

RECOVERY OF PLASTICS FROM THE SEA BY HYDROTHERMAL CARBONIZATION

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Introduction

Plastics are the most abundant debris found in the sea. Once removed from the sea, some plastics cannot be recycled or reused. This debris has high calorific value what makes them suitable for using as fuel. For this reason, hydrothermal carbonization (HTC) of a mixture of plastic materials was carried out using seawater as solvent, to examine the characteristics of the final products obtained and to test the feasibility in converting marine plastic debris to fuel. Results showed that an increase in the temperature of the process reduces the content of the inorganic anions and increases the NCV of the hydrochar (HTC char). In addition, thermobalance was used to look for differences in the thermal decomposition of the different solid residues, being hydrochar at 300 °C the most affected material. The content of inorganic compounds in the HTC-liquor was measured, which increases as the process temperature grows. Organic compounds were also analyzed, being amides, alcohols and alkanes the major compounds in all cases. Finally, gases emissions were measured, showing also an increase with temperature.

Materials and methods

The carbonization of a mixture of the four most common polymers found in the sea (PE, PP, PET and Nylon), was studied. These samples had been submerged in marine water for more than 2 years. The materials were cut to pieces to form the mixture, being the weight proportion of each plastic the same, i.e., 25 wt. % of each one. Seawater was used as the liquid phase of the process.

HTC was conducted in a laboratory scale using a high-pressure batch reactor with stirring. The parameters controlling the process efficiency are temperature, treatment time and solid/liquid ratio (S/L). For the experimental setup, 50 g of the mixture of plastics and 500 mL of seawater were mixed in a 1 L stainless steel liner (S/L equal to 1:10 g/mL). The mixture was heated up to the desired process temperature by a laboratory oven at approximately 3 K·min⁻¹, and once this temperature was reached, the sample was maintained in the reactor for 3 h. Experiments at 200, 250 y 300 °C were carried out.

Hydrochar and liquid fraction were separated by vacuum filtration through Whatman filter paper of 1.2 mm pore size. The hydrochar was dried at 105°C for 24 h. Then, it was stored in a plastic container at room temperature, and the liquid fraction was stored in a plastic dark vessel at 4°C for further analysis. Gases were collected using Tedlar bags.

An elemental analysis was performed to each sample (original mixture and hydrochars obtained at 200 °C, 250 °C and 300 °C), and their carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content were determined using a Perkin-Elmer 2400 (Perkin-Elmer, UK). In all cases, the initial weigh of the sample was 50 mg, and sulfamethazine was employed as internal standard. This experimental system has been described in detail in other previous study¹.

Thermal stability of samples was analyzed by thermogravimetric analyzer. Runs for the TG analysis were carried out on a Mettler Toledo TGA/SDTA851e/SF/1100 Thermal Gravimetric Analyzer. The decomposition temperatures were measured under dynamic conditions in two different atmospheres such as nitrogen and mixture nitrogen:oxygen = 4:1 (20% oxygen, simulating air composition) with a total flow rate of 100 mL·min⁻¹. The samples were heated in the temperature range from room temperature to 950 °C at heating rates of 5, 10 and 20 °C·min⁻¹ in each atmosphere. For all runs, 4 ± 0.3 mg of sample were used.

In order to characterize the liquid fraction after HTC process, the inorganic and organic compounds were analyzed. The inorganic anions content of each sample was measured by ionic chromatography following EPA method 9056 (US EPA, 2007) and the organic compounds in the HTC-liquor were determined using chromatography C18 columns (VARIAN Bond Elut C18) and methanol as solvent.

Gases and volatile compounds were collected in Tedlar® bags (Restek, USA) at the end of the experiments. Carbon dioxide, carbon monoxide, oxygen, nitrogen and hydrogen were analyzed by gas chromatography with thermal conductivity detector (GC-TCD) (Agilent 7820). Light hydrocarbons were analyzed by gas chromatography with flame ionization detector (GC-FID) (Shimadzu GC-17A).

Results and discussion

The results for elemental analysis of the mixture of plastics before and after the hydrothermal carbonization with varying process temperature are illustrated in Table 1. Analysis shows that an increase in process temperature from 200 °C to 300°C increased the carbon content of hydrochar whereas oxygen content decreased. This was reflected by an increase in the NCV from 38.32 to 39.08 MJ/kg. An increase in process temperature also increases the hydrogen content in the solid residue because of side reactions (substitution reaction)².

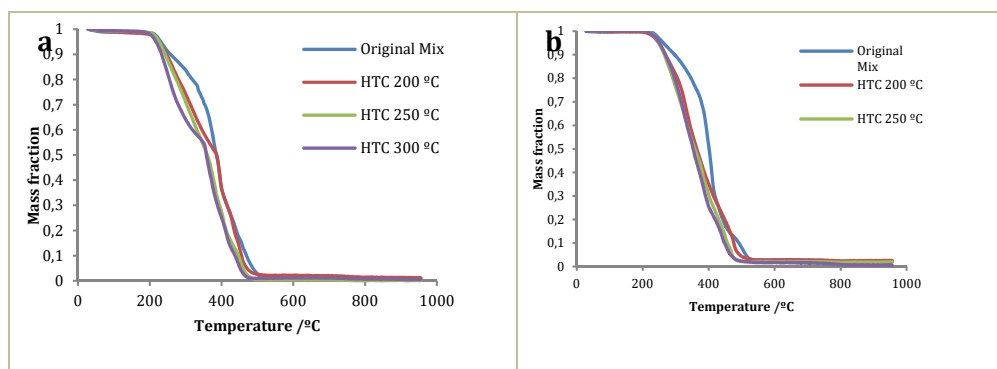
	Original	HTC 200 °C	HTC 250 °C	HTC 300 °C
Immediate analysis				
Moisture	0.02	0.24	0.23	0.29
Ash	5.84	6.95	6.20	5.27
NCV (MJ/kg)	35.60	38.32	38.87	39.08
Elemental analysis				
C	77.39	79.05	80.11	80.91
H	12.57	11.95	12.56	13.05
N	2.99	0.60	n.d.	n.d.
S	n.d.	n.d.	n.d.	n.d.
O (by difference)	1.22	1.45	1.14	0.77
Ionic chromatography				
Fluorine (x 10 ³)	5.34	2.85	1.53	1.07
Chlorine (x 10)	4.58	3.17	3.41	4.13
Bromine (x 10 ⁴)	11.2	0.97	0.81	0.81

*n.d. = not detected

The inorganic anions content was also affected by the process, being the fluorine, chlorine and bromine content lower in the treated material than in the original material. These results are similar to those obtained by other author²

Evolution of the thermal behavior of the Original Mix (before HTC process) and the solid residue (after HTC process) was followed by thermogravimetry. Samples were subjected to decomposition in the thermobalance at 5, 10 and 20 °C·min⁻¹ and were finally compared. As mentioned before, nitrogen and a mixture nitrogen:oxygen = 4:1 were used as carrier gases to test for the behavior of the samples in pyrolytic and combustion conditions. Measures were duplicated to test for the reproducibility that was very good.

Figure 1 shows the decomposition curves of Original Mix, HTC 200 °C, HTC 250 °C and HTC 300 °C obtained in presence of nitrogen and air. As can be seen, the presence of oxygen accelerates the thermal decomposition and causes a similar effect in all materials. This agrees with other authors and works carried out in our laboratory. Also, all samples were affected by the treatment. It is remarkable that the material obtained at 200 °C already shows significant differences with respect to the original sample, especially in the pyrolysis process; but in general, solid residue obtained at 300°C presents a greater degradation than the others. In this way, the temperature at which the decomposition rate is maximum decreases in all solid residue obtained after HTC process with respect to the original material, in both atmospheres and at all heating rates.



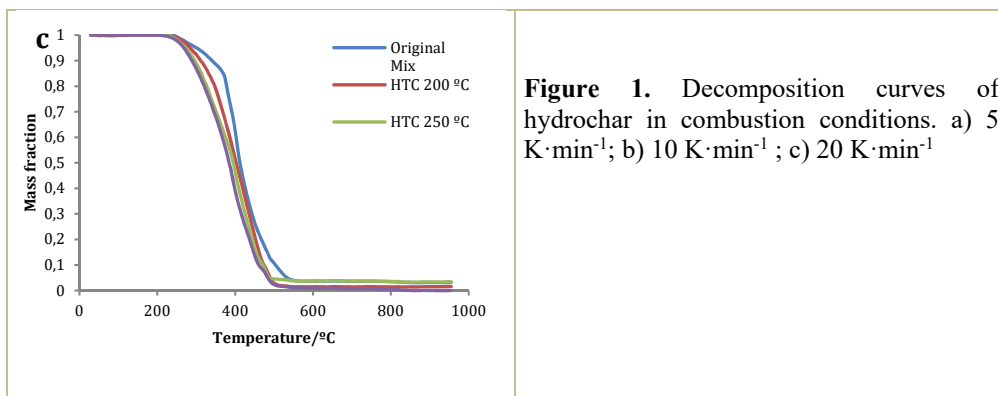


Figure 1. Decomposition curves of hydrochar in combustion conditions. a) 5 K·min⁻¹; b) 10 K·min⁻¹; c) 20 K·min⁻¹

Table 2 shows the inorganic compounds present at the HTC liquid residue which were analyzed by ionic chromatography. Chloride was the most abundant compound found in the HTC-liquor. Note that PVC was not among the plastics used in the study. Nevertheless, chloride abundance is expected since we used seawater for the process. The content of fluoride, bromide and sulfate increased as the process temperature grows, indicating a possible elimination from the plastic materials. The amounts of the rest of the compounds found decrease with the treatment.

Table 2. Inorganic compounds identified in the HTC-liquors generated at 200 °C, 250 °C and 300 °C.

Sample	mg/L						
	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate
HTC 200 °C	0.40	27808	nd	5.72	7.08	7.28	169
HTC 250 °C	0.48	27035	nd	6.16	6.48	5.96	254
HTC 300 °C	0.52	24618	nd	9.16	3.96	3.00	241

n.d = not detected

To find out all the organic compounds that constituted the liquid phase generated in HTC, HTC-liquor samples obtained at 200 °C, 250 °C and 300 °C were fractionated with methanol, and each fraction was analyzed through GC-MS in SCAN mode. Since a relatively high number of species was expected, which were not even known in advance, detected compounds were only identified using NIST databases (NIST MS Library Version 2.0 d, December 2005). However, no quantification of detected compounds was carried out.

Compounds found in the HTC-liquor were grouped by chemical family to estimate the major kind substances. Results, expressed as percentage of total area, are plotted in Figure 2. As can be seen, distribution profiles of the HTC-liquor produced from HTC 200 °C, HTC 250 °C and HTC 300 °C follows different trends. Amides, alcohols and alkanes contribute the most to the total areas, being caprolactam, 4-Methylbenzaldehyde, benzenesulfonamide, n-butyl- and decane the most noticeable compounds in terms of areas.

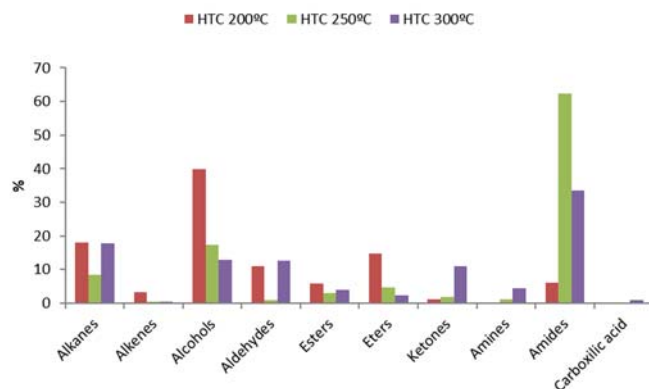


Figure 2. Distribution profiles of the major chemical groups found in the HTC-liquors produced at 250°C.

As mentioned above, HTC of a mixture of plastic was carried out at 200 °C, 250 °C and 300 °C. Table SM1 (Supplementary material) shows the yield (mg/kg sample) of the gases emitted during this process. The main gas emitted was nitrogen, presumably from the air filling the reactor before the runs. In all cases, a low value for the emission of carbon monoxide (CO) was observed. However, the production of CO and CO₂ increased with temperature. In agreement with other published work³ in which combustion experiments of the same plastics were performed, the main light hydrocarbons found were isobutene and methane in all experiments. Additionally, aromatic compounds such as benzene and xylenes were also detected. Moreover, the most abundant non-condensable products detected were acetaldehyde and 2-methyl-1-propene.

The yield of the light hydrocarbons and other non-condensable products increased when increasing the temperature from 200 °C to 300 °C, which indicate that reactions leading to organic compounds are favored at higher temperatures⁴. On the other hand, a greater number of compounds were generated at 300 °C. In terms of total emissions of gas, the higher emissions were produced in the treatment at 300 °C, reaching a value of 822 mg/kg sample (considering high hydrocarbons and other non-condensable products). This value was much higher than those obtained in the processes at 200 °C and 250 °C (116 mg/kg sample and 152 mg/kg sample, respectively).

Conclusions

In this work, hydrothermal carbonization (HTC) of a mixture of the four plastics most frequently found in the sea (PE, PP, PET and Nylon) was performed at three different temperatures (200 °C, 250 °C and 300 °C) to examine the characteristics of the final products obtained and to test the feasibility in converting marine plastic debris to fuel.

With respect to the hydrochar, the inorganic anions content in the solid residue was affected by the process, being lower after the treatment. In addition, the NCV increases, reaching a maximum value of 39.08 MJ/kg in the solid at 300 °C.

Evolution of the thermal behavior of the Original Mix (before HTC process) and the solid residue (after HTC process) was followed by thermogravimetry at different heating rates and atmospheres. The results showed that all samples were affected by the treatment. The presence of oxygen accelerates the thermal decomposition and causes a similar effect in all materials. In general, solid residue obtained at 300°C presented a greater degradation than the others.

Regarding the HTC liquid residue, chloride was the most abundant compound founds in the HTC-liquor. The content of fluoride, bromide and sulfate increase as the process temperature grows. This is expected since during the HTC, the inorganic anions of the solid material pass into the liquid. On the other hand, the organic compounds were also identified, being amides, alcohols and alkanes the major compounds in all waters.

Additionally, the gases emissions during the process were analyzed. Low emissions of CO were founded, and the main gas emitted was nitrogen. Taking into account the high hydrocarbons and other non-condensable products, the higher emissions were detected during the treatment at 300 °C, reaching a value of 822 mg/kg sample.

More investigations on the HTC of marine debris are required. However, the results show that this process could be a good option to remove plastics to the sea (depending on the degradation they present, most of these plastics cannot be recycled) and use them as fuel, since the solid material obtained has good properties as a combustible and the emissions during the process are low. We would be contributing to improve the environment.

Acknowledgements

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