Catalytical seaweed pyrolysis over ZSM-5 and Y-Type catalysts under the different temperature for the gathered products analysis

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Introduction

The most significant part of the global world's energy production is produced from fossil fuels, while renewable energy takes up only around 11 % of the total primary energy consumption [1]. To fulfill the EU commitment to reduce GHG emissions by 40 % till 2030, and also reduce global warming, the usage of fossil fuels must be dramatically reduced. For that reason, biomass feedstock for energy production increased its attention, knowing that it is a sustainable and carbon-neutral material [2]. Moreover, the Baltic Sea is known as one of the most polluted water pools by eutrophication process [3], caused by the intensive agricultural production and excess fertilization with a discharge of inorganic plants like ammonia, nitrogen, and phosphorous, leading to the acceleration of growth of micro- and macro-algae [4]. Based on this literature review, the selected feedstock for the energy carrier recovery was seaweed, contributing to the creation of a circular economy and closing the life cycle. In this investigation the seaweed was used in the laboratory scale pyrolysis plant under three different temperatures: 500, 700, and 900 °C using two different – Y-Type and ZSM-5 – commercial catalysts. A primary investigation was performed by the micro thermal analyzer (TGA) Netzsch Jupiter STA F3 combined with Fourje transform infrared spectroscopy system.

Materials and methods

The characterization of feedstocks was maintained using ultimate and proximate analysis. The chemical analysis of the waste seaweed samples was performed using Fourier transform infrared spectrometer (FTIR). Moreover, the elemental analysis was carried out to investigate nitrogen (N), sulfur (S), carbon (C), and hydrogen (H) content in the samples using the Flash 2000 CHNS analyzer. In addition, the calorific value was measured by an IKA C5000 calorimeter based on LST EN 14918 standard method. Finally, proximate analysis was carried out using the LST EN 15148 for the volatile content, LST EN 14775 for the ash content, and LST EN 14774-1 for the moisture content standard methods.

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 a heating rate of 30 °C/min and a maximum temperature of 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 of 1:1. The gaseous products composition was analyzed using a combined system with TGA-FTIR (Bruker Tensor 27) and GC/MS. The released gas passes through a heated FTIR cell consisting 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 on the laboratory scale was performed. The experimental bench (Fig. 1) could be divided into three parts: the pyrolysis reactor, the liquid products collection, and the gaseous product purification part, and the gaseous product collection and analysis part. The pyrolizer consists of a cylindrical form reactor with a capsule inside and metal sieves on the bottom. During the thermal decomposition emitted gaseous phase passes through those sieves and reaches the second segment, which consists of six flasks with isopropanol in five of them. Into the isopropanol, condensed liquid products could be also called condensable gasses. The purified gaseous phase reaches the third segment for gas collection and analysis.

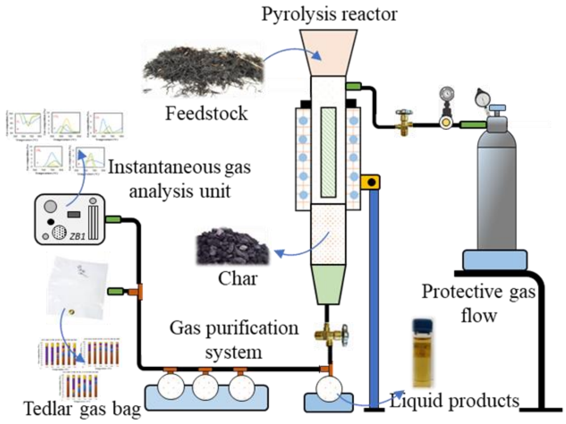

Fig. 1. Schematic view of the experimental rig for the waste's pyrolysis

The formed 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 measurement purposes. The liquid fraction has been taken instantly after the reactor and after the purification process. The pyro-oil products after the purification process are called condensable gases and were analyzed in the same way, as liquids which were 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 matric polymeric chain degradation. Catalyst did not significantly affect the mass loss in both cases during the TGA experiments, which resided in the char fraction due to the inability to decompose.

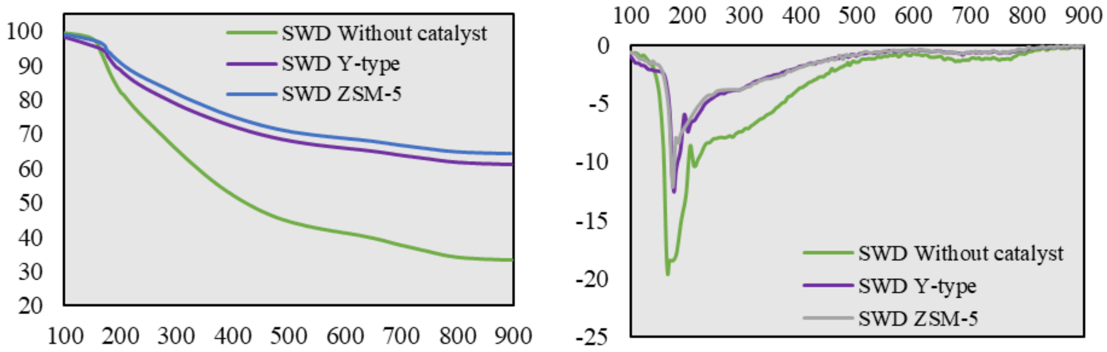

Fig. 2. Thermal decomposition of the seaweed with ZSM-5 and Y-Type catalyst

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, CO2, CH4, and H2. Liquid product analysis showed a high amount of polycyclic aromatic derivatives present.

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

Conclusions

The thermal treatment for primary feedstocks analysis was performed using a thermal gravimetric analyzer combined with Fourier transform infrared spectroscopy (FTIR) and a gas chromatograph with a mass spectrometer detector (GC/MS). The experiments at the laboratory scale bench were processed using a mini pyrolysis plant, where the products for 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's 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 the N-O group.

The product analysis after the laboratory scale bench showed promising results: the main gaseous product compounds are CO, CO_2, CH_4, and H_2. Also, the major derivatives in a liquid state are substituted polycyclic aromatic substances. The commercial catalytical process increased the amount of light hydrocarbons in a liquid phase. All in all, obtained results and analysis of the products could be used for added value energy products generation.

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