**Response to Reviewers**

We thank the reviewers for their critical assessment of our work. In the following, we address their comments one by one.

Comment 1: Page 1: Kindly refrain from including references in the abstract.

Response: Addressed the comment. Thank you.

Comment 2: Page 1: The energy recovery becomes favourable if the energy spent for syngas production is lower than the energy gained by its combustion (the concept of EROEI). Therefore, producing syngas is suitable for recovering energy from the biochar production process, but it should be clearly stated that it is not the goal of the overall procedure.

Response: Thank you for pointing that out. We addressed that the aim of the study is biochar yield, quality and nutrient content.

Comment 3: Page 1: This statement does not appear to be present in the text. Could you clarify or confirm its inclusion?

Response: Thank you for pointing out the mistake. Abstract is revised to address the statements discussed in the manuscript.

Comment 4: Page 1: This aspect has not been addressed in the paper and therefore should not be mentioned in the abstract.

Response: Thank you. The revised abstract addressed the query.

Comment 5: Page 1: Please, explain the acronym before use.

Response: Address in revised abstract.

Comment 6: Page 1: The abstract requires a complete revision, as it fails to adequately convey the context or the purpose of the paper, while including information that is not detailed or supported in the main text of the paper.

Response: Thank you for the detailed review of the abstract. As instructed, we address the concern by completely rewriting the abstract to comply with the objective and findings of the study.

Comment 7: Page 1: Pyrolysis, however, might not allow for recovery of these compounds due to thermal degradation. Please further elaborate regarding this drawback.

Response: The concern is addressed on page 1, lines 38 to 42.

Comment 8, 9: Page 2: Please add this as a reference using the dedicated style.

Response: Thank you. Regulations and certifications were referenced according to the dedicated style.

Comment 10: Page 2: Consider rephrasing this sentence for improved clarity and precision.

Response: The Aim of the study was rewritten for improved clarity. Thank you.

Comment 11: Page 2: Could you please provide a reference for this statement?

Response: Thank you for the concern about this statement. We revised the paragraph discussing the aim of the study. While the statement regarding the purpose behind the selection of a 30 FW: 70 PW mixture was influenced by lab trials. Biochar produced from a mixture with fish waste in the proportion of more than 30% resulted in a higher concentration of Nickel. Thus, not complying with the regulations and suitability for agricultural use.

We have shifted and discussed the reason regarding the selection of this specific mix ratio on page 2, section 2.1, on lines 67-68.

Comment 12: Page 2: Kindly add a brief paragraph between consecutive titles to ensure a smoother transition and improve the document's flow

Response: Thank you. The suggestion for a smoother transition is addressed with a brief paragraph on page 2, lines 59-61

Comment 13: Page 2: Could you clarify or elaborate on the meaning of “homogeneous nature” in this context? Does it refer to uniform composition, structure, or plant species?

Response: Thank you for pointing out the ambiguity of the word. As suggested by reviewers, it refers to the uniform composition of olive tree pruning free from debris and other plant species. As discussed in section 2.1, page 2, lines 62-63.

Comment 14: Page 2: Could you kindly provide the energy consumption of this process? Feedstock drying

Response: Thank you. It is addressed in section 2.1, on page 2, lines 64-66.

Comment 15: Page 2: Could you kindly provide the energy consumption of this process? Pyrolysis reactor

Response: Thank you. Please refer to page 2, lines 75-77, where the energy consumption in kWh for each residence time operation is mentioned. These numbers are calculated based on the amount of treated feedstock capacity (for instance, 5 kg treatment potential at residence time of 30 minutes, etc), and energy consumption per hour to operate the reactor.

Comment 16: Page 2: Why 57 minutes? It looks quite odd

Response: The speed of screw determines the exposure time of sample in the heating chambers. Before initiating the pyrolysis tests, we confirmed the times corresponding to screw speed. We found a slight variation for 60-minute speed, which corresponded to 57 minutes.

Comment 17, 18, 20, 21, 22, 23 Page: 2: Please add this as a reference using the dedicated style

Response: Thank you. References were cited according to a dedicated reference style. All are addressed in section 2.3, page 2, from line 85 to line 94.

Comment 19: Page 2: Kindly remove the extra space in the text

Response: Thank you. Extra space was removed,

Comment 24: Page 3: It seems that an excessive level of detail is being provided about this device. This part might be replaced by further details about the actual work

Response: Thank you for the suggestions. It is addressed by removing the sentence to allow space for actual work.

Comment 25: Page 3: Please use the term “weight” instead

Response: Thank you. The term was corrected to weight.

Comment 26: Page 3: Could you clarify if you intended to refer to bio-oil instead of biochar here?

Response: Thank you. Yes, it was intended to say bio-oil. It is addressed in the revised manuscript.

Comment 27: Page 3: Given the significant uncertainty (±50%), the outcomes may be substantially biased. I recommend utilizing the experimental value obtained during the second round of experiments, conducted after addressing the leakage issue, for greater reliability.

Response: Thank you for the critical assessment of section 3.1. The question is addressed by selecting the reliable test result after corrective measures and by modifying Table 1. There is a need for future studies to confirm the replicability of the equipment as well as the condensation system efficiency. The point is discussed in section 3.1, product yield

Comment 28- 32: Page 3: Concerns about biochar, bio-oil and syngas trends deviations.

Response: Section 3.1 was completely restructured and included the more reliable tests, leaving out the mean and standard deviation numbers. While these tests provide encouraging results for biochar (the main aim of the study), they still point to the need for optimisation of the condensation system for bio-oil collection

Comment 33: Page 3: Ensure consistency in the use of significant figures throughout the data

Response: Thank you. Consistent significant figures are ensured in the updated Table 1.

Comment 34: page 3: Please double-check the value for biochar (42.1%)

Response: Thank you for pointing out the typo error. Figure 1 is corrected for biochar value

Comment 35: Page 3: Please substitute “rise” with “rice”

Response: Addressed in section 3.2, on page 3, line 138

Comment 36: Page 3: The sentence would benefit from rephrasing for improved clarity and precision.

Response: Addressed in section 3.2, on page 3, lines 133- 139

Comment 37: Page 3: Please try to be consistent with significative figures

Response: Thank you. Consistent significant figures are also ensured in the Table 2.

Comment 37: Page 3: Rephrasing the sentence could enhance its readability

Response: Thank you. Concern is addressed in section 3.2, on pages 3, 4, lines 139-142, for better comprehension

Comment 39: Pages 3, 4: Please try to be consistent with significative figures

Response: Thank you. Consistent significant figures are also ensured in the Table 2.

Comment 40: Page 4: Kindly rephrase this for enhanced clarity and accuracy

Response: Thank you. It is addressed in section 3.2, on page 4, lines 149-153 for enhanced clarity and accuracy.

Comment 41: Page 4: Please use the correct font and borders in the Table. Moreover, please shift the biochar column beside the Unit’s one. It’s not clear what does the “x” stand for. Try not to split the table in two pages

Response: Thank you for your valuable insight to enhance table readability. It is addressed in the updated Table 3 on page 4, lines 159-160

Comment 42: Page 4: This sentence lacks clarity and could benefit from revision

Response: Thank you. Sentence is rephrased for enhanced clarity. It is addressed in section 3.3, on page 4, lines 164-165

Comment 43: Page 5: Please relocate Figure 3 to follow the section where it is discussed. Ensure the font matches the text, remove the title, and use black font colour for consistency

Response: Thank you. Figure 3 is relocated to a suitable place, to follow the section where it is discussed. It is addressed in section 3.3, on page 4, lines 197-198. Title was removed, text was changed to black and font was changed to Arial to match the text.

Comment 44: Page 5: Please remove the article “The”

Response: Thank you. Article “The” was removed from the sentence.

Comment 45: Page 5: Please remove the article “The”.

Response: Thank you. Article “The” was removed from the sentence.

Comment 46: Page 5: Please eliminate this symbol here and in the following section.

Response: Symbol “|” was removed from both sections. Thank you.

Comment 47: Page 5: Could you clarify the method or approach used to calculate this?

Response: Thank you for bringing our attention. Methodology of syngas calculation is explained and cited in section 2.3, on page 2, lines 97-101. And also cited on page 5, lines 192-193.

Comment 48: Page 5: High CO2 content typically indicates complete thermal decomposition. Could you explain why the opposite is observed in this case?

Response: Thank you for the correction, sentence is corrected in section 3.4, on page 5, lines 193-195.

Comment 48: Page 5: What is the primary objective of this pyrolysis process? Biochar for soil amendment or fuels for energy recovery? Consequently, which of these should theoretically be prioritized for optimization, biochar or syngas? Please clarify your viewpoint.

Response: Thank you for the concern. Section 4: Conclusion discusses in detail these queries, on page 5, lines 200-208.

Comment 49: Page 6: This reference in not arranged in alphabetical order; please revise for consistency

Response: Thank you for pointing out the alphabetical order mistake. Reference list is updated and arranged in alphabetical order to ensure consistency



# TRANSFER OF COPYRIGHT AGREEMENT

**Corresponding Author**

FIRST NAME\_\_\_\_\_\_\_\_\_\_\_\_\_SALMAN\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_FAMILYNAME\_\_\_\_\_\_\_\_\_\_NISAR\_\_\_\_\_\_\_\_\_\_\_

CONTACT EMAIL\_\_\_\_\_\_\_\_\_\_\_\_\_s.nisar@pm.univpm.it\_\_\_\_\_\_\_\_\_\_\_\_

**Title of Paper VOL. XX, 2025**

CO-PYROLYSIS OF FISH WITH PRUNING WASTE FOR BIOCHAR PRODUCTION AS AN AMENDMENT FOR COMPOSITE COMPOSTING IN THE BIOREFINERY SCENARIO

**Co-Authors:** Nisar S., Gonzalez-Camejo J., Laura Eusebi A., Fatone F.

**STATEMENTS**

**1.** The Undersigned, desiring to publish the above paper in the publication *Chemical Engineering Transaction*by AIDIC Servizi S.r.l., hereby transfers the copyright in the above paper to AIDIC Servizi S.r.l. Via Giuseppe Colombo 81/a, 20133, Milano, Italy – VAT. 11667680158

**2.** The Undersigned retains the following rights in the paper:

a) All proprietary rights over than copyright, such as patent rights.

b) The right to reproduce, have reproduced, revise, adapt, prepare derivative works, present orally or

distribute the above paper for such purpose as teaching (including multiple copies for classroom use),

scholarship or research.

**3.** The Undersigned warrants that the manuscript is the author's original work. If the work was prepared jointly,

the undersigned agrees to inform co-authors of the terms of this agreement. The Undersigned further warrants

that the work has not been published before. The Undersigned also warrants that the manuscript contains no

libellous or unlawful statements, and does not infringe on the right of others.

**4.** This Agreement is in act if the above quoted Paper will be accepted for the publication on *Chemical Engineering Transaction*

 Authorised Signature:

 Date: 15/04/2025

|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS*** ***VOL. xxx, 2025*** | A publication ofaidiclogo_grande |
| The Italian Associationof Chemical EngineeringOnline at www.cetjournal.it |
| Guest Editors: Fabrizio Bezzo, Flavio Manenti, Gabriele Pannocchia, Almerinda di BenedettoCopyright © 2025, AIDIC Servizi S.r.l.**ISBN** 979-12-81206-17-5; **ISSN** 2283-9216 |

CO-PYROLYSIS OF FISH WITH PRUNING WASTE FOR BIOCHAR PRODUCTION AS AN AMENDMENT FOR COMPOSITE COMPOSTING IN THE BIOREFINERY SCENARIO

Salman Nisara\*, Josué González-Camejob, Anna Laura Eusebia, Francesco Fatonea

aDepartment of Science and Engineering of Materials, Environment and Urban Planning-SIMAU, Polytechnic University of Marche, Via Brecce Bianche, 12, 60131, Ancona, Italy

bBETA Technological Centre, University of Vic-Central University of Catalonia, Can Baumann Building Ctra. de Roda, 70, 08500 Vic-Barcelona, Spain

\*s.nisar@pm.univpm.it

Increasing global fish production demands sustainable waste management for the mitigation of process leftovers. Fish waste stabilisation using pyrolysis has the potential to stabilise this putrescible waste, as well production of biochar for sustainable agricultural applications. This study investigated the influence of residence times at a fixed temperature of 400°C on the yield and quality of biochar from co-pyrolysis of fish and pruning waste. The residence time, a key parameter in slow pyrolysis, affects the extent of thermal degradation and the yield and characteristics of the resulting biochar. Results showed a decreasing trend of biochar yield with a decrease in residence time for pruning waste (PW) tests, whereas fish waste (FW) and PW blend (30:70 w/w) resulted in a relatively stable trend. Biochar obtained at 30 minutes residence time accounted for 42.1%, with a higher carbon content of 62.8% and H/C of 0.69, indicating thermal conversion and stable biochar. Furthermore, biochar exhibits a lower concentration of trace elements, complying with safety and quality regulations and certification requirements for biochar.

* 1. Introduction

The circular economy model promotes the valorisation of waste materials from linear process chains by converting them into alternative feedstocks for the recovery of valuable bioproducts. In this context, biorefineries are increasingly recognised for their ability to transform agricultural and organic residues into high-value compounds through biological, thermochemical, and thermal processes (Goswami et al., 2022). Among these residues, those generated by the fishery industry represent a promising resource, especially in coastal regions. Global fish production from capture fisheries and aquaculture is expected to reach 204 million tonnes by 2030, driven by growing demand (FAO, 2020). However, this expansion results in substantial amounts of unavoidable waste—up to 70% of the original fish mass depending on processing methods (Ahuja et al., 2020). These putrefiable residues, which include heads, viscera, scales, and skins, pose significant disposal and environmental challenges if not promptly managed. Nonetheless, they are rich in proteins, lipids, minerals, polysaccharides, and other bioactive compounds, making them suitable feedstock for valorisation strategies (Bruno et al., 2019). Recent research has highlighted the feasibility of developing decentralised biorefineries along the Italian Adriatic coast, leveraging locally available fish and mollusc residues for the production of value-added products such as biochar-compost composites, enzymatic hydrolysates, and calcium carbonate (Andreola et al., 2023).

For the valorisation of such organic waste, a thermochemical approach is suitable for converting the carbon and nutrient content of the biomass into valuable products. Firstly, it provides biochar, which can be used as a soil improver and fertiliser, along with bio-oil and syngas, which are sources of energy. Secondly, compared to biochemical conversion pathways, thermochemical processes are fast and offer a more efficient route for processing complex organic materials (Liu et al., 2022).

Among the various available thermochemical technologies, pyrolysis stands out as one of the efficient processes, particularly slow pyrolysis, operating at moderate temperatures (300–700 °C), low heating rates (0.1–1 °C/s), and extended residence times (10–100 minutes) under oxygen-limited conditions. Moreover, the distribution and quality of these products depend on the feedstock characteristics and pyrolysis parameters, especially residence time, which can be optimised to maximise specific outputs (Pahnila et al., 2023). For instance, Centeno et al. (2023) demonstrated that increasing residence time during pyrolysis enhances biochar yield. The study highlighted that longer residence times allow for more complete thermal decomposition and carbon retention, optimising biochar production efficiency.

Regulatory frameworks such as European regulation (FMFPA, EU (2019) and Italian regulation (RRFF, IG (2010) govern the production and use of biochar, supporting its application as a soil improver or growing medium. Furthermore, voluntary standards, including the European Biochar Certificate (FSBP, EBC (2025) and those of the International Biochar Initiative (GCB, IBI (2020), provide quality guidelines to ensure sustainable use in agriculture.

Based on the discussion mentioned above, the study is designed to investigate the influence of residence time on biochar quality, yield, and nutrient content from co-pyrolysis of fish and pruning waste. In addition, syngas and bio-oil are characterised for energy recovery potential.

* 1. Materials and methods

This section outlines the experimental procedures employed to investigate the pyrolysis of FW with PW. It includes details on feedstock collection and pretreatment, reactor setup, feedstocks and product characteristics, and product yield.

2.1 Feedstock collection and pretreatment

FW was collected from a local fish processing facility, while PW was obtained from olive tree pruning of uniform composition, free from debris and other plant species. Both feedstocks were oven-dried at 80 °C for 48 h to reduce their moisture content, which resulted in 0.7 kWh/kg feedstock of energy consumption normalised against the full capacity of the dryer (160 kg). FW was homogenised using an impact mill. PW was ground using a laboratory grinder. FW to PW proportion of 30%: 70% by dry weight was selected based on lab trials, as the optimal mix ratio, with final biochar complying with regulations in terms of trace elements.

 2.2 Pilot scale pyrolysis setup

Pyrolysis experiments were carried out in a pilot-scale auger-type reactor equipped with a screw mechanism that transports the feedstock and allows control of residence time by adjusting the screw speed. The reactor comprises three independently heated stainless-steel zones, capable of reaching up to 1100 °C, and includes a collection bin for solid residues at the end of the screw shaft. To maintain an inert atmosphere, the system is sealed and equipped with inlet/outlet valves for nitrogen supply. The reactor has a capacity of 2.5 L and is fed semi-continuously via a 20 L hopper. Experiments were conducted at a constant temperature of 400 °C with residence times of 20, 30, 40, 50, and 57 minutes, controlled through screw speed, with energy consumption of 1.66 kWh, 2.49 kWh, 3.32 kWh, 4.15 kWh and 4.98 kWh respectively for each kilogram of feedstock treated. Prior to each run, the reactor was preheated and flushed with nitrogen at 5 L/min for 10 minutes, with the flow maintained throughout the process. Volatile compounds were discharged through a 350 °C exhaust stack to avoid condensation, while condensable vapours were recovered in a chilled spiral condenser. Non-condensable gases passed through an activated carbon column before release, with samples collected in a 2 L gas bag for analysis.

2.3 Feedstock, biochar, bio-oil and syngas characterisation

Biochar obtained from pyrolysis tests was collected and characterised according to FSBP, EBC (2025) and GCB, IBI (2020) guidelines. pH and electrical conductivity (EC) were measured following IBI protocols (IBI, 2020), using a 1:20 (w:v) biochar-to-deionised water solution shaken for 1.5 h, with measurements taken using a Hanna HI-2002 Edge (pH) and XS Cond 70+ meter (EC). Heavy metal content was determined according to the Italian Standards Organization’s method for solid biofuels terminology (UNI, 2015b), using aqua regia extraction followed by analysis via ICP-OES (VISTA-MPX). The elemental composition (C, H, N) of both feedstocks and biochar was assessed through combustion and gas analysis following the method for volatile matter determination (UNI, 2015a). Moisture and ash contents were determined using oven-drying protocols (UNI, 2024; UNI, 2023), while fixed carbon was calculated by difference, based again on the volatile matter standard (UNI, 2015a). Water holding capacity was assessed following the procedure described in Annex A of the gravimetric method standard (UNI, 2014).Bio-oil composition was analysed via Fourier-transform infrared spectroscopy (FTIR). Syngas samples, collected in gas bags, were analysed using a VARIO luxx portable analyser equipped with a built-in pump, filter, and gas cooler. The device uses electrochemical (2- and 3-electrode) and non-dispersive infrared (NDIR) sensors to quantify O₂, CO, NO, H₂S, and SO₂ concentrations. Syngas net calorific value was calculated using Eq (1) based on the intrinsic heating values of CO₂, CO, CH₄, H₂, and O₂ taken from Engineering Toolbox (2005).

NCVsyngas​= ∑(*yi*​×NCV*i*​) (1)

*Where: yi*​ = Volume fraction of component *i* (decimal)

 NCV*i*​ = Net calorific value of component *i* (MJ/m³)

2.4 Pyrolysis product yield

Biochar and bio-oil produced from each test were weighed to calculate their respective yields, expressed as the ratio of each product’s mass to the initial feedstock mass. The syngas yield was determined by difference, obtained by subtracting the combined masses of biochar and bio-oil from the initial feedstock weight to complete the mass balance.

* 1. Results and Discussion

This section presents the analyses of both the feedstock and the resulting biochar, alongside an evaluation of biochar quality parameters and macronutrient content. In addition, the composition of the bio-oil and syngas fractions is discussed to provide a comprehensive assessment of the pyrolysis process and product characteristics.

3.1 Product yield

Table 1 shows the pyrolysis product distribution. As discussed, the influence of residence time on the distribution of biochar, bio-oil, and syngas was investigated for two feedstocks: PW and a fish-to-pruning waste mixture (FW: PW 30:70 by dry weight). For PW tests, biochar yield decreased with shorter residence time, from 55.3 % at 57 minutes to 42.6 % at 20 minutes, and aligns with Pahnila et al., (2023) and Santos et al., (2023), who report that longer residence time results in secondary cracking reactions of volatile vapours, thus resulting in increased formation of biocarbon. While bio-oil yield decreased from 29.9% to 21.2% with fluctuation for tests at 40 and 30 minutes. Similarly, syngas follows an increasing trend (21.2% to 29.9%) except 30-minute test. Moreover, in co-pyrolysis tests (30FW:70PW), biochar and bio-oil yields decline slightly. Differences in biochar yields of PW and co-pyrolysis tests, maybe attributed to influence of fish waste decomposition, potentially increasing the liquid and gas product amounts. While product distribution results are encouraging, particularly for biochar yield from both PW and co-pyrolysis mixtures, further studies are still needed to confirm the efficiency of the condensation system for condensable gas collection, as well as the replicability of product distribution to better understand the feasibility of process scaling from an economic side.

Table 1 Pyrolysis product distribution.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Feedstock | Residence time (min) | Biochar % | Bio-oil % | Syngas % |
| PW | 57 | 55.3 | 29.9 | 14.8 |
| PW | 50 | 49.6 | 23.5 | 26.9 |
| PW | 40 | 45.8 | 20.2 | 34.0 |
| PW | 30 | 45.2 | 24.2 | 30.6 |
| PW | 20 | 42.6 | 21.2 | 36.2 |
| 30FW:70PW | 57 | 43.2 | 25.4 | 31.4 |
| 30FW:70PW | 50 | 40.5 | 24.0 | 35.5 |
| 30FW:70PW | 40 | 43.3 | 23.9 | 32.8 |
| 30FW:70PW | 30 | 42.1 | 20.2 | 37.7 |

PW: Pruning waste only; 30FW:70PW: 30 % fish waste to 70 % pruning waste by dry weight



Figure 1: Pyrolysis products and their characterisation from a 30-minute test.

3.2 Main characterisation of feedstock and biochar from 30-minute pyrolysis test

Table 2 presents the physiochemical properties of FW, PW, and biochar from 30-minute residence time test. The ash content of biochar (19.2%) considerably exceeds that of feedstocks (FW: 11.97%; PW: 4.99%), consistent with the observation by other studies that pyrolysis concentrates inorganic components through volatile matter loss (López-Cano et al., 2018; Chen et al., 2024). Biochar has a higher carbon content of 62.8%, than both FW (53%) and PW (47.8%), suggesting carbon enrichment during pyrolysis and aromatisation of biomass. Biochar exhibits an H/C ratio of 0.69, complying with the stability thresholds (H/C < 0.7) set by the FSBP, EBC (2025) and GCB, IBI (2020), confirming its aromatic structure and thermal alteration under pyrolysis conditions. This ratio aligns closely with values reported for lignocellulosic biochar’s (e.g., rice husk and straw: 0.67 at 400°C) by Jindo et al. (2014). The alkaline pH (9.4) exceeds values documented for tree bark (8.9; Venegas et al., 2014) and corn stover (8.8; Rafiq et al., 2016) at equivalent pyrolysis temperatures (400°C). Electrical conductivity (EC) of the biochar (486 mS/m) aligns with the range reported for woody biomass-derived biochar (370 mS/m; Venegas et al., 2014). Furthermore, both the alkaline pH and EC comply with RRFF, IG (2010), which mandates pH < 12 and EC < 1000 mS/m. This regulatory compliance underscores the biochar’s suitability for agricultural use; however, pot and field trials are recommended to assess long-term impacts on soil salinity.

Table 2: Proximate and ultimate analysis of feedstocks and biochar at 30-minute residence time.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameter  | Unit | Fish waste | Pruning waste | Biochar  |  |
| Moisture contentDry matter | %% | 77.81±0.0322.23±0.03 | 12.97±0.1487.03±0.14  | 5.8094.20 |  |
|  |
| Ash content | % | 11.97±0.51 | 4.99±0.03 | 19.20 |  |
| Fixed carbon1 | % | 16.24±1.41 | 18.42±0.36 | 11.20 |  |
| C | % | 53.00 | 47.80 | 62.80 |  |
| H | % | 8.10 | 6.31 | 3.60 |  |
| N | % | 7.52 | 1.70 | 3.90 |  |
| H/C2 |  | 1.82 | 1.57 | 0.69 |  |
| pH3 |  |  |  | 9.41±0.08 |  |
| EC3 | mS/m |  |  | 486.00±33.94 |  |

1Percentage of dry matter; 2 EBC and IBI specify a H/C (molar ratio) limit of <0.7; 3 pH and EC limits are 4-12 and 1000 in RRFF, IG (2010)

Table 3 presents the macro and trace elements composition of biochar produced in 30-minute test. Macro nutrient presence in biochar is directly related to ash content (19.20%), which is influenced by feedstock composition. Biochar from co-pyrolysis blend possess a high nutrient composition compared to green waste biochar at 400°C, as reported by López-Cano et al., (2018). Also, high Ca (59,054 mg/kg) concentration may possibly be attributed to the presence of fish waste as fish bones are calcium-rich (Ghaly et al., 2013). Similarly, trace elements in biochar respect the limits after being evaluated against four regulatory frameworks: RRFF, IG (2010), FMFPA, EU (2019), FSBP, EBC (2025), and GCB, IBI (2020) guidelines. Both high nutrient content and low trace elements concentration give a potential indication of suitability for agricultural use as soil amendment and compost additives; however, pot and field trials must validate long-term impacts on soil health and compost quality.

Table 3: Biochar macro and trace elements concentration at 30-minute residence time.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Parameter | Unit | Biochar | D. Lgs 75/2017 | EU reg. 1009/2019 | EBC | IBI |
| Macro elements |  |  |  |  |  |
| Na | mg/kg | 9995.8±2896.3 | X | x | x | x |
| K | mg/kg | 14608.3±4314 | X | x | x | x |
| P | mg/kg | 21268.5±5893.4 | X | x | x | x |
| Ca | mg/kg | 59054.3±17653.6 | X | x | x | x |
| Mg | mg/kg | 3308.3±888.2 | X | x | x | x |
| Trace elements |  |  |  |  |  |  |
| Cd | mg/kg | n.m | 1.5 | 2 | 1.5 | 1.4 |
| Hg | mg/kg | n.m | 1.5 | 1 | 1 | 1 |
| Ni | mg/kg | 16.4±4.2 | 100 | 50 | 50 | 47 |
| Pb | mg/kg | n.m | 140 | 120 | 150 | 121 |
| As | mg/kg | n.m | x | 40 | 13 | 13 |
| Cu | mg/kg | 30.5±10.3 | 230 | 300 | 100 | 143 |
| Zn | mg/kg | 138.7±39.7 | 500 | 800 | 400 | 416 |
| Cr | mg/kg | 8.4±2.0 |  |  | 90 | 93 |
| Fe | mg/kg | 262.9±0.5 | x | x | x | x |
| Mo | mg/kg | 1.8±0.4 | x | x | x | 75 |

n.m: not measured; x: limits not specified by regulations

3.3 FTIR characterisation of bio-oil from 30-minute pyrolysis test

FTIR spectrum of bio-oil produced from a mixture of 30 % FW and 70 % PW at 400 °C at 30-minute residence time reveals a complex composition of functional groups characteristic of bio-oil derived from lignocellulosic and protein-rich feedstocks (Figure 2). The spectrum shows two peaks, a broader and a narrow peak at 3000-3600 cm-1 and 1700 cm-1-. The former suggests the presence of hydroxyl functional groups, likely from alcohols, phenols, and water. These compounds are typical of bio-oil and result from the degradation of cellulose and hemicellulose in PW, as well as protein and lipid decomposition from FW. The hydroxyl content is consistent with findings reported in pyrolysis studies by Bridgwater (2012) and Xiu et al. (2012), which attribute similar peaks to lignin derivatives and secondary reactions of pyrolysis vapours. Peaks around 2900 cm⁻¹ correspond to the stretching vibrations of methyl (-CH₃) and methylene (-CH₂) groups, indicating the presence of aliphatic hydrocarbons. The distinct absorption at 1700 cm⁻¹ is attributed to carbonyl functional groups from ketones, aldehydes, and carboxylic acids. These compounds are primarily derived from lipid and carbohydrate breakdown, as documented in slow pyrolysis studies (Xiu et al., 2012). Their presence highlights the oxygenated nature of bio-oil, which contributes to its reactivity and potential for further upgrading. Peaks in the 1500–1600 cm⁻¹ region suggest the presence of aromatic C=C bonds, likely originating from lignin decomposition in PW. Similar findings were reported by Bridgwater (2012), where lignin derivatives were identified as key contributors to the aromatic fraction of bio-oil. Absorptions in the range 1000–1300 cm⁻¹ correspond to C-O bonds in esters, ethers, and alcohols. These compounds are typical of oxygenated intermediates produced during the pyrolysis of both protein-rich and lignocellulosic biomass.

These findings are consistent with previous studies by Bridgwater (2012) and Xiu et al. (2012), which emphasise the significant role of feedstock composition and pyrolysis conditions in determining bio-oil quality. The contribution of fish waste introduces additional complexity due to protein decomposition, potentially resulting in nitrogen-containing compounds. Meanwhile, pruning waste contributes to aromatic and phenolic compounds, enhancing the potential applications of bio-oil in chemical industries. The bio-oil exhibits promising characteristics; however, its high oxygen content could limit its stability and energy density. Additionally, reducing moisture content, as indicated by the broad O-H peak, could enhance bio-oil storage stability.



Figure 2: FTIR spectrum of bio-oil composition at 30-minute residence time.

3.4 Syngas characterisation from 30-minute pyrolysis test

Figure 3 illustrates the syngas composition from co-pyrolysis of FW and PW mixture at 30-minute residence time. Syngas mainly include CO2 (dominant), CO, H2, CH4​, and O2​, with approximately 3.5 MJ/m3 normalised net calorific value calculated excluding N2 using net heating value of each component (Engineering Toolbox, 2005). CO and CH4​ collectively contribute significantly to the syngas energy content, which is crucial for potential applications as a renewable energy source. The high CO2​ fraction potentially suggests complete thermal decomposition of biomass. The relatively low CH4​ content (4 %) may depend on the feedstock composition.

Figure 3 Syngas composition and normalised net calorific value at 30-minute residence time.

* 1. Conclusions

This study focuses on optimising biochar production from co-pyrolysis of fish and pruning waste (30% FW: 70% PW) for agricultural applications as a soil amendment and composting additive. Biochar produced at a 30-minute residence time displays nutrient-rich and stable properties, and lower trace elements, suggesting the synergy of both feedstocks by pyrolysis, that results in biochar having enhanced agronomic potential complying with regulatory standards. While bio-oil and syngas byproducts demonstrated promising results for energy recovery, their optimisation fell outside the scope of this work. Future research will explore the use of biochar in low-carbon composting systems and perform a techno-economic analysis to support the upscaling of sustainable biochar and biochar-compost composite production. This strategy aims to promote nutrient circularity within the fisheries sector through circular economy approaches.

Acknowledgements

The authors acknowledge the European Union’s Horizon 2020 research and innovation programme for its support to fund the “SEA2LAND” project under grant agreement 101000402. The authors also acknowledge CO.PE.MO and Ittica del Conero for providing the seafood residuals for characterisation.

References

Ahuja, E., Dauksas, J. F., Remme, R., Richardsen, A.-K., & Løes, A. (2020). Fish and fish waste-based fertilisers in organic farming – With status in Norway: A review. *Waste Management, 115*, 95–112. [https://doi.org/10.1016/j.wasman.2020.07.025](https://doi.org/10.1016/j.wasman.2020.07.025%22%20%5Ct%20%22_new)

Andreola, C., González-Camejo, J., Tambone, F., Eusebi, A. L., Adani, F., & Fatone, F. (2023). Techno-economic assessment of biorefinery scenarios based on mollusc and fish residuals. *Waste Management, 166*, 294–304. [https://doi.org/10.1016/j.wasman.2023.05.014](https://doi.org/10.1016/j.wasman.2023.05.014%22%20%5Ct%20%22_new)

Bridgwater, A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy, 38*(1), 68–94. [https://doi.org/10.1016/j.biombioe.2011.01.048](https://doi.org/10.1016/j.biombioe.2011.01.048%22%20%5Ct%20%22_new)

Bruno, S. F., Ekorong, F. J. A. A., Karkal, S. S., Cathrine, M. S. B., & Kudre, T. G. (2019). Green and innovative techniques for recovery of valuable compounds from seafood by-products and discards: A review. *Trends in Food Science and Technology, 85*, 10–22. [https://doi.org/10.1016/j.tifs.2018.12.004](https://doi.org/10.1016/j.tifs.2018.12.004%22%20%5Ct%20%22_new)

Chen, L., Al-Dhabi, N. A., Ai, W., Sun, S., Peng, Y., Gao, C., Zhuo, Y., Tang, W., Zhou, Y., & Sun, C. (2024). Impact of low-temperature pyrolysis on ash and physicochemical properties of straw biochar: Multivariate analysis and implications for agricultural and environmental use. *Industrial Crops and Products, 206*, 120431. [https://doi.org/10.1016/j.indcrop.2024.120431](https://doi.org/10.1016/j.indcrop.2024.120431%22%20%5Ct%20%22_new)

FAO. (2020). *The State of World Fisheries and Aquaculture 2020*. FAO. [https://doi.org/10.4060/ca9229en](https://doi.org/10.4060/ca9229en%22%20%5Ct%20%22_new)

FMFPA, EU (2019), European Parliament & Council. (2019). *Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 establishing a framework for the marketing of fertilising products and amending Regulation (EC) No 2003/2003*. Official Journal of the European Union. [https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32019R1009](https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32019R1009" \t "_new)

FSBP, EU (2025), European Biochar Foundation. (2025). *European Biochar Certificate (EBC) - a framework for sustainable biochar production*. European Biochar Foundation. Retrieved April 10, 2025, from [https://www.european-biochar.org/](https://www.european-biochar.org/%22%20%5Ct%20%22_new)

Ghaly, A. E., Ramakrishnan, V. V., Brooks, M. S., Budge, S. M., & Dave, D. (2013). Fish processing wastes as a potential source of proteins, amino acids and oils: A critical review. *Journal of Microbial & Biochemical Technology, 5*(3), 107–129. <https://doi.org/10.4172/1948-5948.1000110>

Goswami, S., Mishra, A., & Pandey, A. (2022). A comprehensive review on the production, properties, and applications of biochar: Environmental, economic, and technological perspectives. *Chemical Engineering Journal, 448*, 137677. [https://doi.org/10.1016/j.cej.2022.137677](https://doi.org/10.1016/j.cej.2022.137677%22%20%5Ct%20%22_new)

GCB, IBI (2020), International Biochar Initiative. (2020). *European Biochar Certificate (EBC) Guidelines for the Certification of Biochar*. [https://biochar-international.org/](https://biochar-international.org/%22%20%5Ct%20%22_new)

Italian Standards Organization (UNI). (2014). UNI EN ISO 14238:2014 – Solid biofuels — Determination of the water holding capacity of biofuels — Method by the gravimetric method. UNI, International Organisation for Standardisation.

Italian Standards Organization (UNI). (2015a). UNI EN ISO 16948:2015 – Solid biofuels — Determination of the content of volatile matter — Method by the gravimetric method. UNI, International Organisation for Standardisation.

Italian Standards Organization (UNI). (2015b). UNI EN 13650 – Solid biofuels — Terminology. UNI, International Organisation for Standardisation.

Italian Standards Organization (UNI). (2023). UNI EN ISO 18122:2023 – Solid biofuels — Determination of moisture content by drying in an oven. UNI, International Organisation for Standardisation.

Italian Standards Organization (UNI). (2024). UNI EN ISO 18134-2:2024 – Solid biofuels — Determination of the moisture content — Oven dry method — Part 2: Total moisture. UNI, International Organisation for Standardisation.

Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. A., & Sonoki, T. (2014). Physical and chemical characterisation of biochars derived from different agricultural residues. *Biogeosciences, 11*(23), 6613–6621. [https://doi.org/10.5194/bg-11-6613-2014](https://doi.org/10.5194/bg-11-6613-2014%22%20%5Ct%20%22_new)

Liu, T., Miao, P., Shi, Y., Tang, K. H. D., & Yap, P. S. (2022). Recent advances, current issues and future prospects of bioenergy production: A review. Science of the Total Environment, 806, 152181. <https://doi.org/10.1016/j.scitotenv.2021.152181>

López-Cano, I., Cayuela, M. L., Mondini, C., Takaya, C. A., Ross, A. B., & Sánchez-Monedero, M. A. (2018). Suitability of different agricultural and urban organic wastes as feedstocks for the production of biochar—Part 1: Physicochemical characterisation. *Agronomy, 8*(11), 290. <https://doi.org/10.3390/agronomy8110290>

Pahnila, S., Tella, S., & Koivumäki, T. (2023). Energy and environmental performance of biomass-based integrated gasification combined cycle (IGCC) plants: A case study. *Energies, 16*(19), 6936. [https://doi.org/10.3390/en16196936](https://doi.org/10.3390/en16196936%22%20%5Ct%20%22_new)

RRFF, IG (2010), Italian Government. (2010). Legislative Decree No. 75 of April 29, 2010: *Reorganization and revision of the regulations concerning fertilisers*, pursuant to Article 13 of Law No. 88 of July 7, 2009. Official Gazette, General Series No. 101. <https://www.ccpb.it/wp-content/uploads/documenti/DLgs_2010_04_29_-_75.pdf>

Rafiq, M. K., Bachmann, R. T., Rafiq, M. T., Shang, Z., Joseph, S., & Long, R. (2016). Influence of pyrolysis temperature on physico-chemical properties of corn stover (Zea mays L.) biochar and feasibility for carbon capture and energy balance. *PLOS ONE, 11*(6), e0156894. [https://doi.org/10.1371/journal.pone.0156894](https://doi.org/10.1371/journal.pone.0156894%22%20%5Ct%20%22_new)

[https://doi.org/10.1016/j.chemosphere.2014.06.009](https://doi.org/10.1016/j.chemosphere.2014.06.009%22%20%5Ct%20%22_new)

Santos, J. L., Centeno, M. A., & Odriozola, J. A. (2023). Biochar production from cellulose under reductant atmosphere: Influence of the total pyrolysis time. RSC Advances, 13(5), 4123–4135. <https://doi.org/10.1039/D3RA03093H>

Venegas, A., Rigol, A., & Vidal, M. (2014). Viability of organic wastes and biochars as amendments for the remediation of heavy metal-contaminated soils. *Chemosphere, 117*, 122–128. [https://doi.org/10.1016/j.chemosphere.2014.06.009](https://doi.org/10.1016/j.chemosphere.2014.06.009%22%20%5Ct%20%22_new)

Xiu, S., & Shahbazi, A. (2012). Bio-oil production and upgrading research: A review. *Renewable and Sustainable Energy Reviews, 16*(7), 4406–4414. [https://doi.org/10.1016/j.rser.2012.04.028](https://doi.org/10.1016/j.rser.2012.04.028%22%20%5Ct%20%22_new)