Valorization of plastic waste with the aid of solar hydrothermal liquefaction

Nikolaos I. Tsongidis^{1,2}, Charikleia A. Poravou¹, Vasiliki A. Zacharopoulou¹, Dimitrios A. Dimitrakis¹, Alexandra Zygogianni¹ and Athanasios G. Konstandopoulos^{1,2}

¹Centre for Research & Technology Hellas (CERTH) 6th km Charilaou-Thermi road, 57001, P.O. Box: 60361, Thermi, Thessaloniki, Greece

²Aristotle University of Thessaloniki (AUTH), Univ. Campus, 54124, Thessaloniki, Greece. Keywords: hydrothermal liquefaction, bio-oil, plastic waste, solar liquefaction Presenting author email: <u>ntsongid@cperi.certh.gr</u>

Introduction

Every year almost 300 million tonnes of plastic waste are accumulated and 5 to 13 million tonnes of them leak into the environment and the seas having a significant impact (Pedersen and Conti, 2017; European Commission, 2017). In addition to the above, less than a third of Europe's plastic waste is recycled (European Commission, 2017). Consequently, the need of utilizing products that otherwise end up in landfills is imperative.

Hydrothermal liquefaction (HTL) is a thermochemical method for converting high moisture organic waste into biocrude oil at moderate to high temperature (250-550°C) and pressure (5-25 MPa) in the presence of a solvent (Akhtar and Amin, 2011; Watson et al., 2019). Through HTL, feedstock is decomposed into various compounds due to water which in sub- and supercritical conditions acts as both a solvent and a catalyst (Wikberg et al., 2015). Although pyrolysis is a proven method for converting waste into energy carriers, it contains an intensive stage of drying which is omitted in the case of HTL and makes the latter method suitable for conversion of wet organic materials (Chen, 2019). Products emerging from the process are gases, solids (char), an aqueous phase and a bio-oil/biocrude oil. Solar HTL is a promising technique based on the combination/merge of HTL with Concentrated Solar Technologies (CST) for providing the thermal requirements of the process.

Materials and Methods

The current study focuses on the application of the HTL technology on plastic waste of various types used as feedstock, which come from recycling companies or are rejections from the paper industry. Regarding their physicochemical characterization, the plastics were subjected to thermogravimetric analysis (TGA), Fourier-Transform Infrared Spectroscopy (FTIR) and Higher Heating Value Analysis (HHV). Experiments were carried out in a 1.8L HP/HT autoclave stirred reactor made of stainless steel and the plastic waste were first pulverized down to 1 μ m. The experimental conditions included three different reaction temperatures (350, 370, 400°C), two initial pressures (1, 20 bar), a retention time of 30 min and constant stirring (300 rpm) and temperature increase (~ 3°C/min) rates. Three different mass quantities of feedstock were tested (300, 450, 600 g) by employing feedstock/water ratio of 10/90 wt%, while N₂ was used as reducing gas. The product separation part was held after each experiment and consisted of the dilution of the products with a solvent for bio-oil extraction and their filtration for char removal. For this purpose, two different extraction solvents were used (Dichloromethane, Ethyl Acetate) in a products/solvent volume ratio of 1:1. The effect of different conditions was investigated in order to optimize the HTL technology for each feedstock.

The bio-oil yield was calculated with the following equation [1]:

Bio – oil yield(%) =
$$\frac{w_{bio-oil}}{w_{feedstock}} x \ 100$$
 [1]

where $w_{bio-oil}$ and $w_{feedstock}$ are the weight of the bio-oil (g) and the dried feedstock (g) respectively. Selected products were characterized in terms of elemental analysis (C, H), Gas Chromatography (GC), Higher Heating Value (HHV), Thermogravimetric Analysis (TGA) and Inductively Coupled Plasma Spectroscopy (ICP). Figure 1 shows a photo of the extracted bio-oil as well as the indicative bio-oil yield (%) results of samples tested at 350 and 370°C respectively, with an initial pressure of 1 bar and bio-oil extraction with the use of Dichloromethane and Ethyl Acetate. The results show that when employing Dichloromethane as the bio-oil extraction solvent, the yield reaches values of up to 40% (370°C reaction temperature, 1 bar initial pressure), while with the use of Ethyl Acetate, the yield is < 10% under the same conditions.





HTL and CST combination proposed in this work (Figure 2) includes a parabolic trough with a metallic absorber tube, possibly in a transparent vacuum envelope and a secondary reflector, used as a batch or semi-batch high-pressure reactor (up to 500 bar), with operational temperature ranging from 300 to over 400°C. The latter is planned to be finalized and constructed in the coming months.



Figure 2. Flowsheet of HTL conceptual coupling with CST

Acknowledgements

This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T1EDK-05079).

References

Akhtar J., Amin N.A.S., 2011. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, Renew. Sustain. Energy Rev. 15, 1615-1624.

Chen W.T., Jin K., Wang N.H.L., 2019. Use os supercritical water for the liquefaction of polypropylene into oil, ACS Sustainable Chem. Eng. 7, 3749-3758.

European Commission leaflet (2017), based on PlasticsEurope study, Plastics- the Fact 2016.

Pedersen T.H., Conti F., 2017. Improving the circular economy via hydrothermal processing of high-density waste plastics, Waste Manag. 68, 24-31.

Watson J., Lu J., Souza R., Si B., Zhang Y., Liu Z., 2019. Effects of the extraction solvents in hydrothermal liquefaction processes: Biocrude oil quality and energy conversion efficiency, Energy 167, 189-197.

Wikberg H., Gronberg V., Jermakka J., Kemppainen K., Kleen M., Laine C., Paasikallio V., Oasmaa A., 2015. Hydrothermal refining of biomass – an overview and future perspectives, TAPPI. 14, 195-207.