



Optimised pyrolysis strategies for energy-dense bio-oil from *Chlorella* sp

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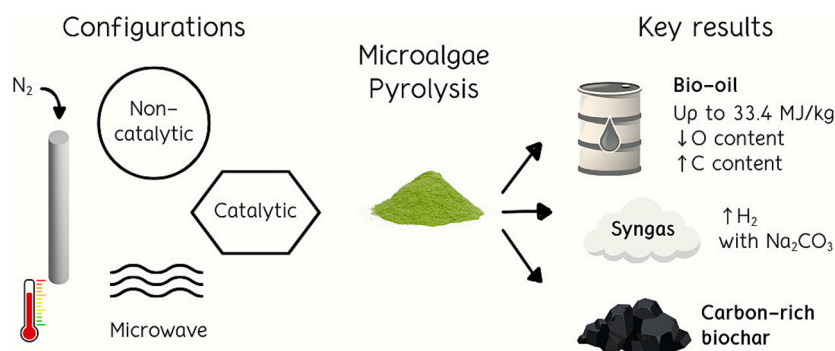
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HIGHLIGHTS

- Optimised pyrolysis of *Chlorella* sp. yielded 43 wt% bio-oil at 550 °C and 60 °C/min.
- Catalysts increased HHV of bio-oil up to 30.8 MJ/kg by enhancing deoxygenation.
- Microwave pyrolysis at 80 W achieved the highest HHV: 33.4 MJ/kg, 16.1 % oxygen.
- Na₂CO₃ produced gas products with highest H₂ content (24.7 vol%).
- Results outperform previous microalgae bio-oils without requiring lipid extraction.

GRAPHICAL ABSTRACT



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ABSTRACT

Microalgae are promising feedstocks for sustainable biofuels due to rapid growth, CO₂ fixation, and non-reliance on arable land. This study investigates the pyrolysis of *Chlorella* sp. under non-catalytic, catalytic, and microwave-assisted configurations to optimise bio-oil composition and energy density. Response surface methodology identified optimal conditions at 550 °C and 60 °C/min, yielding 43 wt% bio-oil. Catalytic pyrolysis with HZSM-5 and Na₂CO₃ improved deoxygenation and increased higher heating value (HHV) to 30.8 MJ/kg. Microwave-assisted pyrolysis at 80 W (~80 W/g for 1 g sample) produced the best bio-oil, with 68.3 % C, 16.1 % O, and HHV of 33.4 MJ/kg. Carbon-rich biochar (~80 wt% C) was also obtained, suitable for soil amendment or activation. Catalyst-dependent gas profiles were observed, with Na₂CO₃. Yielding 24.7 vol% H₂. These results highlight the potential of tuning pyrolysis configuration to upgrade algal biomass without post-treatment. The study supports the development of drop-in microalgal biofuels and reinforces their role in circular, carbon-neutral energy systems.

1. Introduction

The production of biofuels has become a critical strategy in the

global effort to reduce greenhouse gas emissions, mitigate climate change, and transition away from fossil fuels. However, conventional biofuel production, particularly from first-generation feedstocks such as

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food crops, has raised concerns about deforestation, biodiversity loss, and land-use competition, as large-scale agricultural expansion for bioenergy crops can threaten natural ecosystems and food security (IPCC, 2023). To overcome these challenges, next-generation biofuel production must adopt the principles of a circular bioeconomy, minimizing waste and maximizing the valorisation of residues and byproducts (De Schoenmakere et al., 2018). In this context, second-generation feedstocks (e.g., agricultural residues) and third-generation feedstocks (e.g., microalgae) (Ezhumalai et al., 2024) have emerged as promising alternatives. Microalgae, in particular, offer key advantages, including rapid growth, cultivation on non-arable land, and the use of CO₂ and wastewater during growth (Assis et al., 2019; Srimongkol et al., 2022), contributing to both carbon capture and environmental remediation. These characteristics position microalgae as a highly sustainable and versatile feedstock for future biofuel production. Furthermore, many species have the ability to accumulate lipids, which is particularly suitable for pyrolysis, as it promotes the formation of energy-rich liquid products. Among microalgal species, *Chlorella* sp. is especially promising due to its high growth rate, ease of cultivation, and flexible biochemical profile, which can be tailored to enhance lipid or protein yields for thermochemical conversion pathways (Rather and Bano, 2019).

Thermochemical processes, including gasification, liquefaction, and pyrolysis, are widely studied methods for converting biomass into biofuels (Wang and Wu, 2023). Among them, pyrolysis stands out for its versatility, producing three valuable products: bio-oil, biochar, and pyrolysis gas (Laird et al., 2009). Its relatively low operating costs and product flexibility make it a promising route for sustainable biofuel production. Pyrolysis can be configured in several ways, including: non-catalytic pyrolysis, which relies solely on thermal decomposition; catalytic pyrolysis, where catalysts may improve the quality and yield of bio-oil; and microwave-assisted pyrolysis (MAP), an emerging technique that enhances heating efficiency and uniformity through microwave irradiation (Kumar et al., 2017). Unlike conventional heating, MAP allows for volumetric heating of the feedstock, often reducing reaction times and improving energy efficiency, particularly at small scales. Recent studies have reported significant progress in MAP and co-pyrolysis, highlighting improved heating efficiency, product selectivity, and integration with circular bioeconomy frameworks (Bisht et al., 2026; Chen et al., 2025; Elsafi et al., 2025). Different pyrolysis modes influence product distribution: slow pyrolysis, characterized by low heating rates and longer residence times, favours biochar and bio-oil production; fast pyrolysis maximizes bio-oil yield through rapid heating; and flash pyrolysis, operating at even faster rates, prioritizes liquid production but often yields bio-oil of lower quality. Each approach offers specific advantages in terms of energy efficiency and biofuel yield, but achieving economic competitiveness at scale remains a major challenge. Catalysts play a critical role in catalytic pyrolysis by facilitating the breakdown of complex organic structures, improving liquid yield, and reducing the oxygen content in bio-oil – a key step toward enhancing its energy density and stability. However, tailoring catalytic strategies for specific feedstocks, such as microalgae, remains an ongoing area of research.

Despite the promise of microalgae for sustainable biofuel production, significant technological and economic barriers remain. A primary challenge lies in the high cultivation costs (Moshood et al., 2021), driven by the need for controlled environments, nutrient supply, and specialized infrastructure. These factors currently limit the scalability and economic feasibility of microalgae-based biofuels without substantial technological advancements. Although pyrolysis is a well-established technology for lignocellulosic biomass, its application to microalgae requires further optimization, particularly regarding reaction parameters such as temperature and heating rate, to maximize bio-oil yield and improve fuel quality (Ağbulut et al., 2023; Yang et al., 2019). Notably, microalgae-derived bio-oils often exhibit higher energy content compared to other biomasses, but optimizing pyrolysis conditions remains critical to fully leverage this advantage (Lee et al., 2020). The

unique biochemical composition of microalgae – rich in lipids, proteins, and carbohydrates – strongly influences pyrolysis behaviour, making species selection and pretreatment strategies vital for enhancing product yield and quality. Overcoming these technical challenges also demands supportive policies and financial incentives to close the economic gap with conventional fossil fuels, fostering the broader adoption of microalgae-derived biofuels (Khan et al., 2018).

This study addresses critical gaps in the thermochemical valorisation of microalgae by systematically comparing non-catalytic, catalytic, and MAP configurations using the same *Chlorella* sp. feedstock. Unlike previous studies, which often focus on a single configuration or compare results from different feedstocks and experimental setups, this work provides a direct, side-by-side comparison under uniform and controlled conditions, enabling robust assessment of product yields, energy performance, and bio-oil quality. Catalytic pyrolysis was hypothesized to improve deoxygenation and fuel properties, while MAP was expected to offer enhanced energy efficiency and product selectivity. Using Response Surface Methodology (RSM), the optimal process conditions for non-catalytic pyrolysis were identified, providing a reliable baseline for comparative analysis. Through detailed product characterization, this work not only optimizes bio-oil yield and energy density but also offers mechanistic insights into the influence of configuration and catalyst type on fuel upgrading, particularly for low-lipid algal biomass. The findings represent a novel contribution to the field by bridging process optimization with comparative pathway analysis and support the development of more efficient microalgae-based biofuel platforms. They also reinforce the need for supportive policy and investment to scale up these technologies and integrate them into circular, carbon-neutral energy systems.

2. Materials and methods

2.1. Microalgae biomass

Microalgae biomass powder from *Chlorella* sp. was donated by Jongerius Ecoduna® for use in the pyrolysis tests. The quantification of the primary metabolites of the microalgal biomass (proteins, lipids, and carbohydrates) as well as ash and moisture content were carried out based on methods previously reported (Ferreira et al., 2021). Total proteins were measured using the Bradford method and total carbohydrates via the phenol-sulfuric acid assay.

2.2. Pyrolysis reactions

2.2.1. Fixed-bed reactor configuration

Conventional pyrolysis experiments were conducted in a stainless steel fixed-bed reactor, with approximately 5 g of dried *Chlorella* sp. biomass powder loaded per run. Once the target temperature was reached, the reaction was held for 5 min. Microwave-assisted pyrolysis was carried out in a quartz tube reactor using 1 g of biomass per run, corresponding to a power density of 60 or 80 W/g, with a residence time of 2 min. Nitrogen gas was used as an inert carrier at a flow rate of 100 mL/min to ensure an oxygen-free environment. This flow rate was chosen to maintain a fully inert atmosphere and stable sweeping of the reactor system, consistent with typical values reported for laboratory-scale fixed-bed pyrolysis setups. The reactor inner volume was approximately 25 cm³, with a short transfer line connecting to a two-stage condensation consisting of an ice bath and a solvent trap for efficient vapor recovery.

Three different pyrolysis configurations were investigated to assess their impact on bio-oil yield and composition: non-catalytic pyrolysis, catalytic pyrolysis, and microwave-assisted pyrolysis. For conventional pyrolysis, catalytic experiments were conducted in two modes based on catalyst placement: *in situ* and *ex situ* (Fig. 1).

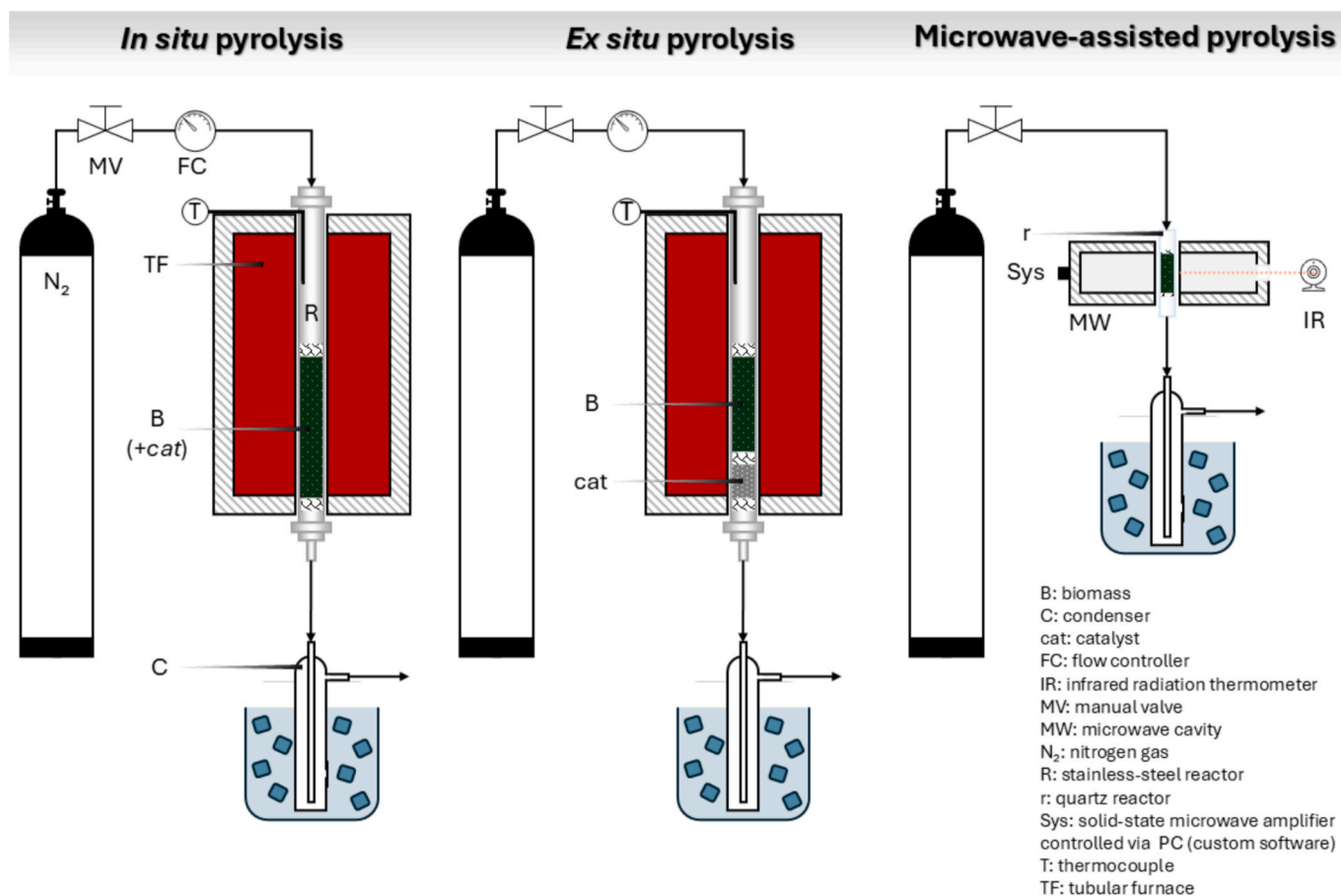


Fig. 1. Schematic representation of the pyrolysis reactor configurations used in this study: conventional pyrolysis (*in situ* and *ex situ* modes) and microwave-assisted pyrolysis.

- Conventional pyrolysis (CP): Two catalytic modes were tested. In *in situ* pyrolysis (abbreviated as *in*), the catalyst was physically mixed with the microalgal biomass, allowing direct interaction during thermal decomposition. In *ex situ* pyrolysis (abbreviated as *ex*), pyrolysis vapours passed through a separate downstream catalyst bed, facilitating catalyst reuse and minimizing char interference.
- Microwave-assisted pyrolysis (MAP): This configuration used volumetric microwave heating to enhance heating efficiency and product selectivity. Although no conventional chemical catalyst was used, the biomass was mixed with a microwave energy susceptor (biochar), making this an *in situ* setup by analogy. Experiments were conducted at 60 or 80 W for 2 min in a quartz tube reactor, with temperature monitored using infrared thermometer.

2.2.2. Non-catalytic and catalytic pyrolysis

Non-catalytic pyrolysis was compared to catalytic pyrolysis using three commercially available catalysts: zeolite ammonium ZSM-5 (Si/Al molar ratio of 23; Zeolyst), sodium carbonate (anhydrous, $\geq 99.5\%$ ACS; VWR Chemicals BDH®), and activated carbon DARCO (100 mesh; Sigma-Aldrich). Catalytic tests were performed in both *in situ* and *ex situ* configurations, in a 1:4 mass ratio related to the biomass.

The ZSM-5 zeolite was calcined before use following a previously described procedure to obtain the HZSM-5 form (Shirazi et al., 2020), while sodium carbonate (Babich et al., 2011; Ferreira and Soares Dias, 2020) and activated carbon (Aswie et al., 2021) were used directly without pretreatment, based on prior studies demonstrating their catalytic activity in pyrolysis processes.

Fresh catalyst was used in all experiments to avoid variability due to deactivation.

2.2.3. Microwave-assisted pyrolysis (MAP)

In the MAP configuration, biochar produced during non-catalytic pyrolysis was employed as a catalyst and energy susceptor (Fan et al., 2022), enhancing microwave absorption efficiency and overall heating performance. Biochar was also employed in a 1:4 mass ratio. Reactor temperature during microwave-assisted pyrolysis was estimated using an infrared thermometer aimed at the tube's outer surface. While this provides only an approximate internal temperature, it is a common limitation in microwave systems, where heating occurs volumetrically through dipole rotation and ionic conduction rather than via external heat transfer, making uniform temperature control inherently more challenging.

2.3. Product yield quantification

The yields of gaseous, liquid, and solid products were determined gravimetrically. The mass of the liquid and solid fractions was measured directly after each pyrolysis experiment, while the yield of the gaseous phase, including non-condensable gases and volatile organic compounds (VOCs), was estimated by mass balance, as shown below:

$$\text{Liquid yield (\%)} = \frac{\text{Liquid weight}}{\text{Feed weight}} \times 100 \quad (1)$$

$$\text{Solid yield (\%)} = \frac{\text{Solid weight}}{\text{Feed weight}} \times 100 \quad (2)$$

$$\text{Gas yield (\%)} = 100 - (\text{Liquid yield} + \text{Solid yield}) \quad (3)$$

2.4. Statistical analysis

2.4.1. Conventional pyrolysis

A Response Surface Methodology (RSM) framework based on a Central Composite Design (CCD) was employed to systematically assess the influence of temperature and heating rate on bio-oil yield. RSM enables evaluation of variable interactions and optimization of response outcomes with a reduced number of experiments, while CCD provides robust estimation of both linear and quadratic effects, making it particularly suitable for nonlinear thermochemical systems such as pyrolysis. Each factor was studied at three levels: low (−1), medium (0), and high (+1), with axial points introduced at $-\alpha$ and $+\alpha$ to better explore the design space. The temperature range investigated was 400–600 °C, and the heating rate varied from 20–80 °C/min. The centre point was included to assess experimental variability.

A total of 11 experimental runs were performed, including factorial, axial, and centre points, as detailed in Table S1.

Bio-oil yield was calculated as the mass percentage of bio-oil relative to the initial biomass input and modelled according to the following second-order polynomial equation:

$$Yield = \beta_0 + \beta_1 \cdot T + \beta_2 \cdot HR + \beta_3 \cdot T^2 + \beta_4 \cdot HR^2 + \beta_5 \cdot T \cdot HR \quad (4)$$

where T and HR are the coded values for temperature and heating rate, respectively; β_0 is the intercept; β_1 , β_2 are linear coefficients; β_3 , β_4 are quadratic coefficients; and β_5 is the interaction coefficient.

Analysis of variance (ANOVA) was conducted to assess the statistical significance of the model and the interaction effects between factors. Model adequacy was evaluated based on the coefficient of determination (R^2) and the lack-of-fit test. Response surface plots and contour maps were generated to visualize the effect of process parameters on bio-oil yield. Optimal conditions were determined by solving the regression model, followed by experimental validation.

2.5. Solid characterisation

2.5.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a TGA 4000 instrument (Perkin Elmer) under a nitrogen (N_2) flow of 20 mL/min. Samples were heated from 30 °C to 900 °C at a constant ramp rate of 10 °C/min.

2.5.2. Surface area and porosity measurements

Surface area and porosity measurements were conducted using a Quantachrome ChemBET chemisorption analyser equipped with a thermal conductivity detector (TCD). Approximately 200 mg of each sample was degassed at 150 °C for 3 h under vacuum prior to analysis. Surface area was determined based on nitrogen (N_2) adsorption, assuming BET theory and the formation of a monolayer of nitrogen molecules on the sample surface.

2.5.3. X-ray diffraction (XRD)

X-ray diffraction patterns were recorded using a PANalytical X'pert Pro diffractometer with Ni-filtered $CuK\alpha$ radiation (operated at 40 kV and 40 mA). The diffraction data were collected over a 2θ range of 10°–80°, with a step size of 0.0168°. Crystalline phases were identified by comparison with the International Centre for Diffraction Data (ICDD) database.

2.5.4. Scanning electron microscopy and EDX (SEM/EDX)

Scanning electron microscopy (SEM) was performed using a Tescan MAIA3 Triglav FEG-SEM. Samples were mounted on aluminium stubs using conductive carbon tape and sputter-coated with a thin layer of gold to enhance conductivity and minimize charging effects. SEM imaging was conducted at an accelerating voltage of 10 kV to balance resolution and sample integrity. Energy dispersive X-ray spectroscopy

(EDX) was used to determine the elemental composition of the samples.

2.6. Bio-oil characterisation

2.6.1. Water content and quantification

Following each pyrolysis experiment, bio-oil was recovered by washing the reactor with acetone. Water content in the liquid products was determined using the Dean-Stark method, following ASTM D95-13 (2018) standard procedures (ASTM D95-13, 2018).

2.6.2. Elemental composition (CHNS analysis)

Elemental analysis (C, H, N, S) of solid and viscous liquid samples was performed using a ThermoFlash 2000 elemental analyser (Thermo Fisher Scientific). Samples were accurately weighed using a Mettler Toledo high-precision balance and sealed in tin capsules. Combustion occurred in a helium stream with excess oxygen added at the start of the run. Combustion gases (CO_2 , H_2O , NO_x) were passed over catalytic beds to ensure complete oxidation and reduction, and were subsequently separated via gas chromatography and quantified using a thermal conductivity detector (TCD). Oxygen content was estimated by mass difference according to Eq. (5). The measurement uncertainty for CHNS was within ± 0.3 wt%.

$$\%O = 100 - \%C - \%H - \%N - \%S - Ash \quad (5)$$

2.6.3. Chemical composition (GC-MS analysis)

Gas chromatography–mass spectrometry (GC-MS) analysis was carried out using a Thermo Scientific Exactive GC system equipped with an electron ionization (EI) source. Chromatographic separation was performed over a retention time (RT) range of 0–40 min. Mass spectra were acquired in full-scan mode over an m/z range of 50–600, using helium as the carrier gas. Identification of major volatile compounds was based on spectral matching against standard mass spectral libraries.

2.7. Bio-gas characterisation

The composition of the pyrolysis gas – including hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and light hydrocarbons (C_1 – C_4) – was analysed using an Agilent 7890B gas chromatograph equipped with a split/splitless inlet and both flame ionization (FID) and thermal conductivity (TCD) detectors. Light hydrocarbons were quantified using the FID, while permanent gases were detected via the TCD. Hydrogen was employed as both the carrier and reference gas. Gas samples were introduced using a manual gas sampling valve, and separation was achieved on packed columns under a programmed oven temperature ramp from 50 °C to 150 °C over 24 min. No methaniser was used; CO and CO_2 were quantified directly by the TCD.

3. Results and discussion

3.1. Solid characterisation

Thermogravimetric analysis (TGA) was performed to investigate the thermal behaviour of *Chlorella* sp. biomass and the three catalysts: HZSM-5, Na_2CO_3 , and activated carbon (AC), as shown in Fig. S1 in the Supplementary Material. The TGA (black line) and derivative DTG (orange line) profiles indicate that the biomass underwent significant mass loss between 200–400 °C, corresponding to the decomposition of organic macromolecules such as proteins, carbohydrates, and lipids. A sharp DTG peak was observed in this region, confirming the main devolatilization event. Beyond 400 °C, the mass loss plateaued, indicating the end of primary degradation and the formation of biochar.

In contrast, the catalysts showed high thermal stability, with minimal mass changes throughout the heating range. Both HZSM-5 and Na_2CO_3 maintained nearly constant mass up to 900 °C, with only ~1–2 % loss below 150 °C due to the desorption of physically adsorbed water,

as evidenced by minor DTG activity. Activated carbon exhibited a more gradual and extended mass loss, beginning near 150 °C and continuing throughout the heating cycle. This behaviour likely reflects the progressive thermal degradation of less stable carbon domains or residual volatiles. These findings suggest that while HZSM-5 and Na₂CO₃ are thermally robust under pyrolysis conditions, AC may experience partial degradation, potentially affecting its catalytic performance and recyclability.

To complement the thermal analysis, X-ray diffraction (XRD) patterns were collected to evaluate the crystallinity of the catalysts (Fig. S2). HZSM-5 exhibited sharp, intense peaks characteristic of the crystalline zeolite framework, which is associated with its high surface area and catalytic efficiency. Sodium carbonate (Na₂CO₃) also showed crystalline peaks, although less intense, suggesting either lower crystallinity or smaller domain sizes. In contrast, AC displayed a broad, diffuse pattern, typical of amorphous materials lacking long-range order.

Surface area and porosity measurements revealed notable differences among the materials (Table S2). HZSM-5 exhibited a specific surface area of 208 m²/g with an average pore radius of 7.4 Å, consistent with its microporous nature and catalytic applications such as fluid catalytic cracking (FCC). Sodium carbonate showed a much lower surface area of 1.2 m²/g, typical of non-porous salts, although its basicity may still render it catalytically active. Activated carbon demonstrated a very high surface area of 1,222 m²/g with a mesoporous structure (average pore radius of 15.7 Å), making it highly effective for both adsorption and catalytic applications, provided pore volume does not limit mass transport.

Elemental analysis (Table S3) showed that the *Chlorella* sp. biomass had a high carbon content (48.9 wt%) and moderate levels of hydrogen (7.0 wt%) and nitrogen (7.2 wt%), reflecting its biochemical composition mostly consistent of proteins, lipids, and carbohydrates. Biochemical analysis revealed a protein content of 55.3 ± 3.7 wt% and a lipid content of 26.1 ± 2.9 wt%, highlighting the nitrogen-rich and energy-dense nature of the biomass.

The high protein content explains the elevated nitrogen levels observed during elemental analysis, which can influence the chemical composition of the resulting bio-oil by promoting the formation of nitrogenous compounds – an important consideration when evaluating biofuel quality. Meanwhile, the substantial lipid fraction contributes to a higher energy content, as reflected by the estimated higher heating value (HHV) of 21.8 MJ/kg, calculated using the Channiwala and Parikh correlation (Channiwala and Parikh, 2002). This value confirms the potential of *Chlorella* sp. as a promising feedstock for biofuel production and exceeds that of typical lignocellulosic biomass such as wood (~18 MJ/kg) (Demirbas, 2002).

3.2. Optimisation of non-catalytic pyrolysis conditions

A CCD was employed to study the influence of temperature (T) and heating rate (HR) on the bio-oil yield from non-catalytic pyrolysis of *Chlorella* sp. The effects of linear, quadratic, and interaction terms were analysed using ANOVA (Table S4), while a Pareto chart and surface response plots were used to visualize the significance and trends of these factors.

The Pareto chart (Fig. S3) confirms that the linear terms of temperature and heating rate are the most significant factors influencing bio-oil yield. The standardized effects for temperature (linear) and heating rate (linear) were 6.97 and 6.16, respectively; both exceeding the critical significance threshold ($p = 0.05$). These findings align with the ANOVA results and are supported by the p -values in the model coefficients table (0.020 for T and 0.025 for HR). The quadratic term for temperature also showed a moderate effect (-4.01 ; $p = 0.057$), while the heating rate quadratic term had a smaller impact (-2.93 ; $p = 0.099$). The interaction between temperature and heating rate ($T \times HR$) was statistically insignificant ($p = 0.877$), confirming its negligible contribution to the model.

The bio-oil yield was modelled using a second-order polynomial function of temperature and heating rate, following Eq. (4). The coefficients (β_i) determined from regression analysis were $\text{Yield} = 26.53 + 3.22T + 2.85HR - 2.21T^2 - 1.61HR^2 - 0.12T \cdot HR$. The intercept and linear terms confirm that increasing both temperature and heating rate tends to enhance bio-oil yield up to a certain point. However, the negative quadratic terms for T^2 and HR^2 indicate the presence of an optimum region, beyond which further increases in these variables reduce the yield, likely due to secondary cracking reactions. The small, negative interaction coefficient (-0.12) confirms that temperature and heating rate act largely independently in this system.

The predictive capability of the model was evaluated by comparing the predicted and observed values of bio-oil yield (Fig. S4). The data show good agreement, with most points clustering near the parity line, indicating that the regression model accurately represents the experimental data within the tested design space. The coefficient of determination ($R^2 = 0.78$) suggests that 78 % of the variability in bio-oil yield could be explained by the model. Although the adjusted R^2 value (0.56) was lower, reflecting the limited number of experimental runs and the inclusion of higher-order terms, it still supports the use of the model for identifying optimal pyrolysis conditions for *Chlorella* sp. This indicates that, while useful for guiding optimisation, the model's predictive power is moderate and may benefit from additional variables or interaction terms not captured in the current design. This further validates the response surface methodology as a reliable tool for fast pyrolysis optimisation.

As shown in the contour and surface plots (Fig. 2), bio-oil yield increased with both temperature and heating rate up to a maximum, beyond which secondary cracking of volatiles likely reduced liquid production. The highest yields were predicted near 550 °C and 60–70 °C/min, aligning with the expected thermal behaviour of fast pyrolysis. Although heating rate is generally associated with higher bio-oil production, extremely rapid rates may offer diminishing returns or even reduce yield if residence time becomes insufficient for complete volatilization at lower temperatures (Morgan et al., 2015; Wright et al., 2010). The fitted response surface model demonstrated good predictive accuracy, with a lack-of-fit p -value of 0.099 indicating acceptable performance. Based on the model, the optimal conditions were identified at approximately 550 °C and 60 °C/min. A confirmatory experiment under these conditions yielded ~43 wt% of total liquid product, with 38 wt% of that corresponding to water as quantified by the Dean-Stark method, validating the prediction for the organic phase yield. These parameters were subsequently adopted as the operational baseline for further pyrolysis experiments. With this baseline established for maximizing liquid yield, the next stage of the study examined the impact of catalyst selection and microwave-assisted heating on product distribution and fuel quality.

3.3. Effect of catalysts and MAP on product distribution

3.3.1. Product yields comparison

The yields of total bio-oil, biochar, and pyrolysis gas obtained from the pyrolysis of *Chlorella* sp. biomass with different catalysts (HZSM-5, Na₂CO₃, and AC) in both *in situ* and *ex situ* configurations are presented in Fig. 3. A non-catalytic (NC) pyrolysis experiment was also performed for comparison. In this context, “total bio-oil” refers to the full liquid fraction recovered after condensation, without any subsequent phase separation into aqueous and organic layers.

Among the tested catalytic configurations, inNa₂CO₃ achieved a high liquid yield (40.9 wt%) with a moderate gas fraction (26.1 wt%) and char at 33.0 wt%. ExNa₂CO₃ produced a lower liquid yield (33.6 wt%) and slightly more gas (29.1 wt%), likely due to more extensive cracking as vapours interact with the catalyst in the heated downstream zone. InHZSM-5 showed stronger cracking activity, leading to a lower oil yield (35.2 wt%) and higher gas formation (39.0 wt%), while char was reduced to 25.8 wt%. The exHZSM-5 configuration slightly increased

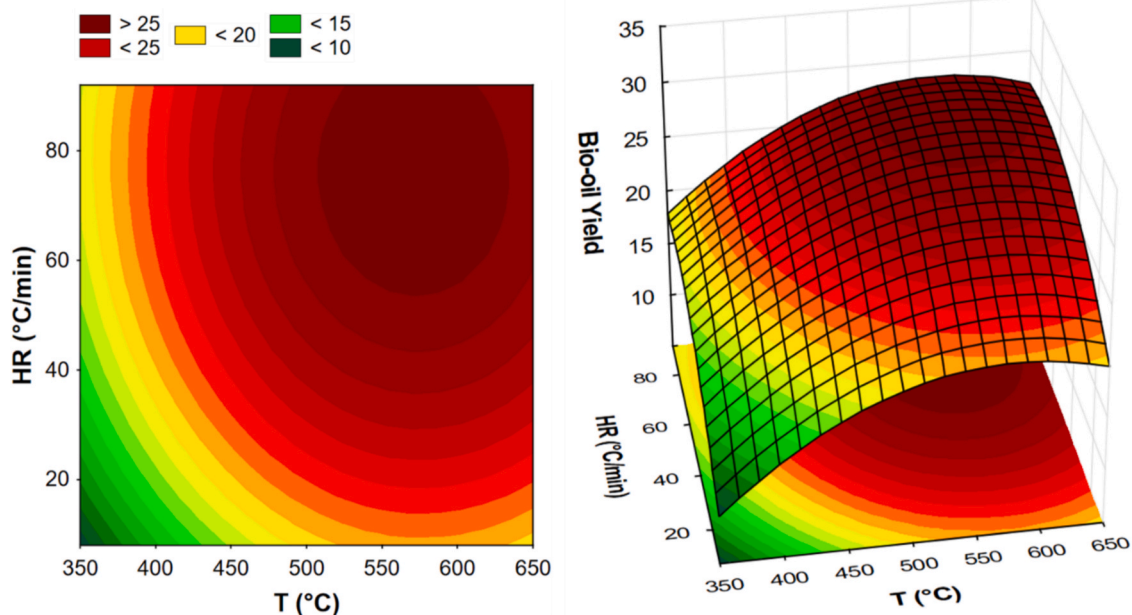


Fig. 2. (Left) Contour plot and (Right) 3D surface response plot showing the effect of temperature and heating rate on bio-oil yield from non-catalytic pyrolysis of *Chlorella* sp. Colour scale indicates predicted bio-oil yield (wt%).

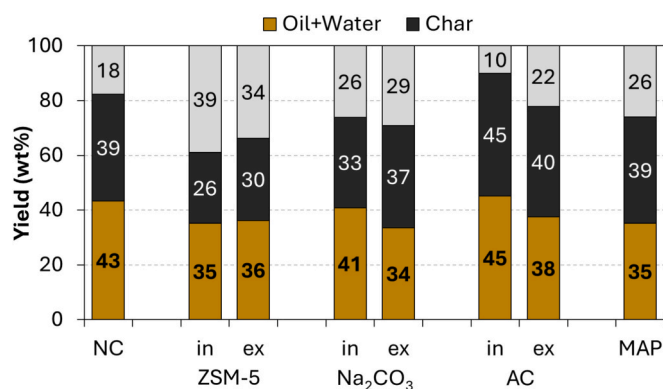


Fig. 3. Product yields (total bio-oil, biochar, pyrolysis gas) from pyrolysis of *Chlorella* sp. biomass using different catalytic and non-catalytic configurations. Yields typically showed a standard deviation of ± 2.7 wt%, indicating low experimental variability.

gas formation further (42.0 wt%) but produced more liquid products (36.2 wt%) than its *in situ* counterpart. These results reflect how the positioning of the catalyst and its interaction with vapours during peak thermal exposure critically affect product distributions.

Activated carbon performed particularly well in the *in situ* setup, achieving the highest liquid yield (45.2 wt%) and the lowest gas fraction (10.0 wt%), indicating milder cracking activity. This highlights its potential as a sustainable catalyst alternative. Notably, if AC becomes more catalytically effective, it could be produced from the microalgal-derived biochar itself (Han et al., 2019), improving the overall circularity and economics of the process.

The MAP configuration produced a moderate liquid yield (35.3 wt%), comparable to that of *in situ* HZSM-5, with a balanced product distribution and a gas fraction of 26.0 wt%. At the applied power density of approximately 80 W/g (based on 1 g of biomass and 80 W input), MAP enabled rapid energy transfer and effective volatilization while avoiding excessive secondary cracking. This supports MAP's potential as a less thermally severe yet efficient pyrolysis route. The volumetric and selective heating provided by microwaves can reduce local overheating

and secondary cracking reactions, preserving more condensable volatiles and enhancing overall bio-oil quality (Beneroso et al., 2017).

3.3.2. Bio-oil composition and energy content

To further assess the influence of pyrolysis conditions and catalysts on bio-oil quality, elemental analysis was performed for each bio-oil sample after water removal to isolate the organic-rich phase (Table 1). For the following sections, the term “bio-oil” refers specifically to the organic phase, excluding the aqueous fraction, unless otherwise stated. The composition (%C, %H, %N, %S, %O) and estimated HHVs were then compared with literature values from *Chlorella vulgaris* pyrolyzed at 500 °C (Gong et al., 2014), lignocellulosic biomass (wood), and fossil-derived oils (Czernik and Bridgwater, 2004). As shown in Table 1, the carbon content and HHV obtained here under both thermal and microwave-assisted catalytic conditions exceed or match those reported in comparable studies, despite using low-lipid algal biomass.

Non-catalytic pyrolysis in this study produced bio-oil with 54.4 % carbon (C), 9.0 % hydrogen (H), 7.9 % nitrogen (N), 0.7 % sulfur (S), and 28.0 % oxygen (O), and an estimated HHV of 26.7 MJ/kg. These values are similar to those reported by Gong et al. (2014) for *Chlorella vulgaris* bio-oil obtained at 500 °C (51.4 % C, 33.3 % O), with slightly higher carbon and lower oxygen in the present work. On the other hand, enhanced deoxygenation and hydrocarbon yield can be found in the literature, as the values reported by Ly et al. (2016) for *Saccharina japonica*, whose bio-oils reached 72.31 % C and 15.24 % O at 600 °C. Such variations may be attributed to differences in algal strain, cultivation conditions, and biochemical composition, particularly lipid and carbohydrate content, which strongly influence bio-oil quality and energy density.

Catalytic pyrolysis, especially with HZSM-5 and Na₂CO₃, significantly enhanced bio-oil quality. The carbon content increased to 60.4–62.8 wt%, while oxygen content dropped to as low as 20.5 wt%, resulting in HHVs of 29.5 and 30.8 MJ/kg, respectively. Compared to the non-catalytic oil (26.7 MJ/kg), these catalysts improved energy density by approximately 3–4 MJ/kg, primarily through enhanced deoxygenation. Microwave pyrolysis at 80 W further advanced performance, achieving the highest HHV of 33.4 MJ/kg alongside an oxygen content of just 16.1 wt%, a level approaching that of upgraded bio-oils, which typically contain less than 5 wt% oxygen after catalytic

Table 1

Elemental composition and higher heating value (HHV) of bio-oils from different catalysts and methods compared to literature data.

	Bio-oil from <i>Chlorella</i> sp. [this study]						<i>C. vulgaris</i> bio-oil (Gong et al., 2014)	Wood bio-oil (Czernik and Bridgwater, 2004)	Fossil oil
	NC	HZSM-5	Na ₂ CO ₃	AC	MAP60W	MAP80W			
% C	54.4 ± 1.4	60.4 ± 1.7	62.8 ± 1.5	54.5 ± 1.2	65.0 ± 1.1	68.3 ± 1.3	51.4	56.0	85.0
% H	9.0 ± 0.1	9.2 ± 0.2	9.4 ± 0.3	8.9 ± 0.1	9.5 ± 0.2	9.6 ± 0.1	7.8	5.8	11.0
% N	7.9 ± 0.3	8.1 ± 0.1	7.3 ± 0.1	8.0 ± 0.3	3.7 ± 0.2	6.0 ± 0.1	7.1	0.1	0.3
% S	0.7 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	0.3 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.4	0.0	0.0
% O	28.0 ± 1.2	22.1 ± 1.0	20.5 ± 1.0	28.3 ± 1.4	21.8 ± 1.1	16.1 ± 1.3	33.3	37.5	1.0
HHV, MJ/kg	26.7 ± 1.5	29.6 ± 1.5	30.8 ± 0.9	26.5 ± 1.3	31.6 ± 1.4	33.4 ± 0.9	23.6	22.4	42.5

hydrotreatment (Mortensen et al., 2011). Consequently, it may reduce the need for intensive downstream upgrading. In contrast, although AC improved overall yield, it had a less pronounced effect on elemental composition, with C and O contents remaining close to those observed in the non-catalytic case. This highlights a key trade-off: while AC may enhance liquid production, it does not significantly improve oil quality. For practical applications, this suggests that AC may be more suitable when the volume of liquid product is prioritised over fuel-grade properties. In contrast, catalysts like Na₂CO₃, which moderately reduce yield but enhance deoxygenation and HHV, may be more viable for producing drop-in fuels.

It is worth noting that in the study by Adamczyk and Sajdak (2018), bio-oils from *Nannochloropsis gaditana* initially contained 24.6–34.8 % carbon, but after purification of the organic phase using dichloromethane (DCM), the carbon content increased significantly to 58.9–64.1 %, with HHVs up to ~ 32 MJ/kg. This improvement is attributed to the removal of the aqueous phase and polar oxygenated compounds (e.g., acids, alcohols, and small ketones), which are poorly soluble in DCM. These oxygenates contribute to lower carbon content and reduced energy density. By isolating the energy-rich, non-polar fraction of the bio-oil, the DCM extraction concentrates hydrocarbon-like components, thereby enhancing both carbon content and overall fuel quality. Similarly, Aboulkas et al. (2017) reported 51.1 % C in bio-oil from algal waste pyrolyzed at 500 °C, and Gong et al. (2014) found carbon contents ranging from 30.6 to 56.3 % in bio-oils from different algal sources, depending on temperature.

These comparisons highlight two key insights: first, carbon content in algal bio-oils tends to increase with pyrolysis temperature, as seen across all referenced studies; second, post-pyrolysis purification, particularly solvent-based separation of the organic phase, can substantially enrich the hydrocarbon content of bio-oils. This step goes beyond simply removing water; it also extracts polar oxygenated compounds, thereby concentrating the energy-dense, non-polar fraction of the bio-oil.

Furthermore, catalytic treatments did not significantly reduce the nitrogen content of the bio-oil (remaining around 7–8 wt%), since many nitrogenous compounds formed during protein pyrolysis are transferred to the oil phase. In contrast, the microwave approach, particularly at 60 W, resulted in a lower N content (3.7 wt%), possibly by favoring nitrogen retention in the char or release into the gas phase. This observation suggests that microwave heating might help mitigate nitrogen incorporation into the bio-oil to some extent, although the 80 W sample still contained 6 wt% N. Similar synergistic effects have been recently reported during microwave-assisted co-pyrolysis of biomass and microalgae, where improved heat transfer and uniform energy distribution enhanced product quality and process efficiency (Bisht et al., 2026).

However, to meet conventional fuel specifications, nitrogen content typically must be below 0.1 wt%, especially for drop-in applications such as diesel (ASTM D975, 2021) or jet fuel (ASTM D1655-22a, 2022), where higher nitrogen levels can lead to NO_x emissions and catalyst fouling during upgrading (Bridgwater, 2012). Therefore, further strategies would be necessary to reduce nitrogen content, such as catalytic

deamination, hydrotreatment, or phase separation post-treatment. These upgrading techniques have shown promise in removing nitrogenous functional groups while retaining the carbon-rich structure of the oil. Achieving this while preserving high carbon and hydrogen levels is critical for producing drop-in biofuels with both high energy quality and improved environmental performance.

When compared to lignocellulosic feedstocks like wood, *Chlorella*-derived bio-oils consistently showed higher nitrogen content, ranging from 3.7 % to 8.1 %, depending on the pyrolysis conditions. As a result, the pyrolysis vapours carry a greater proportion of nitrogen-containing species (e.g., amines, pyrroles, pyridines). The elevated nitrogen levels come from the inherently high protein content of microalgae, which contributes to the formation of nitrogenous compounds during pyrolysis, a known drawback for combustion quality due to the risk of NO_x emissions and thermal instability. This affects not only the heating value but also presents serious barriers for downstream upgrading and engine performance.

To better understand the compositional changes underlying these elemental improvements, we analyzed the bio-oil by GC–MS to identify major compounds and functional groups.

3.3.3. GC–MS analysis of bio-oil compounds

The chemical composition of bio-oil derived from *Chlorella* sp. biomass differs markedly from that of lignocellulosic-derived pyrolysis oils. Despite the absence of lignin, aromatic hydrocarbons such as benzene, toluene, and ethylbenzene were detected (Fig. 4), likely originating from the thermal degradation of proteins and lipids. Phenolic compounds were less prominent, consistent with the lack of lignin in microalgae. Instead, naphthalene derivatives and alkylbenzenes, primarily derived from lipid breakdown, were among the most abundant species. These light aromatics are desirable intermediates for high-octane fuels following catalytic upgrading.

Catalytic configurations, particularly with HZSM-5, produced bio-oils enriched in aromatic hydrocarbons and depleted in heavier oxygenates compared to non-catalytic pyrolysis, indicating effective deoxygenation. The MAP-derived oil showed a comparable composition dominated by aromatics, with lower phenolic content relative to conventional pyrolysis oils from lignocellulosic feedstocks. This reflects the selective heating and reduced secondary cracking typical of microwave processes.

In addition to aromatics, oxygenated compounds such as acids and furans were detected. Acetic acid, a major product of carbohydrate degradation, poses upgrading challenges due to its corrosivity but can be converted into hydrocarbons through hydrodeoxygenation. Furans, particularly furfural (2-furaldehyde), are also valuable precursors for biofuel synthesis, offering routes to more stable, energy-dense molecules.

The bio-oil also contained long-chain hydrocarbons (e.g., neophytadiene) and fatty alcohols, predominantly originating from the microalgal lipid fraction. These molecules are relevant to the production of diesel and aviation fuels due to their favorable molecular structure and high energy content. Thus, *Chlorella* sp.-derived bio-oil presents a diverse array of valuable hydrocarbons and upgrading intermediates.

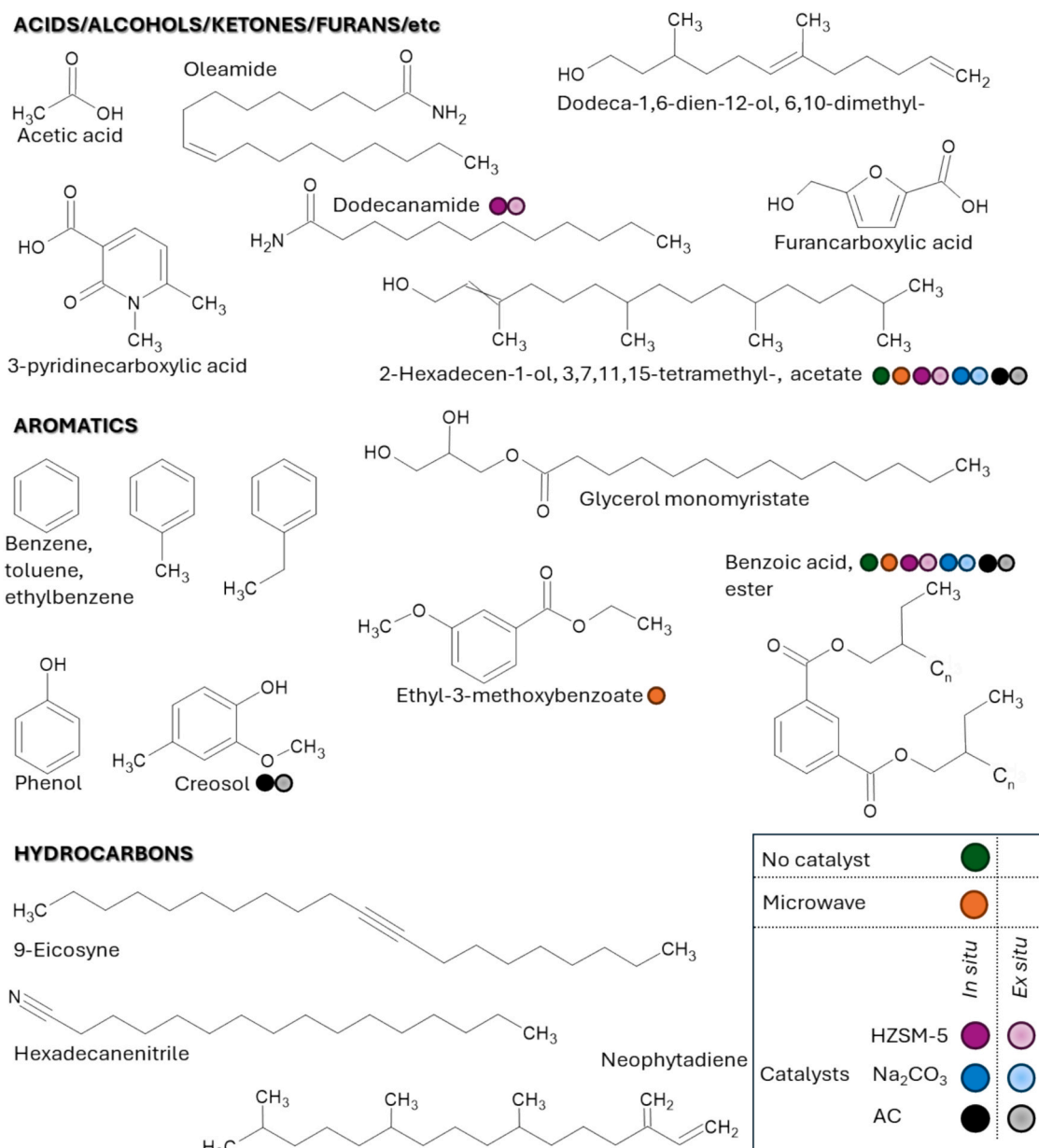


Fig. 4. GC-MS identification of the most abundant molecules in bio-oil from microalgae: reaction specific patterns [Each colour corresponds to one pyrolysis configuration. Molecules with several colours were among the top two most abundant species in multiple reactions. Compounds without coloured dots were present in more than one configuration but not all, and are shown for reference.] [Colour code: non-catalytic (green), MAP (orange), catalytic acidic (pink), catalytic basic (blue), and catalytic neutral (black). *Ex situ* configurations are represented by the same colour as their *in situ* counterpart but in a lighter shade.].

However, the relatively high oxygen content, particularly from acids and polar oxygenates, necessitates further deoxygenation to meet fuel quality standards. Upgrading steps are essential to reduce oxygen levels below 2 wt% (de Miguel Mercader et al., 2010), ensuring stability, energy density, and compatibility with transportation fuel specifications.

Similar compound classes were reported in other microalgae pyrolysis studies. Mahfud et al. (2024) identified phenols (5.01 %), nitrogenous aromatics such as indole (3.37 %) and quinoline (0.57 %), FAMES (4.52 %), and PAHs (e.g., 2-naphthalenemethanol, 4.55 %) in bio-oils from *Chlorella* sp. under MAP. Aboulkas et al. (2017) reported phenolic-rich bio-oils (24.79 %) along with indoles and pyridines formed from protein decomposition. Adamakis et al. (2018) also detected indole, quinoline, and PAHs in *Chlorella vulgaris* bio-oil, linking their presence to protein and lipid thermolysis. Although detailed nitrogen speciation was beyond the analytical scope of this study, it remains an important aspect to be addressed in future work.

Compared to the present study, the higher phenol and p-cresol content observed in previous reports may be attributed to variations in pyrolysis temperature, reaction duration, and the specific microwave absorbers employed. These factors influence the severity of cracking reactions and the extent of compound volatilization, ultimately shaping the bio-oil's molecular profile. Although this study did not include time-resolved product analysis, the results indicate that tuning operational parameters, particularly absorber type and residence time, represents a promising strategy for directing product composition toward desired fuel properties. Notably, despite the expected benefits of MAP, such as reduced thermal severity and enhanced selectivity, the product distribution in this work was comparable to that of conventional catalytic runs. This may suggest that, under the tested conditions, MAP alone was not sufficient to drive substantial changes in product selectivity. Integrating catalytic systems into MAP configurations may therefore be a more effective approach for exploiting selective heating effects and

further shifting product composition toward high-quality fuel intermediates.

3.4. Biochar and pyrolysis gas characterisation

As shown in Fig. 5, the elemental composition of *Chlorella* sp. biomass, non-catalytic (NC) pyrolysis biochar, and MAP biochar was determined by SEM-EDX analysis, focusing on key elements including carbon, nitrogen, oxygen, sodium (Na), magnesium (Mg), silicon (Si), phosphorus (P), sulphur, and potassium (K).

The most notable observation is the substantial increase in carbon content following pyrolysis, with both biochar (NC and MAP) exhibiting approximately 80 % carbon compared to just over 60 % in the original biomass. This enrichment indicates that pyrolysis effectively concentrates the carbon matrix by volatilizing oxygenated compounds. Oxygen content decreased significantly after pyrolysis, reflecting the thermal degradation of oxygen-rich organics. Although MAP biochar retained slightly more oxygen compared to NC biochar, this suggests milder devolatilization under microwave conditions. Extended residence time can further enhance devolatilization but may also lead to structural degradation and reduced biochar yield (Wang et al., 2019).

Nitrogen retention was also improved in MAP-derived biochar, which could enhance its value as a soil amendment by providing a slow-release nitrogen source. Mineral elements (Na, Mg, Si, P, S, K) were present at low levels, but slightly concentrated in the biochar due to the loss of organic matter and the formation of mineral-rich ash. It should be noted that SEM-EDX provides semi-quantitative data and results should be interpreted accordingly.

Overall, the results confirm that pyrolysis enhances the carbon stability of biomass, producing biochar with improved properties for long-term carbon sequestration and potential agronomic applications. The use of MAP further contributes to the retention of nitrogen, offering additional environmental benefits. Furthermore, the NC pyrolysis char had surface area of 51 m²/g, indicating potential as a catalyst or adsorbent itself after activation. Due to its high carbon content (~80 wt %) and porosity, the obtained biochar may serve as a precursor for various value-added applications, including activated carbon, catalyst support materials, or even nanostructured carbon materials such as carbon nanotubes. Recent studies have explored similar valorisation pathways using carbon-rich waste streams or biomass residues to produce carbon nanomaterials (Cheng et al., 2025, 2024). These potential uses further support the integration of microalgae pyrolysis into circular economy strategies.

In addition to biochar production, significant quantities of gas were generated during pyrolysis, as shown in Fig. 3. The gaseous products were analysed to determine the major components, including H₂, CO, CO₂, CH₄, and C₂-C₄. As shown in Table 2, more than half of the gaseous stream consisted of H₂ and CO, aligning with typical syngas compositions and indicating potential for energy recovery or further upgrading.

The gas composition provides insight into the energy potential and

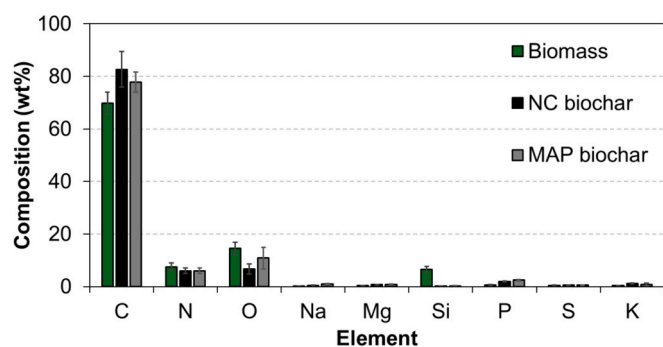


Fig. 5. SEM-EDX elemental analysis of *Chlorella* sp. biomass, NC pyrolysis biochar, and MAP pyrolysis biochar.

Table 2

Pyrolysis gas composition (vol% on a dry, N₂-free basis).

Gas	NC	HZSM-5	Na ₂ CO ₃	AC	MAP
CO	34.6 ± 1.2	39.5 ± 1.3	29.8 ± 0.9	36.9 ± 1.2	35.3 ± 1.0
CO ₂	32.2 ± 0.8	25.8 ± 0.7	35.5 ± 1.4	28.1 ± 0.9	28.5 ± 1.1
H ₂	17.5 ± 0.5	19.4 ± 0.9	24.7 ± 0.9	21.6 ± 0.8	22.3 ± 1.0
CH ₄	11.8 ± 0.4	7.2 ± 0.3	6.9 ± 0.3	8.4 ± 0.4	8.0 ± 0.3
C ₂ -C ₄	3.9 ± 0.1	8.1 ± 0.2	3.1 ± 0.1	5.0 ± 0.0	5.9 ± 0.2

Note: Absolute concentrations in the reactor effluent are diluted by the N₂ carrier gas, but here percentages reflect the makeup of the produced gas.

reusability of the gaseous fraction. Catalytic pyrolysis influenced the gas profile substantially: HZSM-5 increased CO and light hydrocarbons, suggesting enhanced cracking and deoxygenation activity. Na₂CO₃ led to the highest hydrogen content (24.7 vol%) and CO₂ production, possibly indicating greater decarboxylation reactions. Activated carbon yielded a more balanced composition, with notable CO and H₂ content and moderate levels of CH₄ and light hydrocarbons. These results demonstrate that catalyst selection can be used to tune the gas composition for potential applications in combustion, reforming, or syngas-to-liquid conversion routes. In addition, hydrogen- and CO-rich streams may be valorised *in situ* for heat and power generation or as hydrogen donors for catalytic upgrading, contributing to process integration and circularity.

3.5. Microalgae pyrolysis prospects

To further enhance product quality, the choice of pyrolysis configuration plays a critical role. While both microwave-assisted and conventional pyrolysis convert microalgae into bio-oil, their outcomes differ significantly. MAP offers more uniform and selective heating, which reduces secondary cracking and results in higher-quality bio-oil with lower levels of oxygenated compounds such as acids. Consequently, MAP-derived bio-oils show improved fuel stability and higher energy density compared to those produced by conventional pyrolysis. They also tend to be richer in phenolic and aromatic hydrocarbons, which are desirable intermediates for fuel upgrading. In contrast, conventional pyrolysis produces a broader spectrum of oxygenated by-products and often requires more intensive downstream upgrading. Additionally, MAP is particularly well-suited for wet biomass, reducing the need for energy-intensive drying steps and offering a key advantage for the direct thermochemical conversion of microalgae into advanced biofuels. Although this work used dried biomass, in practice MAP could directly process algal paste, reducing drying costs.

As highlighted by Forruque Ahmed et al. (2023), the fast pyrolysis of *Chlorella protothecoides* at 500 °C has been shown to produce bio-oil with high carbon and nitrogen content, and reduced oxygen compared to lignocellulosic biomass, demonstrating the species-specific advantages of microalgae. Moreover, the authors emphasize that, although alternative methods like hydrothermal liquefaction (HTL) can yield more consistent oil quality, pyrolysis technologies remain more accessible and economically viable for near-term implementation. These insights support the relevance of the current study's focus on optimising pyrolysis conditions to improve energy density and reduce oxygenates in microalgae-derived bio-oils. The presented results support these insights: microalgae pyrolysis can indeed yield higher energy-content oils (HHV > 33 MJ/kg) with suitable configuration. The fact that this was achieved via fast pyrolysis underlines the potential of pyrolysis as a nearer-term solution compared to HTL, especially given the simpler infrastructure of pyrolysis.

Further improvements could include exploring upgrading strategies such as fractionation, catalytic hydrotreatment, or solvent-based extraction to enhance fuel stability and compatibility with existing infrastructure.

To support future deployment, environmental and economic

performance must also be evaluated. While this study focused on product quality and process optimisation, integrating life cycle assessment (LCA) and techno-economic analysis (TEA) would be essential to quantify the overall sustainability and feasibility of microalgae pyrolysis routes. As noted in recent reviews, MAP may offer lower energy inputs and improved carbon efficiency (Inayat et al., 2022), but system-wide impacts such as cultivation emissions, energy use, and capital costs require further analysis to guide commercial-scale implementation. Recent techno-economic reviews suggest that minimum fuel selling prices (MFSPs) from pyrolysis can be competitive if bio-oil upgrading and co-product valorisation (e.g., biochar) are included, but estimates still vary significantly depending on plant size, feedstock costs, and product yields (Makepa et al., 2023). Addressing these system-level challenges will be key to translating the present laboratory-scale findings into real-world biofuel solutions.

4. Conclusions

This study presents a comprehensive assessment of *Chlorella* sp. pyrolysis under non-catalytic, catalytic, and microwave-assisted configurations. Response surface methodology identified optimal non-catalytic conditions near 550 °C and 60–70 °C/min, yielding ~43 wt% total bio-oil. Catalytic pyrolysis with Na₂CO₃ and HZSM-5 improved deoxygenation and energy quality (HHVs up to 30.8 MJ/kg), while MAP achieved the highest HHV (33.4 MJ/kg) and lowest oxygen content (16.1 wt%), despite high nitrogen content (3.7–8.1 wt%) still requiring upgrading to meet drop-in fuel standards. Gas composition also varied: HZSM-5 favoured CO and light hydrocarbons, while Na₂CO₃ promoted hydrogen-rich streams. Although MAP offers energy efficiency and short reaction times, its scalability, along with catalyst dosage optimisation and recyclability, requires further study. Overall, this work demonstrates the flexibility of pyrolysis strategies and supports the integration of microalgal biorefineries with life cycle and techno-economic assessment (LCA/TEA) to guide commercial feasibility.

CRedit authorship contribution statement

Gabriela F. Ferreira: Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **James S. Hayward:** Resources, Investigation. **Mathew Nelson:** Writing – review & editing, Investigation. **Daniel R. Slocombe:** Writing – review & editing, Resources. **Jonathan K. Bartley:** Writing – review & editing, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2025.133628>.

Data availability

The dataset supporting this publication is openly available in Figshare at <https://doi.org/10.6084/m9.figshare.30604220>.

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