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Advancements in ZSM-5 Catalytic Torrefaction of Microalga Chlorella sp. for Biochar Production

Baron Joseph Magdaraog[a], Aristotle Ubando[a,*], Wei-Hsin Chen[b]

[a]Department of Mechanical Engineering, De La Salle University, 2401 Taft Ave, 0922 Manila, Philippines
[b]Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan
aristotle.ubando@dlsu.edu.ph

With the growing studies on microalgae as a sustainable source of biomass and other high-value products, the demand for microalgal biomass has increased. Hence, microalgae waste accumulation has become a growing environmental issue, threatening marine ecosystems and water quality. Torrefaction is a promising method for converting this waste into a solid product called biochar, contributing to carbon capture and reducing greenhouse gas emissions. Inert and oxidative torrefaction have become the primary methods, but both often require high energy and long processing times. Catalysts offer a pathway to improve these limitations by enhancing carbon retention and promoting deoxygenation and decarboxylation reactions. This study utilizes zeolite ZSM-5 as a catalyst for biochar production derived from microalga *Chlorella sp.* under inert and oxidative conditions. The main objective is to investigate the effects of torrefaction parameters and zeolite on the solid yield, higher heating value, and carbon content of the raw and torrefied microalgae. Results show that ZSM-5 can effectively increase the carbon content up to 58.21 %, and achieve an HHV of 25.82 $MJ \cdot kg^{-1}$. Comparison with existing literature confirms that catalytic torrefaction improves energy content and shifts biochar properties closer to those of fossil fuels such as lignite and coal. These findings demonstrate the potential of catalytic torrefaction as a sustainable strategy for microalgal waste management and solid biofuel production. Future work will focus on the analysis and characterization of liquid and gaseous byproducts to further elucidate the catalyst's role in reaction pathways and overall system efficiency.

1. Introduction

The increasing global demand for energy, driven by population growth and industrial development, has renewed interest in sustainable alternatives to fossil fuels due to their significant greenhouse gas emissions (Drozdov et al., 2020). Biomass has recently been considered a viable energy alternative to reduce reliance on fossil fuels (Kalak, 2023), as it is derived from organic materials such as agricultural and industrial waste. The two major biomass types are lignocellulosic and algal. Lignocellulosic biomass, obtained from agricultural waste, forestry residues, and urban solid waste, is the most abundant feedstock and benefits from mature supply chains (Barskov et al., 2019). In contrast, algal biomass—particularly microalgae—offers several advantages as a third-generation feedstock (González-Delgado et al., 2022). It has a higher growth rate, greater photosynthetic efficiency, and can be cultivated on non-arable land using wastewater or saline water, reducing competition with food crops. Microalgae are also rich in energy-dense compounds and can thrive in diverse aquatic environments, making them highly adaptable for solid biofuel production.

Bioenergy is renewable and often considered a carbon-neutral energy source. It can be converted into biofuels through thermochemical processes, particularly relevant for industrial applications. The primary thermochemical conversion techniques in microalgal torrefaction are gasification, pyrolysis, and torrefaction (Sirohi et al., 2022). Gasification (700–1,100 °C) and pyrolysis (250–900 °C) operate at high temperatures to produce gaseous and liquid biofuels. In contrast, torrefaction—also referred to as mild pyrolysis—is performed under inert conditions at a lower temperature range (200–300 °C) and atmospheric pressure. It is particularly suitable for solid biofuel production, as it improves energy density, stability, and handling while requiring less energy input than other methods.

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Recently, the torrefaction of microalgae has attracted interest as a method for producing solid biofuels, owing to its effectiveness in improving properties like energy content, moisture resistance, and ease of handling. It is also associated with the lowest average global warming potential in producing bioenergy streams compared to other thermochemical methods (Ubando et al., 2019). However, optimizing torrefaction conditions remains a challenge, especially for microalgal biomass, which contains high moisture content (Sirohi et al., 2022). While increasing temperature and residence time can improve biochar quality by enhancing volatile release, overly severe conditions may lead to excessive degradation, resulting in high ash content and reduced calorific value (Felix et al., 2023).

To improve biochar quality without relying solely on harsh thermal conditions, alternative approaches have been explored. Catalysts have been utilized to serve as a reaction accelerator by promoting better deoxygenation and decarboxylation (Mustapha and Isa, 2025). In this study, zeolite ZSM 5 is utilized in the torrefaction of microalga *Chlorella sp.* under inert and oxidative environments. The main objective is to assess the impact of ZSM-5 on fuel quality by examining changes in higher heating value, carbon content, and solid yield under varying torrefaction conditions. By comparing selected trials and benchmarking against existing literature, this work highlights the potential of catalytic torrefaction for producing high-quality biochar from microalgal feedstocks.

2. Materials and methods

2.1 Materials

This study utilized microalga *Chlorella sp.* (MCS), which was sourced from a laboratory in Southern Taiwan, as shown in Figure 1. The catalyst employed was zeolite ZSM-5, with a SiO_2/Al_2O_3 ratio of 23 and a surface area of 425 $m^2 \cdot g^{-1}$. This zeolite was obtained from Alfa Aesar Company in the USA. Prior to its use in torrefaction experiments, the zeolite was activated by heating it in a muffle furnace at 550 °C for 5 h to remove impurities and volatiles.

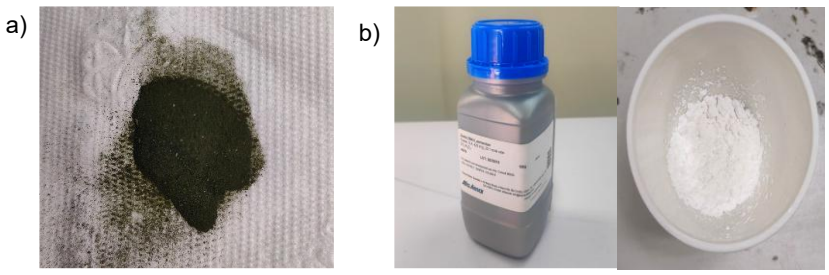

Figure 1: (a) Microalga Chlorella sp. and (b) zeolite ZSM-5 for inert and oxidative torrefaction

2.2 Torrefaction setup

The microalgal torrefaction was conducted using a tubular furnace with controlled temperature settings and a gas mixer, as illustrated in Figure 2. Two layers of quartz wool were utilized to separate the MCS and ZSM-5 within the quartz glass tube. The mass of the MCS was fixed at 1 g, while different masses of the catalyst were tested, including 1 g, 2 g, 3 g, and 4 g. Furthermore, torrefaction experiments were performed in both inert and oxidative environments, employing a nitrogen tank (0 % O_2) and two oxygen tanks (12 % and 21 % O_2). The gas mixer allowed for varying oxygen concentrations, providing a combined gas flow rate of 200 $mL \cdot min^{-1}$. The holding times for torrefaction at each temperature were set to 15, 30, 45, and 60 min. Each duration was recorded 5 min after the target temperature was attained. The spacing of all selected parameters—catalyst dosage, temperature, residence time, and oxygen concentration—was deliberately arranged to ensure a wide yet practical range for effective optimization. The selected oxygen concentrations represent typical oxidative environments for partial and full oxidation scenarios in torrefaction, where 0 % and 21 % O_2 serve as baseline values for inert (nitrogen) and oxidative (air) carrier gases, respectively. The holding times for torrefaction at each temperature were set to 15, 30, 45, and 60 min, while durations beyond 60 min were avoided to prevent excessive thermal degradation, which could reduce solid yield and adversely affect biochar quality. Temperatures ranging from 200 °C to 300 °C were chosen to represent the typical torrefaction window for microalgal biomass. Catalyst dosages of 1 g to 4 g (equivalent to biomass-to-catalyst ratios of 1:1 to 1:4) were selected to explore the effect of increasing catalytic influence without overwhelming the feedstock.

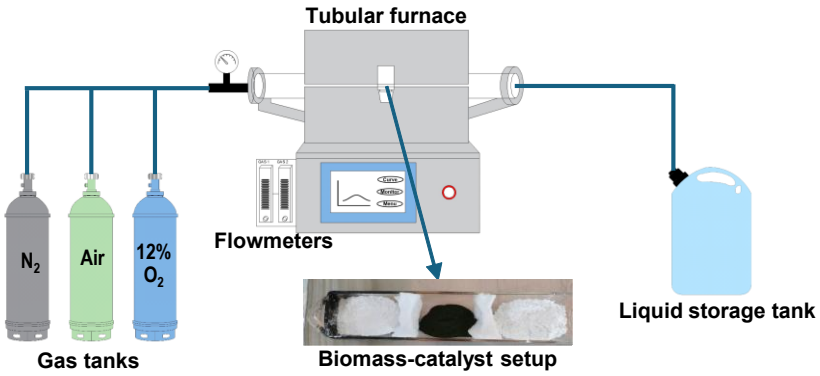

Figure 2: Schematic diagram of the torrefaction experimental setup

The solid yield was calculated by measuring each sample's weight before and after torrefaction, as shown in Eq(1). This parameter is defined as the ratio of the final mass of the torrefied sample to the initial mass of the raw microalgae.

$$SY\ (\%) = \frac{m_{final}}{m_{initial}} \times 100 \quad (1)$$

2.3 Experimental design and characterization

A Taguchi design experiment was originally used to systematically investigate the effects of catalyst dosage, oxygen concentration, temperature, and residence time on the catalytic torrefaction of microalgae. The application of the L16 orthogonal array permitted effective screening of interactions between factors with minimal runs. All experiments were carried out in duplicate to provide reproducibility and compensate for any variability in the observations. To illustrate key findings, this paper emphasizes selected trial results that exhibited the most promising fuel properties, e.g., higher carbon content and heating value. The selected trials indicate the scope of experimental conditions that proved to be best suited for improving biochar quality.
Thermogravimetric analysis of the raw MCS was studied using a PerkinElmer TG/DTA analyzer, as shown in Figure 3. This analysis was used to identify the volatile matter, ash content, and carbon content on a dry basis. Additionally, it investigated the combustion performance of the raw sample measured from ambient temperature up to 800 °C. To evaluate the energy content, the higher heating values of the raw and torrefied MCS were measured using a bomb calorimeter (IKA C6000). Furthermore, the elemental composition, such as carbon, hydrogen, nitrogen, and oxygen, was determined using PerkinElmer elemental analyzer to assess chemical changes following torrefaction.

Figure 3: Instruments used for sample characterization: (a) thermogravimetric analyzer, (b) bomb calorimeter, and (c) elemental analyzer

3. Results and discussion

3.1 Thermochemical characteristics of raw feedstock

This study investigates the inherent properties of the microalga *Chlorella sp.* (MCS) on a dry basis. The sample has a volatile matter content of 58.52 %, indicating high thermal reactivity suitable for conversion processes. Its ash content of 7.19 % is higher than that of lignocellulosic biomass, while its fixed carbon content (34.29 %). contributes to a relatively high heating value of 20.84 MJ·kg^{-1}.
The thermogravimetric analysis (TGA) curve profile of raw MCS indicates three clear thermal decomposition phases, as shown in Figure 4. The initial phase (<150 °C) is attributed to moisture evaporation; the second

(200–400 °C) reflects rapid decomposition of volatiles and proteins (Zhang et al., 2021); and the third (500–650 °C) involves the breakdown of stable compounds such as lipids and ash formation. Complementing the TGA profile, the derivative thermogravimetry (DTG) curve shows the two distinct peaks: one at 280 °C linked to the degradation of carbohydrates and volatiles, and another at 570 °C associated with more thermally stable lipids. These findings validate the feedstock's high reactivity and its suitability for torrefaction.

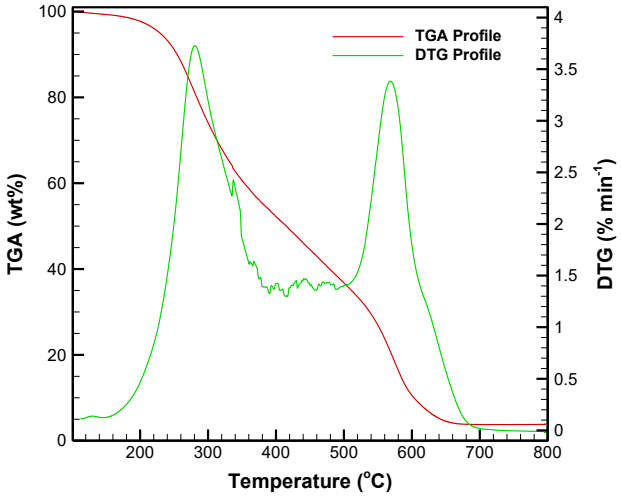

Figure 4: Thermogravimetric (TGA) and derivative (DTG) analysis of raw microalga Chlorella sp

3.2 Effect of torrefaction conditions on biochar properties

Table 1 shows the solid yield, HHV, and elemental composition of the raw and torrefied MCS. The HHV and carbon content significantly increase after torrefaction, indicating an enhancement in fuel quality. The highest HHV and carbon content recorded are 25.82 MJ·kg^{-1} and 58.21 %, respectively. These are observed in an inert environment with a 1:4 MCS-ZSM-5 ratio under 300 °C for 30 min. This suggests that the catalyst addition to an inert environment promotes effective deoxygenation and decarboxylation, likely due to the acidic and microporous nature of ZSM-5, which enhances the removal of oxygenated volatiles while preserving carbon-rich compounds. (Sirohi et al., 2022). However, this process requires an extended residence time compared to oxidative torrefaction (15 min), resulting in the lowest solid yield of 33.01 %. This highlights a compromise between maximizing energy content and preserving material, where enhancing the HHV often comes at the expense of reduced solid yield, emphasizing the need to balance energy density with feedstock retention.

Table 1: Biochar yield and composition of raw and selected torrefied microalga Chlorella sp. samples

Conditions	Solid yield (%)	HHV (MJ·kg^{-1})	Carbon (%)	Oxygen (%)	Hydrogen (%)
Raw	–	20.84	47.54	35.64	7.30
0 % O_2, 4 g ZSM-5, 300 °C, 30 min	33.01	25.82	58.21	25.88	5.43
6 % O_2, 4 g ZSM-5, 260 °C, 15 min	56.33	24.22	56.51	26.63	5.97
12 % O_2, 2 g ZSM-5, 300 °C, 15 min	47.70	23.77	58.03	26.88	4.33
21 % O_2, 3 g ZSM-5, 220 °C, 15 min	71.21	23.16	49.72	34.03	6.01

3.3 Comparison with existing literature

The studies about microalgal torrefaction for solid biofuel production were sourced from the Scopus database using the search strings "microalga*", "biochar", and "torrefaction". To establish a consistent basis for comparison, only the maximum HHV values and their corresponding solid yield and carbon content were considered.

The presence of catalysts appears to significantly enhance the fuel quality of the torrefied microalgae, as illustrated in Table 2. Zhang et al. (2024) achieved the highest HHV of 32.79 MJ·kg^{-1}, mainly attributed to KOH

activation and water washing. In terms of the carbon content, Chen et al. (2022) recorded the highest value of 69.05 %, using MgO as a catalyst. In contrast, studies without catalysts—such as those by Felix et al. (2023) and Zhang et al. (2021)—reported slightly lower HHVs of 25.85 MJ·kg^{-1} and 26.17 MJ·kg^{-1}, respectively. Although the HHV in this study (25.82 MJ·kg^{-1}) is comparable to those non-catalytic cases, the increase in carbon content to 58.21 % at a moderate temperature and short residence time highlights the selective advantage of catalytic torrefaction with ZSM-5 in optimizing carbon enrichment.

Table 2: Summary of torrefaction conditions and resulting fuel properties of microalgal biochar from this study and selected literature

Conditions	Microalgae feedstock	Catalyst	Solid yield (%)	HHV (MJ·kg^{-1})		Carbon (%)		Reference
				Raw	Torrefied	Raw	Torrefied	
0 % O_2, 4 g ZSM-5, 300 °C, 30 min	*Chlorella sp.*	ZSM-5	33.01	20.84	25.82	47.54	58.21	This study
0 % O_2, 5 wt % MgO, 630 W, 25 min	*Chlorella vulgaris FSP-E*	Magnesium oxide	35.40	20.22	26.22	51.06	69.05	Chen et al. (2022)
0 % O_2, 0.2 M H_2SO_4, 170 °C, 10 min	*Chlorella vulgaris ESP-31*	Sulfuric acid	~23	19.23	32.35	47.98	68.71	Yu et al. (2020)
0 % O_2, 2.5 g KOH, 300 °C, 60 min	*Nannochloropsis oceanica*	Potassium carbonate	–	21.08	32.79	53.89	64.89	Zhang et al. (2024)
3 % O_2, 300 °C, 60 min	*Chlorella sorokiniana*	–	51	20.77	25.85	48.73	–	Felix et al. (2023)
21 % O_2, 300 °C, 60 min	*Nannochloropsis oceanica*	–	60.76	21.02	26.17	53.98	63.28	Zhang et al. (2021)

3.4 Fuel quality evaluation via van Krevelen diagram

The van Krevelen diagram in Figure 5 demonstrates enhanced fuel properties of the torrefied microalgal samples based on their atomic O/C and H/C ratios. The study of Felix et al. (2023) is excluded due to the absence of elemental data from their highest HHV run. The placement of the samples in the diagram confirms the effectiveness of catalytic torrefaction in shifting biochar characteristics toward those of fossil fuels like lignite and coal. Although some non-catalytic processes also approached properties similar to lignite, the catalyst-assisted methods consistently demonstrated a greater transformation towards coal-like attributes, likely due to the catalyst's role in selectively promoting dehydration and decarboxylation reactions. This mechanistic advantage underscores their superior performance in upgrading biochar.

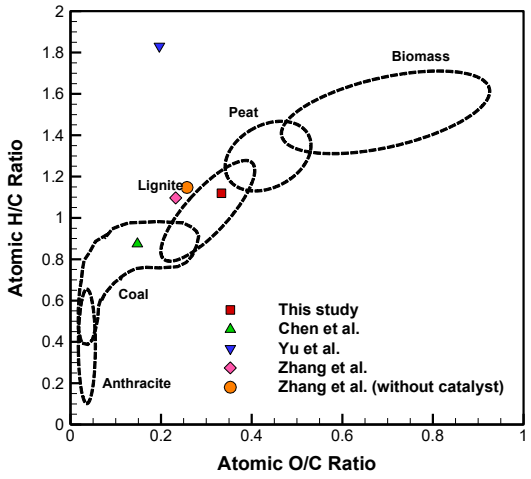

Figure 5: Van Krevelen diagram comparing atomic O/C and H/C ratios of torrefied microalgae from this study and existing literature

The data shown in the van Krevelen diagram is further supported in terms of the energy content relative to coal. In the study conducted by Go and Conag (2018), the maximum HHV for coal, derived from 8310 data samples

globally, was 36.26 $MJ \cdot kg^{-1}$. This value was associated with high-grade anthracite coal. As shown in Table 2, the highest HHV obtained in catalytic microalgal torrefaction is 32.79 $MJ \cdot kg^{-1}$. Given the narrow gap in calorific performance and the improved elemental composition seen in catalyst-treated samples, microalgal biochar torrefied with catalysts shows significant potential as a sustainable, energy-dense alternative or supplement to traditional coal.

4. Conclusions

This study highlights the potential of zeolite ZSM-5 as a catalyst for the torrefaction of microalga *Chlorella sp.* under inert and oxidative environments for biochar production. Catalyst loading, oxygen concentration, temperature, and residence time are systematically varied. The maximum HHV and carbon content are 25.82 $MJ \cdot kg^{-1}$ and 58.21 %, respectively, under torrefaction conditions of 0 % O_2 concentration, 1:4 biomass-catalyst ratio, 300 °C, and 30 min. These results indicate that inert torrefaction is significantly enhanced by the highest catalyst loading at elevated temperature and moderate residence time. Compared to existing non-catalytic studies, this work achieves a comparable HHV with a shorter residence time, confirming ZSM-5's catalytic advantage. Van Krevelen diagram further indicates that catalytic torrefaction improves fuel characteristics, aligning biochar properties more closely with those of lignite and coal. These findings support the practical viability of using ZSM-5 for efficient biochar production from microalgal biomass. Future work should assess the economic feasibility, process scalability, and environmental impacts of catalytic torrefaction. This includes the comprehensive characterization of gaseous and liquid byproducts to optimize system integration in bioenergy applications.

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