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Abstract
The ongoing eutrophication processes and water pollutions caused by marine biomass and plastic waste are one of the most relevant ecological problems. Collected wastes are possible alternative feedstock for additional higher added value energy product generation. The thermal treatment could be offered to solve the ecological problems and contribute to creating a circular economy. Usually, catalysts are used in thermal treatment to refine pyrolysis products and to increase their yield. In order to study pyrolysis process and the effect of the catalyst on the formulated products, this work aims at the analysis of seaweed and used fishing nets, using TGA-DTG-FTIR systems, and mini pyrolysis plant. Experiments were conducted with ultra-stable Y-type zeolite catalyst with a ratio 1 by 3. Micro-thermal analysis using the TGA-DTG-FTIR system was processed for feedstock characterization purposes, which showed that marine biomass could decompose in two different periods, while the fishing gear only in one, with a total weight loss of 61 wt.% and 83 wt.%, respectively. The FTIR analysis exhibits that aromatic and aliphatic C-H, CO₂, and C=O (aldehyde or ketone) represents the major functional groups and compounds in the released volatile components. Catalyst slightly increased the intensity of the C-H peak in both samples and added one additional O-H peak in the seaweed sample. Pyro-oils analysis showed that the main fractions could be assigned to aromatic and aliphatic hydrocarbons, such as naphthalene, styrene, and toluene. Meanwhile, the seaweed and fishing nets samples subjected to thermal treatment produced 17% and 72% of liquid products, respectively.

Keywords: Biomass; Macroalgae; Plastic wastes; Pyrolysis; Used fishing nets;

1. Introduction
During the last few decades, environmental problems attract more and more attention. Moreover, the depletion of fossil fuels leads scientists and fuel industries to explore alternative sources and methods for energy production. The best solution for both of these problems could be waste utilization, gathering higher added value energy products, and making an environment clear. Plasctics (fishery) and biomass wastes (seaweed) are significant threats to seas and water pools [1]. Uncollected marine bio-wastes causes eutrophication problems which lead to water blooming process. Moreover, this process accelerates seaweed growth, enhances biomass wastes formation on shores, and also oxygen consumption [2]. Nevertheless, one of the major human-induced damages to ocean, sea and other water pools ecosystems is fishery [3] [4]. The total abundance and weight of plastics wastes were estimated about 5.25 trillion particles with a weight about 268,000 tons [5]. Used fishing nets with fishing gear also have a high-level contribution to the seas and ocean pollution in fishery activities [6].

Both of these issues (eutrophication and plastic pollutants) could be solved by thermal treatment using the pyrolysis process. During the thermal decomposition in anoxic ambient three different types of products (gases, liquids, and solids) could be obtained. The yields of the products strongly depend on the feedstock selection and
the main pyrolysis parameters. R. Kumar et al. [7] investigated the influence of biomass composition and nature to the yield of pyrolysis products. It was determined that pyrolysis of lignocellulosic biomass at 500-550 °C results in pyro-oil yield in the range of 60-80 wt.%, pyro-gas – 20-25 wt.%, and pyrolytic char in the range of 20-30 wt.%. Moreover, Xun Hu et al. [8] confirmed the previous scientists and determined that yields of pyrolysis products from lignocellulosic biomass, resulting in 50-70 wt.% (liquids), 13-25 wt.% (char), and 12-15 wt.% (gas). These results show that the topic of biomass pyrolysis is relevant and ongoing.

Used fishing nets thermal utilization were not so widely explored. R. Skvorčinskienė et al. [9] investigated the main thermal characteristics of fishing gear. Scientists determined that the most significant decomposition peak during the micro-thermal analysis is in the range of 400-440 ºC, depending on the heating rate. Moreover, it was determined that the main components in the waste fishing net structure are Nylon 6, Polypropylene (PP), Polyethylene (PE), and some Polyesters [10]. The major part of the structure belongs to Nylon 6, which has high strength, dimensional and chemical stability, and wear-resistant. Considering that, recycling of Nylon 6, which is the significant component in the used fishing net, is desirable, and thermal treatment could be the possible solution for utilization and gathering higher added value energy products from this waste. The temperature and heating rate influence on pyrolysis oils composition and the yield was reported by A. M. Pannase et al [11]. Scientists determined that with a lower heating rate, the obtained pyro-oil has a lower density and high volume compared to a high heating rate. The higher maximum temperatures and heating rates lead to the higher yield of pyro-oil. The obtained liquid pyrolysis products range from 85 to 88 wt.%, while the gaseous products detected about 12-14 wt.%, and only a negligible amount of char was obtained. This analysis shows that fishing nets pyrolysis is relevant, and the literature is rare.

In order to reach the pollute-less environment by utilizing the wastes and contributing to energy products generation, the pyrolysis process could be maintained for both of the selected (used fishing nets and seaweed) refuses. Moreover, to obtain higher added value energy products in better quality, the catalytic pyrolysis process could be maintained. Biomass thermal conversion, using ZMS-5 catalyst, was widely described by E.F.Iliopoulou et al. [12]. Authors determined that produced pyro-oils was enriched in aromatics and phenols and maintains fewer oxygenates [13]. The liquid phase yield varies from 34.33 wt.% (without catalyst) to 58.67 wt.%, depending on the catalyst concentration.

The fishing nets catalytic thermal conversion into valuable high quality energy products was widely described by Chaidan et.al. [6]. The authors investigated used fishing nets thermal treatment over calcined scallop shells for the recovery of ε-caprolactam monomer. It was determined that the highest yield of purposive products reaches around 66% at 410 °C with 2 minutes resident time and 1:5 waste fishing nets: calcined scallop shells ratio. Other manuscripts with used fishing nets thermal and catalytical utilization are challenging to find. For that reason, it is necessary to explore the field of the fishing nets utilization by pyrolysis process. In order to contribute to the creation of cleaner seashores and water pools, the wastes must be collected and utilized. One of the promising alternative paths for utilizing the waste could be the thermal treatment in anoxic ambient. During this process, three different energy carriers can be obtained and reused in valuable technologies or systems. Moreover, by searching on the "Web of Science" for publications concerning pyrolysis and catalytic pyrolysis of fishing gear and seaweed, we noted the absence of scientific paper analysis. This topic is important for energy recovery from water pool wastes in terms of reducing ecological problems.
2. Experimental methodology

Material

The feedstock for all experiments were collected in Melnragė beach, Klaipėda city, Lithuania. The seaweed for thermal treatment were washed to remove the highest part or sand and other abrasive particles. After that, the feedstock was dried using 2V 151 dryer and milled. For further analysis fishing nets was only dried according to ISO 579 and chopped without any primary treatment.

Analysis of selected feedstock

The main characterisation and feedstock investigation were 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 analyser. 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. The results are presented in Table 1.

Table 1. Main characteristics selected feedstocks

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Used Fishing nets</th>
<th>Seaweed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, wt.%</td>
<td>53.20</td>
<td>46.93</td>
</tr>
<tr>
<td>Hydrogen, wt.%</td>
<td>8.17</td>
<td>4.73</td>
</tr>
<tr>
<td>Nitrogen, wt.%</td>
<td>7.44</td>
<td>4.13</td>
</tr>
<tr>
<td>Sulphur, wt.%</td>
<td>&lt;0.01</td>
<td>5.13</td>
</tr>
<tr>
<td>Chloride, wt.%</td>
<td>1.14</td>
<td>0.05</td>
</tr>
<tr>
<td>Oxygen, wt.% (diff.)</td>
<td>25.53</td>
<td>29.61</td>
</tr>
<tr>
<td>Moisture, wt.%</td>
<td>0.8</td>
<td>0.60</td>
</tr>
<tr>
<td>Volatiles, wt.%</td>
<td>82.07</td>
<td>58.30</td>
</tr>
<tr>
<td>Fixed carbon, wt.%</td>
<td>12.27</td>
<td>32.23</td>
</tr>
<tr>
<td>Ashes, wt.%</td>
<td>4.86</td>
<td>8.87</td>
</tr>
<tr>
<td>LHV, MJ/kg</td>
<td>25.68</td>
<td>16.51</td>
</tr>
</tbody>
</table>

Chemical and micro-thermal analysis of seaweed and fishing nets using TG-FTIR system

Thermal degradation of the selected feedstocks was investigated using thermogravimetric analyser combined with Fourier transform infrared spectrometer system (TG-FTIR). All experiments were maintained with 15-20 mg of each batch in anoxic ambient using nitrogen with a flow rate of 60 ml/min. The catalytical pyrolysis experiments, using ultra stable Y-type Zeolite, were performed using the same conditions with added catalyst in ratio 1:3 (catalyst: feedstock, respectively).

Pyrolysis experiments at laboratory scale bench

The pyrolysis experiments using the fishing nets and seaweed samples were maintained in a laboratory scale mini pyrolysis plant of 150 g working useful volume in nitrogen ambient. The pyrolysis plant consists of the
main reactor chamber with a cylinder form capsule in it. The capsule is connected with a refinery at its end, which contains small holes (2-3 mm) allowing the formulated gaseous and liquid products to exit, keeping the char fraction inside the reactor. The gathered liquid products set down in the storage at the end of the reactor, while the gaseous products pass through a piping system and start colling, purification, analysis, and collection. The purification process of the formulated gaseous products was maintained simultaneously, by passing through five tanks loaded with isopropanol. The composition of the purified gasses was analysed in continuous mode using VISIT 03H gas analyser. Collected liquid products were analysed using GC/MS system, and the main compounds were determined using NIST database. The used carrier gas flow in GC/MS system are 1.5 ml/min, while the main investigation interval is 30-600 m/z. The column of the used system is HP-5MS with a (5%-phenyl)-methylpolysiloxane filling. Detailed laboratory scale bench scheme is depicted in Figure 1.

Fig. 1. Schematic view of mini pyrolysis plant

3. Results and discussion

TGA-DTG data analysis

Figure 2 shows the results of TGA-DTG data of the selected feedstock in anoxic ambient. As depicted in TGA curves, fishing nets has only one decomposition peak (X₁) around 440 °C, while the seaweed thermally decompose at two stages (X₂ and X₃): around 260 °C and 710 °C. The fishing nets degradation could be explained by the main components in the feedstock, which is Nylon 6. As reviewed in the literature, the highest degradation point of this polymer varies from 400 °C to 460 °C depending on the heating rate [14]. The seaweed thermal decomposition in two stages could be explained by different composition of the biomass. The first peak represents cellulose and hemicellulose β-glycosidic bonds polymeric matrix decomposition [15]. The second peak could be assigned to lignin thermal depolymerization and bond-break reactions. Lignin material has stronger aromatic matrix, compared to cellulose and hemicellulose, and it helps to avoid degradation at the lower temperatures [16].
Catalytical micro-thermal analysis showed that the catalyst significant increase the thermal resistance of samples decomposition in terms of total weight loss. This effect could be explained by the inability to decompose Y-type catalyst and stays it as a residue during the pyrolysis process. Thus, the residual mass in TGA experimental data must be recalculated to evaluate accurate results [17]. Analysis of the recalculated results leads to the statement, that adding of catalyst did not affect the weight loss in the main decomposition areas. The DTG curves indicates one sharp peak with the seaweed (around 210 °C) and one with the fishing nets sample (around 440 °C), so it does not significantly change the kinetic of the decomposition.

**Chemical analysis of the obtained volatile products during the micro-thermal analysis**

In order to evaluate the volatile products during the micro-thermal analysis, the combined TGA-FTIR systems has been used. Figure 3 shows 2-3D FTIR spectra results of the obtained volatile products at 260 °C and 440 °C for seaweed and fishing nets, respectively. The sharp peak in fishing net sample was noticed around 3000 cm$^{-1}$ referring to C-H (methane and aromatic) compounds formation [18]. Also, the presence of aromatic compounds could be confirmed by visible peaks at the zone of 600 - 1000 cm$^{-1}$ [19]. Minor vibrations at 2300 cm$^{-1}$ indicates C=O presence, which could be assigned to typical CO$_2$ compound [20]. Strong valence carbonyl group oscillations around 1700 cm$^{-1}$ indicates aldehydes and ketones presence. Comparing to fishing net spectra, the seaweed has only small valence oscillations around 3000 cm$^{-1}$ and 600 - 1000 cm$^{-1}$. However, high intensity peak around 2300 cm$^{-1}$ could be referred to higher amount of CO$_2$ presence. Two peaks at 1300 cm$^{-1}$ and 1500 cm$^{-1}$ could be assigned to N-O group presence [20], which was not detected with fishing net sample. Small intensity
valence oscillation peak could be obtained around 1700 cm\(^{-1}\). These functional groups agree with other authors’ papers on marine biomass and fishing gear thermal decomposition [9], [19].

**Fig. 3.** The 3D-2D FTIR spectra analysis of seaweed and fishing nets

In case of ultra-stable Y-type zeolite/fishing nets sample, the same functional groups were observed. However, the absorbance of C-H (methane) and aromatic compounds increased significantly, because the non-stable hydrocarbons were combined together to form polyolefins. During this process, the higher number of flammable compounds and oil was obtained [21], [22]. Analysis of the ultra-stable Y-type zeolite/seaweed sample showed interesting results (Figure 4). The catalyst split decomposition area into different peaks at distinct temperatures. As can be seen from the results, catalyst increased C-H bond around 3000 cm\(^{-1}\) and 600-1000 cm\(^{-1}\) referring to methane and aromatic compounds formation (435 °C and 530 °C). Also, the valence oscillation around 3600 cm\(^{-1}\) could be assigned to O-H group, which could be obtained from alcohols or carboxylic acid residues (210 °C). Increased formation of aldehydes and ketones could be assigned to the higher C=O peak intensity at 1700 cm\(^{-1}\) (210 °C)

**Fig. 4.** The 3D-2D FTIR spectra analysis of the decomposed ultra-stable Y-type zeolite/selected feedstock samples

**Temperature influence to gaseous pyrolysis products generation during pyrolysis at laboratory scale bench**

Commonly, the volatile products after the thermal treatment of biomass and plastic wastes are most likely composed of carbon monoxide (CO) and dioxide (CO\(_2\)), hydrogen (H\(_2\)), methane (CH\(_4\)), and other light hydrocarbons, such as C\(_2\)H\(_2\), C\(_2\)H\(_4\), C\(_3\)H\(_6\), etc. [23]. The gaseous products composition during the full continuous pyrolysis process were analysed using online unit (VISIT 03H) measurements. The results of the obtained data are depicted in Figure 5. The gaseous products formation starts around 300 °C and continuous until the end of the
conversion. The amounts of products range from 15 to 21% with seaweed sample, while the fishing nets samples ranges from 19 to 25%.

**Fig. 5.** The gaseous products analysis during the pyrolysis process. Orange – Seaweed, Blue – Fishing nets.

The catalyst influence to the gaseous products formation is clearly visible. The methane concentration increased with the seaweed and fishing nets sample by 14 and 21%, respectively, while the CO concentration was slightly decreased. The conversion kinetic did not significantly change: the gas emission start around 300 °C and finish at 900 °C. However, the maximum peak of methane shifted to the higher temperature side. It could be explained by increased gasses exit time, because of the catalyst layer. The amount of hydrogen slightly increased by 5 and 8% with seaweed and fishing nets sample, while CO2 did not significantly change. The results of the obtained data are presented in Figure 6.

**Fig. 6.** The gaseous products analysis during the catalytical pyrolysis process. Orange – Seaweed, Blue – Fishing nets.

**Analysis of the pyro-oil products**

Figure 7 shows GC/MS analysis of pyrolysis liquid products obtained during thermal treatment. Pyrolysis tars from both samples containing typical compounds in bio-oils: Alcohol, Styrene, Ethane, pyridine, Naphthalene...
and other light aromatic and aliphatic derivatives [24] [25]. Moreover, the amount of toluene reaches 11 and 16 wt.% with the seaweed and fishing nets, respectively. The pyro-oil from used fishing nets sample consist of 32 wt.% of caprolactam, and it is typical compound in liquid pyrolysis products from the waste fishing gear [6]. Both samples consist of aromatic and aliphatic compounds and reaches 18 and 20 wt.% in the seaweed and fishing net sample, respectively.

Figure 7. GC/MS spectra of the formulated pyro-oils

Figure 8 represents GC/MS analysis of liquid products obtained after catalytical thermal conversion. It was estimated, that the amounts of benzene and light aromatic derivatives increased by 11 and 19 wt.% in seaweed and used fishing nets sample, respectively. Also, the toluene content in the seaweed and used fishing nets pyrolysis oil increased by 4 wt.% and 2 wt.%, respectively. Moreover, the amount of caprolactam in used fishing nets sample increased by 8 wt.% These tendencies show alternative pyro-oils uses obtaining high-quality hydrocarbons and caprolactam monomers, which could be recovered and used in nylon-6 synthesis.

Figure 8. GC/MS spectra of the formulated pyro-oils during the catalytical pyrolysis
Conversion efficiency during pyrolysis

The conversion efficiencies have been calculated to evaluate the product yields and catalyst influence on the product formation. A mass balance was calculated for pyrolysis products: it was determined by primary feedstock mass and terminal mass of formed pyrolysis oil, pyro-gas, and biochar. Also, the conversion of the selected feedstock to liquid and gaseous product percentage was estimated. The results are presented in Table 2.

Table 2. Feedstock’s conversion and product yield to valuable energy products

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seaweeds</th>
<th>Fishing nets</th>
<th>Seaweed (with catalyst)</th>
<th>Fishing nets (with catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis oil, wt.%</td>
<td>17.2</td>
<td>72.4</td>
<td>36.2</td>
<td>78.4</td>
</tr>
<tr>
<td>Pyrolysis gas, wt.%</td>
<td>43.7</td>
<td>12.2</td>
<td>34.9</td>
<td>8.7</td>
</tr>
<tr>
<td>Biochar, wt.%</td>
<td>39.1</td>
<td>15.4</td>
<td>28.9</td>
<td>12.9</td>
</tr>
<tr>
<td>Conversion of feedstock to oil and gas, %</td>
<td>60.9</td>
<td>84.6</td>
<td>71.1</td>
<td>87.1</td>
</tr>
</tbody>
</table>

The higher conversion was reached with the fishing net sample (84.6%), while more char was produced with the seaweed sample (39.1%). The major part of the composing products with the seaweed sample is pyrolysis gas (43.7 wt.%), while the main part of the fishing nets products is in the liquid phase (72.4 wt.%). The catalyst increased the yields of liquid products with seaweed and fishing nets by 19 and 6 wt.%, respectively. The different nature and feedstock composition could explain the distribution of liquids, gases, and char. Biomass typically decomposes, forming a high amount of biochar during the slow pyrolysis process. Moreover, it is known that plastics have a low amount of char and a high amount of liquid and gaseous products. A process with catalyst increased useful higher added value energy carrier’s formation, thus increasing the conversion to valuable products.

4. Conclusions

Water pollutants and eutrophication problems caused by plastics and marine biomass on seashores is one of the most relevant ecological issues. Collected wastes could be utilized using pyrolysis process. First of all, the characterization of selected feedstocks was maintained using TGA-DTG-FTIR system. It was assumed, that biomass has two decomposition peaks and could be explained by cellulose-hemicellulose and lignin thermal decomposition.

The waste fishing nets has one minor peak, which belong to moisture evaporation, and the second one, which could be assigned to Nylon-6 thermal degradation. Most relevant functional groups in gaseous products are C-H, C=O, O-H which represents aliphatic and aromatic hydrocarbons, CO₂, aldehydes and ketones, and also alcohols present.

The gaseous, liquid and solid fractions were obtained during the pyrolysis at laboratory scale bench. Investigated, that most relevant compounds in gaseous products are CO, CO₂, CH₄ and H₂. Moreover, the catalyst increased methane and hydrogen content in both samples, while CO was slightly decreased. Amount of CO2 was not significantly affected.

The highest amount of the both samples tars content belongs to alcohol, styrene, ethane, pyridine, naphthalene and other light aromatic and aliphatic derivatives. Moreover, high amount of caprolactam was investigated in fishing net sample. Catalyst increased benzene derivatives present by 11 and 16 wt.% in seaweed
and fishing net sample, respectively, while the caprolactam content increased by 8 wt.%. The calculation of mass balance showed that the highest part of obtained products with the seaweed sample are gases (43.7 wt.%), while the major part with fishing nets belong to liquid phase (72.4 wt.%). Catalytical pyrolysis increased liquid fraction by 19 wt.% and 6 wt.% in the seaweed and fishing nets, respectively.

All in all, it is clear that pyrolysis process is suitable for biomass and plastic wastes utilization obtaining additional energy products. Moreover, high content of caprolactam could be recovered from the fishing net sample. This monomer could be re-used for the synthesis of Nylon-6. Therefore, both materials showed potential as a feedstock for higher added value energy products production contributing to the creation of circular economy.

References


