

# Hydrothermal liquefaction of fish processing by-products towards biofuel intermediates

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Fish processing residues constitute a heterogeneous and highly biodegradable waste stream characterized by elevated moisture content, significant lipid fractions and substantial protein levels, often accompanied by mineral-rich components such as scales and bone fragments. The management of these by-products presents both environmental and logistical challenges, particularly due to their rapid degradation and high organic load. From a thermochemical perspective, their intrinsic biochemical composition (rich in triglycerides and nitrogen-containing macromolecules) renders them attractive candidates for hydrothermal liquefaction (HTL), a process capable of converting wet biomass directly into energy-dense liquid intermediates under subcritical water conditions. Thus, in this study, selected marine residues, including intestines and scales from European sea bass and gilthead seabream, as well as striped mullet roe, were investigated as HTL feedstocks. These materials exhibit varying lipid contents even after mechanical or preparatory treatments, allowing assessment of how differences in residual lipid fraction, protein concentration and mineral content influence carbon partitioning, product distribution and biocrude characteristics during HTL conversion.

Two experimental investigations were conducted. First, an optimization study was performed using striped mullet roe as the model feedstock to evaluate the effect of reaction temperature on HTL performance. Experiments were carried out at 280, 300, 320, 350 and 360 °C with a fixed residence time of 30 min and a solid-to-liquid ratio of 1:10 using deionized water as the reaction medium. All experimental conditions were tested in duplicates to ensure reproducibility, and product yields are reported on a dry basis. Following identification of the optimal operating temperature, all selected marine residues were subsequently processed under identical HTL conditions to enable direct comparison of product distribution and biocrude characteristics as a function of feedstock composition.

HTL experiments were conducted in a bench-top, high-pressure stirred batch reactor (Parr 4576A) with an internal vessel volume of 250 mL. The reactor is equipped with a J-type thermowell for controlled heating and an internal U-type cooling coil enabling rapid quenching after reaction. For each run, 10 g of freeze-dried feedstock were mixed with 100 mL of deionized water. The reactor was sealed and purged three times with nitrogen to eliminate oxygen and ensure an inert reaction environment. Subsequently, the system was pressurized to 30 bar with nitrogen in order to maintain water in the liquid phase during heat-up and reaction. No catalyst or chemical pretreatment was applied. After reaching the desired temperature, the reaction was maintained for the specified residence time and then rapidly cooled to ambient conditions prior to product recovery and phase separation. The methodology is depicted in Figure 1.

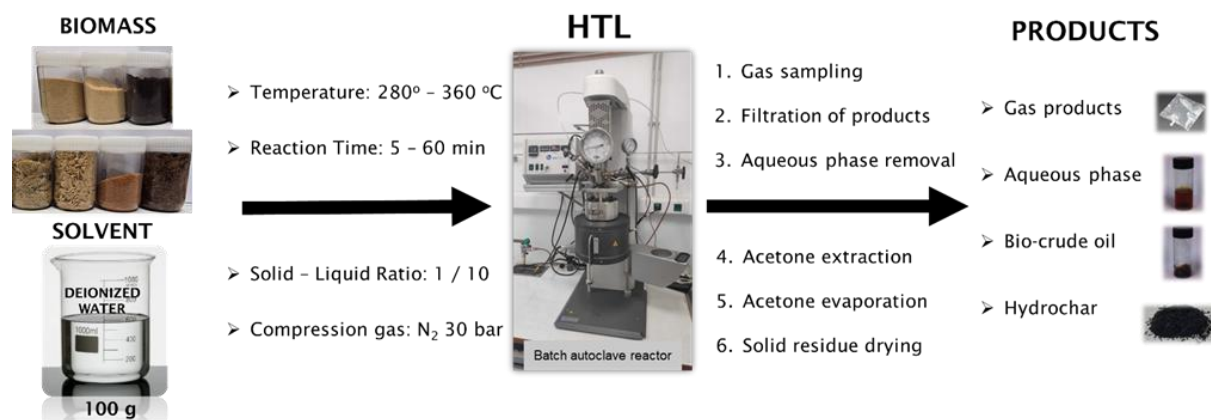


Figure 1. Methodology of hydrothermal liquefaction experimental procedure

The optimization study performed on striped mullet roe demonstrated a clear temperature-dependent product distribution across the investigated range (280–360 °C) with the maximum oil yield obtained at 350 °C. Biocrude

yield increased from 37.80 wt.% at 280 °C to a maximum of 41.90 wt.% at 320 °C, before slightly decreasing to 39.75 wt.% at 360 °C. This indicates that intermediate severity conditions favor oil production, while excessive temperature promotes secondary reactions. Gas yield decreased progressively with decreasing temperature, ranging from 12.43 wt.% at 360 °C to 7.99 wt.% at 280 °C, whereas the aqueous phase showed the opposite trend, increasing from 47.52 wt.% at 360 °C to 53.71 wt.% at 280 °C. Solid residue formation remained negligible under all tested conditions (<0.5 wt.%), suggesting extensive decomposition of the organic fraction even at the lowest temperature. Elemental analysis of the biocrudes revealed carbon content between 74.68 and 76.86 wt.%, with the highest carbon enrichment observed at intermediate temperatures. Hydrogen content remained stable (~10.8–11.0 wt.%), while nitrogen levels were comparatively moderate (2.9–3.0 wt.%) and showed no significant temperature dependence. Oxygen content varied between 9.14 and 11.57 wt.%, without a monotonic trend across the severity window. These results indicate that temperature primarily influences carbon redistribution among phases rather than substantially altering oil elemental composition within the investigated range. The results from the optimization study are presented in Figure 2.

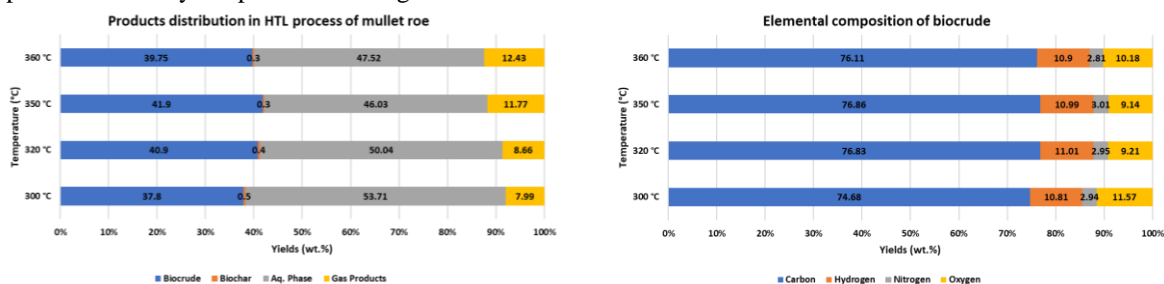


Figure 2. HTL optimization study results on mullet roe

At the selected optimal temperature of 350 °C, substantial differences in conversion behavior were observed among the investigated marine residues. The highest biocrude yield was obtained for *Togarodes sagittatus* (44.2 wt.%), followed by mullet roe (41.9 wt.%) and gilthead seabream intestines/stomach (39.5 wt.%). In contrast, European sea bass (intestines, liver) and gilthead seabream trimmings exhibited significantly lower oil yields (17.3–21.4 wt.%), accompanied by elevated biochar formation (17.3–21.4 wt.%). Striped mullet roe samples showed moderate oil yields (19.4–22.6 wt.%) but negligible solid formation (<0.5 wt.%), with carbon predominantly partitioned into the aqueous phase ( $\approx 71$  wt.%). Aqueous phase production varied widely (40.66–71.44 wt.%), indicating strong feedstock-dependent redistribution of water-soluble nitrogenous and oxygenated compounds. Gas formation remained comparatively moderate across all samples (6.22–11.77 wt.%).

Elemental analysis of the resulting biocrudes revealed carbon contents between 70.65 and 76.86 wt.% and hydrogen levels around 10 wt.%. Nitrogen content ranged from 2.41 wt.% (gilthead seabream intestines/stomach) to 5.02 wt.% (European sea bass intestines/liver), highlighting variability in protein-derived nitrogen incorporation into the oil phase. Oxygen content showed broader variation (8.57–16.33 wt.%), with higher oxygen levels corresponding to lower carbon enrichment. These findings confirm that biochemical heterogeneity among fish processing residues significantly influences carbon partitioning, char formation and heteroatom retention during HTL. The results from the optimization study are presented in Figure 2.

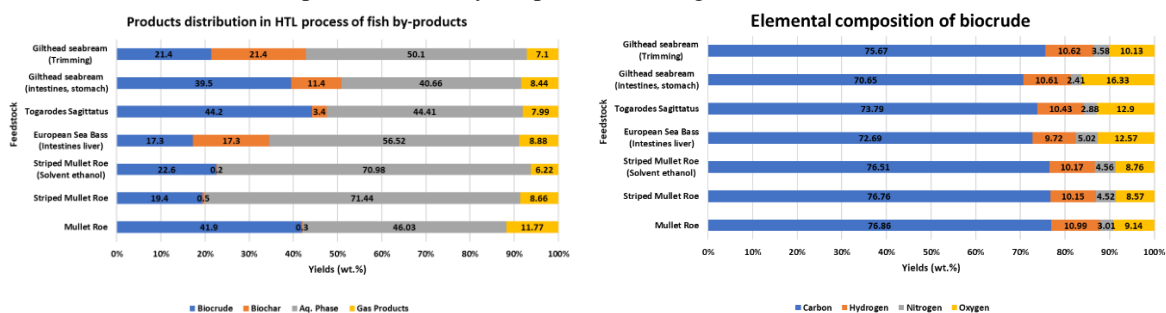


Figure 3. Comparative HTL study results on various fish by-products