,29
3.2	2,448	950	Butene	1,65
4.1	3,242	2450	Isopentane	4,26
4.2	3,362	4901	n-pentane	8,51
5	4,272	303	Pentene	0,53
6.1	5,302	579	Hexane	1,01
6.2	5,440	3230	Hexene	5,61

As it was expected, the components present in the gas are lighter, from C2 to C6.

#### 4.3.2 To the liquid product

After collecting the liquid from the reactor, 2  $\mu$ l of liquid were injected through the injection membrane. The resulting chromatogram is presented in the figure 23, along with the designation of the peaks in table 7. Since there were 140 peaks, the



designation was carried out between intervals.

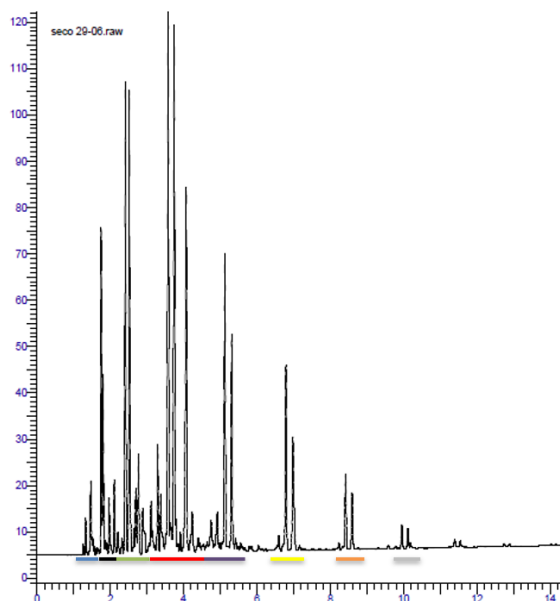


Figure 23 - Liquid's chromatogram

Table 7 - Liquid sample's components

Zone	Time (min)	Area's sum (μV.s)	Term	Composition (%)
Blue	1,262-1,696	71865,32	C5	3,07
Black	1,749-2,208	244083,88	C6	10,46
Green	2,323-3,111	507081,23	C7	21,67
Red	3,155-4,600	857443,31	C8	36,63
Purple	4,641-5,599	331540,14	C9	14,16
Yellow	6,397-7,301	181924,33	C10	7,77
Orange	8,147-8,965	74187,23	C11	3,16
Grey	9,702-10,463	28978,48	C12	1,22

As previously expected, the heavier components are present in the liquid product, from C5 to C12.

## 5. Conclusion and future work

In the study with different heat rates, it was verified that with higher heat rate comes a later degradation. Tied with this, the peak's intensity also increased, which was expected because the energy required was the same, but it was supplied faster, resulting in bond's breaks.

From the sea's samples, it was shown that the sea's and sun's action in the plastic bags resulted in a weakening of the material, although the pre-treatment may have influenced these results, due to the mass loss.

In the kinetic study, by and large, the activation energy followed a decrease with the heat rate increase and in the sea's samples, although these results may not meet the reality, since the values were too high for this process, when compared to literature values. In the future, a more complex model that could fit entirely this process could improve the veracity of the results.

Using the reactor as a differential calorimeter showed that the sea's samples, when compared to the virgin one, lost some of their characteristics, resulting in a heat resistance loss. The model used could once again be more complex since the gas's mass wasn't taken in account. In the long run, a kinetic study would be interesting.

Overall, although there were some differences between the samples, their behavior was relatively similar throughout the tests, wherefore they're suitable to be treated the same way as the other plastics. However, a better washing/drying treatment should be thought of.

It would also be interesting a deeper study in HDPE and other types of polymers, for longer periods of time, because sadly this work's samples disappeared. This is a very hot topic nowadays, and it's aggravating all marine life, which in turn can be extremely harmful to human life.

## 6. References

- [1] "Plastic's characteristics", Plastval, 2008 [Online]. Available: <http://www.plastval.pt/index.asp?info=plastico/caracteristicas> [Visited on 21st April 2022]
- [2] "Plastics – The Facts 2021", Plastics Europe, 2021 [Online]. Available: [https://plasticseurope.org/wp-content/uploads/2021/12/AF-Plastics-the-facts-2021\\_250122.pdf](https://plasticseurope.org/wp-content/uploads/2021/12/AF-Plastics-the-facts-2021_250122.pdf) [Visited on 22st April 2022]
- [3] "Plastic in the Ocean: Statistics 2020-2021", CondorFerries, 2022 [Online]. Available: <https://www.condorferries.co.uk/plastic-in-the-ocean-statistics> [Visited on 1st May 2022]
- [4] "Life cycle of a plastic product", American Chemistry Council, 2010 [Online]. Available: [https://web.archive.org/web/20100317004747/http://www.americanchemistry.com/s\\_plastics/doc.asp?CID=1571&DID=5972](https://web.archive.org/web/20100317004747/http://www.americanchemistry.com/s_plastics/doc.asp?CID=1571&DID=5972) [Visited on 2nd May 2022]
- [5] "Thermoset vs Thermoplastic (What is the difference?)", The Welding Institute, 2022 [Online]. Available: <https://www.twi-global.com/technical-knowledge/faqs/thermoset-vs-thermoplastic> [Visited on 6th May 2022]
- [6] R. Geyer, J. R. Jambeck, K. L. Law, *Production, use, and fate of all plastics ever made*. Sci. Adv.3, e1700782 (2017)
- [7] Basmage, Osama M. (2019). *Reference Module in Materials Science and Materials Engineering* || Plastic Products in Hospital and Healthcare Systems, pp. 2
- [8] "What is a circular economy", Ellen MacArthur Foundation, [Online]. Available: <https://ellenmacarthurfoundation.org/topics/circular-economy-introduction/overview> [Visited on 13th July 2022]
- [9] "Circular economy: definition, importance and benefits", News European Parliament, 26 April 2022 [Online]. Available: <https://www.europarl.europa.eu/news/en/headlines/economy/20151201STO05603/circular-economy-definition-importance-and-benefits> [Visited on 13th July 2022]
- [10] "Circular economy as a way of increasing efficiency in organizations", Paulo Fernandes [Online]. Available: <https://www.europarl.europa.eu/news/en/headlines/economy/20151201STO05603/circular-economy-definition-importance-and-benefits> [Visited on 13th October 2022]
- [11] "Pyrolysis, chemical reaction", Sarah E. Boslaugh, 2022 [Online]. Available: <https://www.britannica.com/science/pyrolysis> [Visited on 19th August 2022]
- [12] STAUFFER, E (2008). *Fire Debris Analysis || Chemistry and Physics of Fire and Liquid Fuels*, 85–107.
- [13] Oasmaa A, Qureshi MS, Pihkola H, Deviatkin I, Mannila J, Tenhunen A, Minkkinen H, Pohjakallio M, Laine-Ylijoki J, *Pyrolysis of Plastic Waste: Opportunities and Challenges, Journal of Analytical and Applied Pyrolysis* (2020)
- [14] Haoyu Li; Ondřej Mašek; Alan Harper; Raffaella Occone; (2021). *Kinetic study of pyrolysis of high-density polyethylene (HDPE) waste at different bed thickness in a fixed bed reactor*. The Canadian Journal of Chemical Engineering, (), -. doi:10.1002/cjce.24123