

Co-Pyrolysis of Fish with Pruning Waste for Biochar Production as an Amendment for Composite Composting in the Biorefinery Scenario

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Increasing global fish production demands sustainable waste management for the proper disposal of process leftovers. Fish waste stabilisation using pyrolysis has the potential to stabilise this putrescible waste, as well as production of biochar for sustainable agricultural applications. This study investigated the influence of residence times at a fixed temperature (400 °C) on the yield and quality of biochar by co-pyrolysis of fish and pruning waste. 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 low concentration of trace elements, complying with safety and quality regulations for biochar.

1. Introduction

The circular economy model promotes waste valorisation for recovering valuable bioproducts. Biorefineries are gaining attention for converting agricultural and organic waste into value-added products via biological and thermochemical processes (Goswami et al., 2022). Fishery waste, especially in coastal areas, offers significant potential. With global fish production expected to reach 204 million tonnes by 2030 (FAO, 2020), up to 70% of the original fish becomes waste (Ahuja et al., 2020). These putrescible residues, heads, viscera, scales, and skins pose environmental risks if not properly managed, but are rich in valuable compounds suitable for resource recovery (Bruno et al., 2019). Recent studies highlight the feasibility of decentralised biorefineries along Italy's Adriatic coast, utilising local fish and mollusc waste to produce high-value products such as biochar-compost composites, enzymatic hydrolysates, and calcium carbonate (Andreola et al., 2023).

Thermochemical techniques are well-suited for valorising organic waste, converting its carbon and nutrients into valuable outputs such as biochar, useful as a soil improver and fertiliser, alongside bio-oil and syngas, both energy sources. Compared to biochemical pathways, thermochemical processes are faster and more efficient in processing complex organic materials (Liu et al., 2022).

Among thermochemical approaches, slow pyrolysis is highly efficient. It operates at moderate temperatures (300–700 °C), low heating rates (0.1–1 °C/s), and long residence times (10–100 minutes) in oxygen-limited conditions. The quality and yield of products depend on feedstock and process parameters, with residence time playing a key role. For example, Centeno et al. (2023) showed that longer residence times improve biochar yield by allowing more complete decomposition and better carbon retention, boosting production efficiency (Pahnila et al., 2023). The study highlighted that longer residence times allow for more complete thermal decomposition and carbon retention, optimising biochar production efficiency.

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. Voluntary standards, like European Biochar Certificate (FSBP, EBC (2025) and those of the International Biochar Initiative (GCB, IBI (2020), provide quality

ensure quality and sustainability in agriculture. Based on the discussion mentioned above, this 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.

2. Materials and methods

This section covers the experimental setup for co-pyrolysis of fish waste (FW) and pruning waste (PW), including feedstock preparation, reactor setup, product characterisation, and product distribution.

2.1 Feedstock collection and pretreatment

FW was sourced from a local fish processor, and PW of free from debris and of uniform composition, came from olive tree pruning. Both were dried at 80 °C for 48 hours, consuming 0.7 kWh/kg of energy (based on a 160 kg dryer). FW was milled, and PW was ground. A 30:70 dry weight mix of FW to PW was chosen as optimal from lab trials, producing biochar meeting regulatory trace element limits.

2.2 Pilot-scale pyrolysis setup

Pyrolysis was performed in a pilot-scale auger reactor with a screw mechanism for feedstock transport and residence time control via screw speed. The reactor, made of three independently heated zones (up to 1100 °C), has a treatment capacity of 2.5 L/h and a 20 L semi-continuous hopper to allow semi-continuous operation. To ensure an inert environment, the sealed system was flushed and maintained with nitrogen (5 L/min). Experiments ran at 400 °C with residence times of 20–57 minutes, corresponding to energy use of 1.66 kWh, 2.49 kWh, 3.32 kWh, 4.15 kWh and 4.98 kWh respectively for each kilogram of feedstock treated. Volatiles exited via a 350 °C stack; condensable gases were recovered in a chilled spiral condenser, and non-condensable filtered through activated carbon and collected in 2 L gas bags for analysis.

2.3 Feedstock, biochar, bio-oil and syngas characterisation

Biochar from pyrolysis was characterised following FSBP, EBC (2025) and GCG, IBI (2020) standards. pH and electrical conductivity (EC) were measured using a 1:20 biochar-to-water solution, shaken for 1.5 h, with readings taken by Hanna HI-2002 (pH) and XS Cond 70+ (EC) meters (GCG, IBI, 2020). Heavy metals were analysed via aqua regia extraction and ICP-OES, following UNI (2015b). Elemental composition (C, H, N) of feedstocks and biochar was assessed by combustion and gas analysis (UNI, 2015a). Moisture and ash were determined through oven-drying (UNI, 2023; 2024), with fixed carbon calculated by difference. Water holding capacity followed the gravimetric method (UNI, 2014). Bio-oil was analysed by FTIR, while syngas was assessed using a VARIO luxx analyser with electrochemical and NDIR sensors for gases like O₂, CO, NO, H₂S, and SO₂. Syngas' net calorific value was calculated (Eq. 1) using heating values from Engineering Toolbox (2005).

$$NCV_{\text{syngas}} = \sum (y_i \times NCV_i) \quad (1)$$

Where: y_i = 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 yields were calculated as the ratio of each product mass to the initial feedstock mass. Syngas yield was determined by difference, subtracting the combined masses of biochar and bio-oil from the original feedstock to complete the mass balance.

3. Results and Discussion

This section presents analyses of feedstocks and biochar, focusing on quality parameters and macronutrient content. It also examines the composition of bio-oil and syngas to evaluate pyrolysis process products.

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 Pahnla 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. Whereas 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 the influence of fish waste decomposition,

potentially increasing the liquid and gas product proportion. The yields, mainly biochar, is promising, but further investigation is needed to validate condensation system efficiency for bio-oil collection, and consistent product distribution for assessing economic viability of scaling up the process.

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

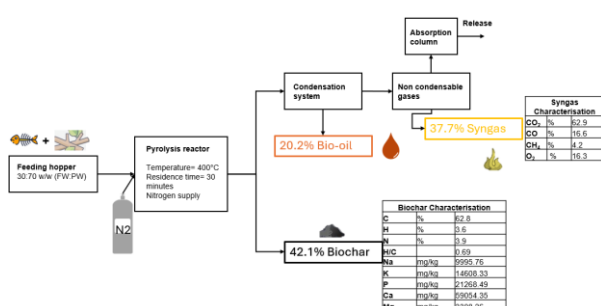


Figure 1: Pyrolysis products and their characterisation from a 30-minute test.

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

Errore. L'origine riferimento non è stata trovata. presents the physicochemical properties of FW, PW, and biochar (30-minute test). Produced biochar shows higher ash content (19.2%) compared to original feedstocks (FW: 11.97%; PW: 4.99%), consistent with prior studies that pyrolysis concentrates inorganic components through loss of volatile matter (López-Cano et al., 2018; Chen et al., 2024). Biochar contains 62.8% carbon, higher than both FW (53%) and PW (47.8%), indicating carbon enrichment during pyrolysis and aromatisation. Its H/C ratio of 0.69 meets the stability threshold ($H/C < 0.7$) set by FSBP, EBC (2025) and GCB, IBI (2020), confirming aromatic structure and thermal alteration. This value is consistent with lignocellulosic biochar (e.g., rice husk and straw: 0.67 at 400°C; Jindo et al., 2014). The alkaline pH (9.4) of biochar exceeds that of tree bark (8.9; Venegas et al., 2014) and corn stover (8.8; Rafiq et al., 2016) biochar at similar pyrolysis temperatures. Its electrical conductivity (EC; 486 mS/m) aligns with the range reported for woody biomass-derived biochar (370 mS/m; Venegas et al., 2014). Both pH and EC meet RRF, IG (2010) standard ($pH < 12$ and $EC < 1000$ mS/m), supporting biochar's suitability for agricultural use. Pot and field trials are advised to evaluate long-term effects 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 content	%	77.81±0.03	12.97±0.14	5.80
Dry matter	%	22.23±0.03	87.03±0.14	94.20
Ash content	%	11.97±0.51	4.99±0.03	19.20
Fixed carbon ¹	%	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/C ²		1.82	1.57	0.69
pH ³				9.41±0.08
EC ³	mS/m			486.00±33.94

¹Percentage of dry matter; ²EBC 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: 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

Errore. L'origine riferimento non è stata trovata. summarises the macro and trace element composition of biochar produced in a 30-minute test. Macro nutrient level in biochar is related to ash content (19.20%), which is influenced by feedstock composition. Biochar from co-pyrolysis possess a high nutrient composition compared to green waste biochar at 400°C, as reported by López-Cano et al. (2018). The elevated calcium concentration (59,054 mg/kg) likely results from fish waste, given the calcium-rich nature of fish bones (Ghaly et al., 2013). Trace element concentrations comply with regulatory limits set by RRFF, IG (2010), FMFPA, EU (2019), FSBP, EBC (2025), and GCB, IBI (2020). High nutrient content and low trace element levels suggest suitability for use as a soil amendment or compost additive, though pot and field trials are needed to confirm long-term effects on soil health and compost quality.

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

The FTIR spectrum of bio-oil produced from a 30-minute co-pyrolysis test reveals a complex composition of functional groups derived from both protein-rich and lignocellulosic feedstocks. The broad absorption band at 3000–3600 cm⁻¹, indicates O–H stretching, consistent with presence of hydroxyl-containing compounds such as alcohols, phenols, and water from cellulose, hemicellulose, and protein breakdown. Peaks near 2900 cm⁻¹, correspond to C–H stretching in aliphatic hydrocarbons, while a strong absorption at 1700 cm⁻¹ is attributed to carbonyl groups (ketones, aldehydes, and carboxylic acids), reflecting the oxygenated nature of the bio-oil. Additional peaks at 1500–1600 cm⁻¹ and 1000–1300 cm⁻¹ indicate aromatic C=C and C–O bonds, respectively. These findings align with previous studies [Bridgwater, 2012; Xiu et al., 2012], highlighting the synergistic chemical complexity and the need for further upgrading to enhance bio-oil quality.

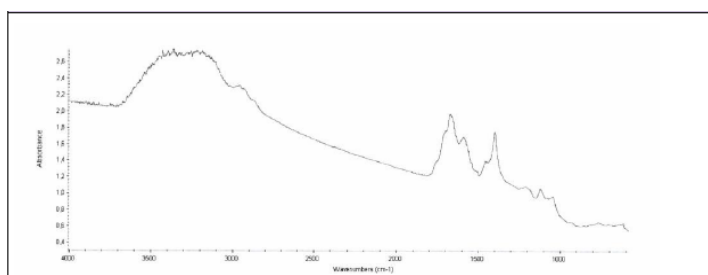


Figure 2: FTIR spectrum of bio-oil composition at 30-minute residence time.

3.4 Syngas characterisation from 30-minute pyrolysis test

Errore. L'origine riferimento non è stata trovata. illustrates the syngas composition from the co-pyrolysis of FW and PW mixture at a 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 the 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.

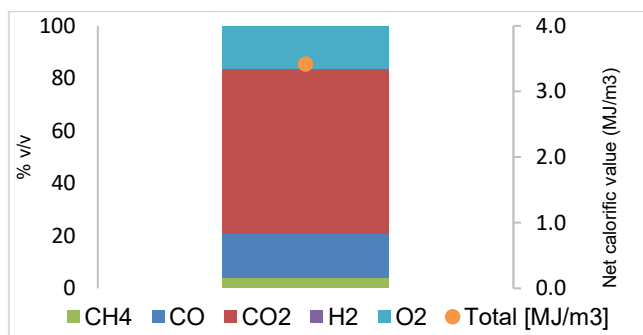


Figure 3: Syngas composition and normalised net calorific value at 30-minute residence time.

4. Conclusions

This study focuses on optimising biochar production from the 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 exhibits nutrient-rich and stable properties, and lower trace elements, suggesting the synergy of both feedstocks by pyrolysis, showing potential for agronomic use, as well as 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 techno-economic analysis to support the upscaling of sustainable biochar and biochar-compost composite production. This approach aims to enhance nutrient circularity within the fisheries sector by applying circular economy principles

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