

# The exploration of catalytic pyrolysis of discarded fishing nets aiming to recover energy-based products

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## Introduction

The persistent environmental concern of marine plastic waste leading to eutrophication and water contamination highlights the necessity for environmentally sustainable remedies. Repurposing gathered waste materials offers potential as an alternative resource, producing more valuable energy-related items. Additionally, extracting caprolactam from discarded nylon 6 fishing nets could help conserve resources, improve waste management economics, and establish a closed loop within the circular economy of the fishing net industry. This research delves into the examination of the pyrolysis process and the influence of catalyst interactions at different temperatures on the resultant outputs, contributing to circular economy initiatives. We scrutinize used fishing nets utilizing TGA-DTG-FTIR analysis and a miniature pyrolysis setup. Initial micro-thermal analysis characterizes the raw material, revealing minimal degradation at approximately 200 °C and a significant peak at 450 °C, leading to an 88 wt.% reduction in weight. Analysis of the pyrolysis oils reveals considerable quantities of aromatic and aliphatic hydrocarbons. Moreover, the recovery of caprolactam not only produces energy-related products but also valuable chemical derivatives. The combined effect of temperature and catalysts suggests that the optimal condition for generating the most refined, superior-quality products is 700 °C. According to the results, catalytic thermal treatment at 700 °C with a Y-type catalyst displays potential as an efficient approach for caprolactam extraction, yielding a substantial output (96%).

## Materials and methods

The feedstock's characterization was upheld through ultimate and proximate analyses, adhering to specific standards. LHV determination followed LST EN 14918 guidelines using an IKA C5000 calorimeter. Volatile content was evaluated per LST EN 15148, while ash content was assessed in line with LST EN 14775. Moisture content adhered to LST EN 14774-1, and CHNS content was determined following LST EN 15104 using a Flash 2000 CHNS analyzer. Examination of heavy metals and mineral content was conducted according to LST EN 15411: 2011 and LST EN 15297: 2011 utilizing an Induced Plasma Optical Emission Spectrometer (ICP-OES) Optima 8000.

The thermal decomposition at micro-scale analysis of the specified feedstock was carried out using a thermogravimetric analyzer (Netzsch Jupiter F3, Germany) linked with a Fourier transform infrared spectrometer (Bruker Tensor 27, Germany), referred to as TG-FTIR. All experimental procedures were conducted in a nitrogen-rich oxygen-free setting, maintaining individual batches at 15-20 mg and a nitrogen flow of 60 ml/min. Following established literature, catalytic pyrolysis experiments utilized Y-type Zeolite and ZSM-5 catalysts, with catalyst-to-feedstock ratios of 1:3 and 1:8, respectively, under identical conditions. The experimental range encompassed temperatures from 40 to 850 °C. Differentiation of thermogravimetric analysis (DTG) curves was accomplished by deriving thermogravimetric analysis (TGA) curves, aiding in pinpointing the zone of peak thermal decomposition for each sample under analysis.

The experimental investigations involving the pyrolysis of samples from fishing nets were conducted using a laboratory-scale pyrolysis setup. Considering discrepancies among various authors' findings in the introductory context, an exploration was undertaken to analyze product distribution at maximum temperatures of 500, 700, and 900 °C, incorporating a 20-minute isothermal hold at the peak temperature. The heating rate was set around 20 °C/min, in accordance with specifications from a prior publication. A detailed depiction of the laboratory-scale bench apparatus is provided in Figure 1. Each pyrolysis trial employed a sample mass of 100 g. A nitrogen atmosphere, flowing at a rate of 3 L/min, was established for gas generation.

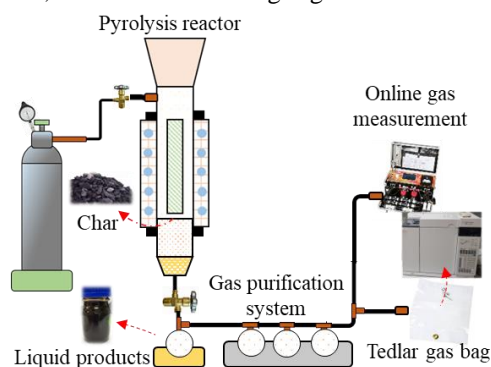


Fig. 1. Laboratory-scale experimental bench

The pyrolysis setup consisted of a primary reactor chamber linked to a condenser at its end, featuring small openings (up to 2-3 mm) for the release of produced gaseous and liquid components while retaining the char residue within the reactor. Liquid products were collected in a container placed at the end of the reactor, while gaseous products underwent a series of processes including cooling, purification, analysis, and collection through a conduit system. Purification of the produced gaseous components involved passage through five scrubbing vessels filled with isopropanol. Continuous analysis of the purified gases' composition was performed using a VISIT 03H gas analyzer.

## Results

### *Thermal analysis at micro scale*

Figure 2 illustrates the findings derived from TGA-DTG analyses performed while investigating the pyrolysis of the specified feedstock. Notably, the fishing nets exhibit a minor degradation phase around 200 °C, attributed to the evaporation of impurities and remnants from seawater. This process may contribute to the breakdown of secondary polymeric chains alongside the primary nylon 6 polymer, including materials like PP and PE. Moreover, a significant degradation stage occurs at approximately 440 °C, characterized by the linear condensation and thermal breakdown of the polymeric chains within nylon 6 (identified by recurring amide bonds, -NH-CO-). Consequently, a substantial portion of elongated polymeric chains undergoes decomposition, resulting in the formation of pyrolysis byproducts comprising volatile liquids (paraffins, aromatic hydrocarbons, etc.), gaseous components (H<sub>2</sub>, CH<sub>4</sub>, monomers), and solid char residues. Existing literature indicates variability in the upper temperature threshold for degradation of these polymers, ranging from 400 °C to 460 °C, contingent upon the heating rate. Additionally, the catalytic micro-thermal analysis distinctly indicates that the inclusion of a catalyst leads to a noticeable increase in the sample's thermal resistance during decomposition, evident in the overall pattern of weight loss. This phenomenon arises from the inherent resistance of ZSM-5 and Y-type catalysts to decomposition, resulting in their residual presence throughout the pyrolysis process. Consequently, adjusting the residual mass within the TGA data becomes crucial to ensure precise result evaluation.

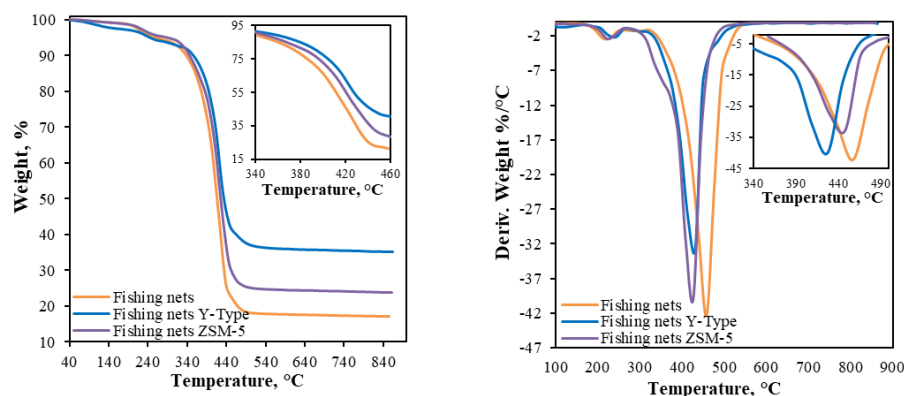


Fig. 2. Thermal decomposition of the seaweed with ZSM-5 and Y-Type catalyst

### *Pyrolysis products (liquid and gaseous) analysis*

The examination of gaseous and liquid products involved the utilization of gas chromatographs (Agilent 7890 A) equipped with TCD for gases and GC/MS for liquids. Predominant constituents identified in the generated pyrolysis gases encompass CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>. Analysis of the liquid products revealed a notable presence of derivatives derived from polycyclic aromatic compounds. An industrial catalytic enhancement of the produced items exhibited encouraging trends, particularly an observable rise in the quantity of lighter aromatic compounds. Based on the acquired findings, it can be inferred that the resulting products hold potential for conversion into valuable energy-based products suitable for use as transportation fuel.

## Conclusions

This investigation focused on catalytic pyrolysis of discarded fishing nets utilizing Y-Type and ZSM-5 catalysts at temperatures ranging from 900 to 500 °C. Initial assessment of the starting material involved TGA-DTG analysis, revealing a prominent peak at 440 °C and an 88 wt.% mass loss attributed to the thermal degradation of the primary polymer, Nylon-6.

This research highlights the potential of utilizing waste fishing nets through pyrolytic processes to generate additional energy products. The considerable recovery of caprolactam from these nets not only offers a pathway to extract higher-value products but also provides opportunities for its use in Nylon-6 synthesis. Ultimately, this study emphasizes the material's potential as a resource for producing valuable energy products, thereby contributing to the circular economy.