

# Marine biomass and plastic waste thermal utilization over the commercial and biochar catalyst for energy products recovery

J. Eimontas<sup>1</sup>, N. Striūgas<sup>1</sup>, K. Zakarauskas<sup>1</sup>, I. Kiminaitė<sup>1</sup>

<sup>1</sup>Laboratory of Combustion Processes, Lithuanian Energy Institute, Kaunas, LT-44403, Lithuania

Keywords: Biomass, Macroalgae, Bio-char catalyst, Plastic wastes, Pyrolysis.

Presenting author email: [Justas.Eimontas@lei.lt](mailto:Justas.Eimontas@lei.lt)

## Introduction

Marine biomass and plastics wastes could be the potential feedstock for the additional energy carrier's generation, capturing the energy and utilizing the wastes [1]. These refuses could be collected from the seashores, reducing the eutrophication processes and contributing to the creation of a cleaner environment. In the best case, the collected seaweed could be used as fertilizers. However, the sea biomass (seaweed) during the growth cycle consumes not only nutrients and minerals but also pollutants, such as heavy metals, leading to biomass not being appropriate for fertilization purposes. Also, the used fishing nets cannot be separated and recycled because of the heterogenous fraction. The different polymers inside the fishing gear must be separated before recycling. It consumes energy and human resources, which makes the process not efficient. The utilization method for additional energy capturing could be offered pyrolysis process. This topic with catalytical thermal decomposition of plastics and biomass wastes is relevant and ongoing for energy recovery from seashores, reducing ecological problems. Moreover, this investigation will present a pyrolysis test and formed products analysis over commercial ZSM-5 and self-prepared bio-char catalyst.

## Materials and methods

The seaweed char-basis catalyst preparation starts with the washing procedure. The feedstock was washed by the tap water to remove the highest part of sand and other abrasive particles. After the washing procedure, the seaweed was dried and mixed with the potassium hydroxide (KOH) by the ratio 1:1 to increase the surface area. The characterization of feedstocks was maintained using ultimate and proximate analysis. Those analysis was performed in accordance with LST EN 14918 for the LHV by an IKA C5000 calorimeter, LST EN 15148 for the volatile content, LST EN 14775 for the ash content, LST EN 14774-1 for the moisture content, and LST EN 15104 for the CHNS content by a Flash 2000 CHNS analyzer. The heavy metals and minerals content were investigated following LST EN 15411: 2011 and LST EN 15297: 2011 using Induced Plasma Optical Emission Spectrometer (ICP-OES) Optima 8000.

Primary investigation of the feedstock and catalyst influence for the formed products were analyzed using microthermal analysis via Netzsch Jupiter STA 449 F3 thermogravimeter (TGA). The mass of the samples ranges between 10 – 30 mg, with the heating rate of 30 °C/min and the maximum temperature about 900 °C. The carrier gas flow was set around 60 ml/min. For the catalytical thermal conversion with commercial catalyst used ZSM-5 and Y-Type zeolite catalyst in a ratio 1:3 and 1:8, respectively. The gaseous products composition was analyzed using combined system with TGA-FTIR (Bruker Tensor 27) and GC/MS. The released gas passes through a heated FTIR cell consisted of an internal KBr and external ZnSe window. The MCT (mercury cadmium telluride) detector with a liquid nitrogen cooling was used for gas functional groups investigation.

In order to evaluate the conversion efficiency and formed products (gases and liquids) composition, the pyrolysis test in the laboratory scale was performed. The experimental bench (Fig. 1) could be divided into three parts: pyrolysis reactor, the liquid products collection and the gaseous product purification part, and the gaseous product collection and analysis part. The pyrolizer consist of cylindrical form reactor with a capsule inside and the metal sieves on the bottom. During the thermal decomposition emitted gaseous phase passes through those sieves and reaches second segment, which consist of six flasks with an isopropanol into five of them. Into the isopropanol condensed liquid products could be also called condensable gasses. Purified gaseous phase reaches the third segment for a gas collection and analysis.

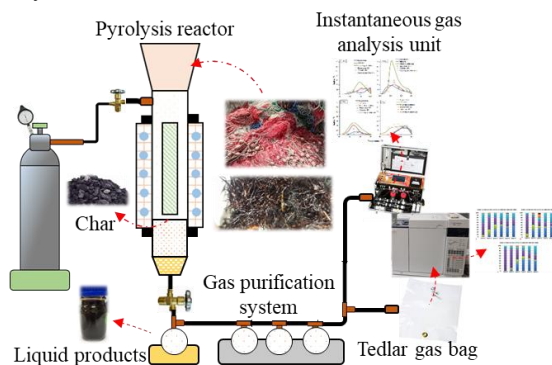


Fig. 1. Schematic view of the experimental rig for the waste's pyrolysis

The main parameters of the process were obtained from the TGA analysis: the heating rate was 30 °C/min with the maximum process temperature of 900 °C. Also, experiments with catalyst load were maintained on the same conditions. The product analysis was maintained using “Agilent 7890 A” gas chromatographs with TCD (for gases) and GC/MS (for liquids) detectors. The gases were analyzed from the “Tedlar” bags for comparison with continuous measurements purposes. The liquid fraction has been taken instantly after the reactor, and after purification process. The pyro-oil products after purification process are called condensable gases and were analyzed on the same way, as liquids which was obtained after the reactor.

## Results

### Thermal analysis at micro scale

Primary investigation of feedstock and commercial catalyst influence on the whole process was performed using TGA analysis. The results are presented in Fig. 2. As can be seen, the seaweed has two decomposition peaks, around 300 °C, and 700 °C. The first peak could be assigned for cellulose and hemicellulose 1,4 β-glycosidic bond decomposition, while the second could present lignin stronger aromatic matrix polymeric chain degradation. Used fishing nets thermal analysis showed two decomposition peaks. Minor peaks around 200 °C could be related to water and small molecular mass volatiles evaporation. The main part (about 80 wt.%) occurred at 440 °C and could be assigned to polymeric matrix decomposition of different plastics, such as Nylon 6, polyethylene, polypropylene, etc. Catalyst did not significantly affect the mass loss in both cases during the TGA experiments, which resided into the char fraction due to the inability to decompose.

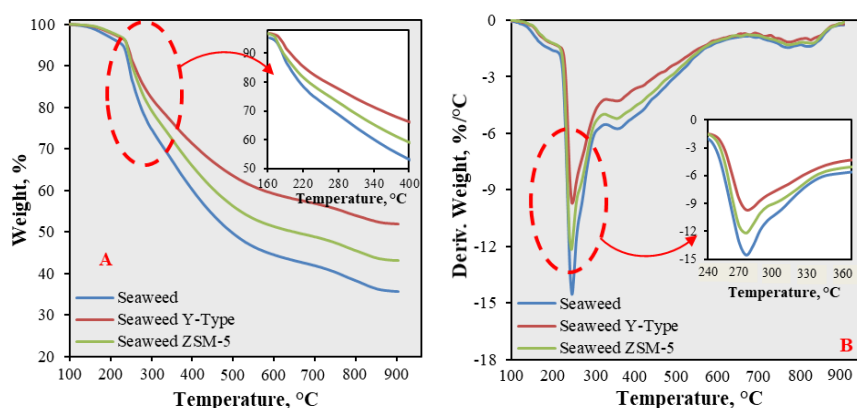


Fig. 2. Thermal decomposition of the seaweed with ZSM-5 and Y-Type catalyst

### Pyrolysis products (liquid and gaseous) analysis

The gaseous and liquid products were analyzed using “Agilent 7890 A” gas chromatographs with TCD (for gases) and GC/MS (for liquids) systems. The main components of formed pyrolysis gases are CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. Liquid products analysis showed high amount of polycyclic aromatic derivatives present.

Commercial catalytical upgrade of formed products showed promising tendencies. The amount of light aromatic compounds increased significantly. According to gained results could be stated, that obtained products could be converted into valuable energy products and used for transportation fuel.

## Conclusions

The main purpose of this investigation is to analyze the self-prepared char-basis catalyst influence to the pyrolysis process and to compare the results with commercial catalyst. The thermal treatment for primary feedstocks analysis were performed using thermal gravimetric analyzer combined with Fourier transform infrared spectroscopy (FTIR) and gas chromatograph with mass spectrometer detector (GC/MS). The experiments at laboratory scale bench were processed using mini pyrolysis plant, where the products for the further analysis were also obtained.

Microthermal analysis showed that the catalyst did not affect the total mass loss of the sample. The different residual mass shows the commercial catalyst inability to decompose. The main functional groups in volatile fraction were detected to be carbon dioxide, some aromatic and aliphatic C-H groups and also a minor oscillation of N-O group.

The products analysis after laboratory scale bench showed promising results: main gaseous products compounds are CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. Also, the major derivatives in liquid state are substituted polycyclic aromatic substances. Commercial catalytical process increased amount of light hydrocarbons in liquid phase. All in all, obtained results and analysis of the products could be used for added value energy products generation.

## References

- [1] Kim JH, Jung S, Lin KYA, Rinklebe J, Kwon EE. Comparative study on carbon dioxide-cofed catalytic pyrolysis of grass and woody biomass. *Bioresour Technol* 2021. <https://doi.org/10.1016/j.biortech.2020.124633>.