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TÍTULO DO TRABALHO:

Catalytic conversion of *Chlorella* sp. microalgae into hydrocarbon-rich liquid biofuel promoted by an environmentally friendly catalyst

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Abstract

Microalgae-based CO_2 biological fixation is deemed a promising method for post-combustion CO_2 capture. Its dual objectives are mitigating CO_2 emissions and generating microalgal biomass suitable as feedstock for third-generation biofuels. Therefore, microalgal-based biorefinery is an important contributor to producing bioenergy with carbon capture, demonstrating significant potential for decoupling reliance on fossil fuels and generating carbon credits through effective CO_2 capture. In this regard, the bio-oil produced from the catalytic pyrolysis of microalgal biomass holds considerable potential as a substitute for non-renewable transportation fuels. However, the occurrence of oxygenated compounds in bio-oil renders it unsuitable as a liquid biofuel for real-world applications. One feasible approach to overcoming this barrier is catalytic pyrolysis, but the high expense associated with commercially available catalysts for producing hydrocarbon-rich bio-oil continues to be a critical obstacle, hindering its practical scalability. This motivates the current study, which concentrates efforts on evaluating a new environmentally friendly CaO-based catalyst derived from industrial waste, named CCKD, for inducing the production of a deoxygenated precursor for low-carbon liquid biofuel from *Chlorella* sp. microalgae through catalytic pyrolysis. To capture CO_2 from flue gas and cultivate algal biomass for energy conversion, *Chlorella* sp. microalgae were cultivated in 5-L bubble column photobioreactors with flue-gas level aeration. Operated in an *ex-situ* configuration, a micro-furnace temperature-programmable pyrolyzer interfaced with gas chromatographic separation and mass spectrometry detection (Py−GC/MS setup) was employed to investigate the catalytic pyrolysis of *Chlorella* sp. microalgae and compare it to non-catalytic conversion. In Py−GC/MS experiments, the catalyst demonstrated high deoxygenation activity, resulting in a condensable volatile product with a hydrocarbon content reaching 61.8%, and a high selectivity for monocyclic aromatic hydrocarbons. This study also illustrates the potential of utilizing CCKD as an efficient, low-cost catalyst for flash pyrolysis to produce hydrocarbons within the gasoline range (C_5−C_{12}). This suggests that the condensable volatile products may be an alternative precursor for low-carbon transportation fuel. The catalytic activity of CCKD, in terms of cracking, deoxygenation, and aromatization reactions, was effectively mediated by the substantial presence of basic sites in surface catalyst originating from CaO. In conclusion, this study provides valuable insights into a practical and cost-effective route for converting *Chlorella* sp. microalgae into a hydrocarbon-rich liquid biofuel.

Keywords: flash pyrolysis, microalgae, low-cost catalyst, drop-in biofuel precursor.

Resumo

A fixação biológica de CO_2 utilizando microalgas é vista como um método promissor para a captura de CO_2 pós-combustão. Seu duplo propósito é reduzir as emissões de CO_2 e gerar biomassa de microalgas adequada como matéria-prima para biocombustíveis de terceira geração. Neste contexto, o bio-óleo produzido a partir da pirólise catalítica da biomassa de microalgas possui um considerável potencial como substituto para combustíveis de transporte não renováveis, demonstrando um potencial significativo para reduzir a dependência de combustíveis fósseis. No entanto, a presença de compostos oxigenados no bio-óleo o torna inadequado como biocombustível líquido para aplicações práticas. Uma abordagem emergente para superar essa barreira é a pirólise catalítica. No entanto, o alto custo dos catalisadores comercialmente disponíveis para a produção de bio-óleo rico em hidrocarbonetos continua

sendo um obstáculo crítico, dificultando a escalabilidade dessa abordagem. Isso motiva o estudo atual, que concentra esforços na avaliação de um novo catalisador ambientalmente amigável à base de CaO derivado de um resíduo industrial, denominado CCKD, para promover a produção de um precursor desoxigenado para biocombustíveis líquidos de baixa pegada de carbono a partir da microalga *Chlorella* sp. por meio da pirólise catalítica. Para capturar CO_2 e cultivar biomassa de microalgas para conversão energética, as microalgas *Chlorella* sp. foram cultivadas em foto-biorreatores de coluna de bolhas com aeração com um nível de CO_2 similar ao encontrado em gás pós-combustão. Operado em uma configuração *ex-situ*, um micro-pirolisador com identificação em linha dos produtos voláteis condensáveis evoluídos por meio de separação cromatográfica em fase gasosa e detecção por espectrometria de massa (Py-GC/MS), foi empregado para investigar a pirólise catalítica da microalga *Chlorella* sp. e compará-la à conversão não catalítica. O catalisador demonstrou alta atividade de desoxigenação, resultando em um produto volátil condensável com um teor de hidrocarbonetos atingindo 61,8% e alta seletividade para hidrocarbonetos monoaromáticos. Este estudo também ilustra o potencial de utilização do CCKD como um catalisador eficiente e de baixo custo para pirólise rápida para produzir hidrocarbonetos dentro da faixa de gasolina (C_5–C_{12}). A atividade catalítica do CCKD, em termos de craqueamento, desoxigenação e reações de aromatização, é justificada pela presença de sítios básicos na superfície do catalisador derivados do CaO. Em conclusão, este estudo fornece resultados favoráveis sobre uma rota prática e econômica para converter microalgas *Chlorella* sp. em um precursor de biocombustíveis avançados.

Palavras-chave: pirólise rápida, microalga, catalisador de baixo custo, precursor de biocombustíveis avançados.

Introduction

Owing to environmental concerns associated with climate change and potential future energy crises, immediate action and energy transition through the utilization and advancement of renewable and sustainable energy sources are urgently required. Biofuels derived from biomass are widely acknowledged as a promising alternative to fossil fuels due to their carbon neutrality, acceptance as renewable energy, and potential to mitigate global warming by displacing fossil fuels. The energy stored in biomass, originating from sunlight, can be utilized either directly through combustion or converted into energy-rich biofuels using thermochemical processes such as gasification and pyrolysis (Pattiya et al., 2010). Pyrolysis is a thermally induced, low-emission technology becoming increasingly attractive for biofuel production due to its relative simplicity and compatibility with existing energy industry infrastructure (Valizadeh et al., 2022).

Microalgae are recognized as promising sources for producing biomass rich in lipids, carbohydrates, and proteins, classified as third-generation feedstock for value-added products such as liquid biofuels and platform chemicals (Marques et al., 2024). An additional advantage is that microalgae can utilize CO_2 as their carbon source during growth, positioning them as one of the most promising techniques for post-combustion CO_2 capture, while also providing a sustainable approach for microalgal biomass production (Leflay et al., 2021). Flash pyrolysis represents a promising pathway for microalgal biomass conversion into low-carbon liquid biofuel, termed bio-oil, accompanied by useful energy-rich by-products, including carbon-rich solid biochar and non-condensable gases. The main product, bio-oil, can be easily stored and transported, serving either as a biofuel or a source of renewable chemicals (Kassim and Meng, 2017).

Bio-oil derived from microalgae is rich in oxygenated compounds, predominantly derived from carbohydrates. These compounds are primarily responsible for their lower heating value and higher viscosity than conventional fuel oils and their instability, which restricts direct utilization as a biofuel

(Marques et al., 2024). The catalytic upgrading of bio-oils from the flash pyrolysis of biomass is crucial for removing reactive oxygen species and enhancing hydrocarbon content, resulting in a liquid biofuel suitable for direct use as a fossil fuel replacement or blending with petroleum-based fuels (Onwudili and Scaldaferri, 2023). Using low-cost materials, such as biomass ash, coal fly ash and industrial waste, has been identified as a potential alternative to expensive commercial zeolites to reduce overall upgrading costs in obtaining high-grade bio-oil. Therefore, employing widely available, efficient, and affordable catalysts during bio-oil upgrading is essential for achieving a viable and sustainable way to convert oxygen-rich bio-oils into ready-to-use hydrocarbon-rich biofuel. Our research endeavors to use industrial waste rich in $CaCO_3$ as a potential precursor for obtaining a CaO-based catalyst for pyrolysis, named CCKD, are motivated by its high annual generation rate and the presence of an active metal oxide, which can catalyze the conversion of algal biomass into high-energy-density hydrocarbons. Thus, the current work addresses the scientific question of how the CCKD, used as a catalyst in microalgae pyrolysis, impacts the composition of condensable volatile products towards producing a deoxygenated precursor for low-carbon liquid biofuel.

The present work addresses this knowledge gap by intending to shed light on using CCKD in flash pyrolysis to convert microalgal biomass into a potential hydrocarbon-rich liquid biofuel. A Py–GC/MS system assessed how CCKD influences the pyrolysis vapor composition compared to a catalyst-free pyrolysis scenario. The major innovation in this study was using an environmentally friendly CaO-based catalyst derived from industrial waste, CCKD, to upgrade condensable volatile products by removing oxygenated compounds and enhancing hydrocarbon content. This investigation is expected to provide novel insights that expand the limited existing knowledge on new environmentally friendly catalysts, which is attractive for resource-limited countries, particularly those unable to afford expensive conversion routes and catalysts for producing high-grade bio-oil from biomass.

Materials and methods

The microalga *Chlorella* sp. was cultivated for 10 days in a vertical tubular photobioreactor containing BG-11 medium, using a simulated flue gas as the carbon source. This condition replicates the typical CO_2 concentration in flue gas from the cement industry (Premaratne et al., 2021). After collection, the microalgal biomass sample was lyophilized for 72 h using a FreeZone 4.5-liter benchtop freeze dryer (Labconco, Kansas City, United States) at −53 °C under high-vacuum conditions. It was then stored in plastic airtight zip bags until further use. The lyophilized microalga *Chlorella* sp. was subjected to proximate analysis, ultimate analysis, and heating value determination following standard methods established by the American Society for Testing and Materials (ASTM). The proximate analysis provided information on the mass contents of moisture, volatile matter, ash, and fixed carbon. For moisture content determination, the sample was dried at 105 ºC in a forced-convection oven until reaching constant mass following ASTM D4442−20; volatile matter was determined by heating the sample in a covered crucible in a muffle furnace at 950 ºC for 7 min following ASTM E872−82; ash content was determined by heating the sample in an uncovered crucible in a muffle furnace at 575 ºC for 3 h following ASTM D1102−84; and mass balance was used for specifying fixed carbon content. The sample's elemental composition was determined by ultimate analysis using a CE 1108 elemental analyzer (Carlo Erba Instruments, Wigan, England) according to ASTM D3176−24, providing carbon, hydrogen and nitrogen mass contents. Oxygen content was calculated by mass balance (subtracting the combined mass contents of carbon, hydrogen, and nitrogen from 100 wt.%). The sample's higher heating value (HHV) was determined using an adiabatic bomb calorimeter model 1341 (Parr Instruments, Moline, United States), according to ASTM E711−23e1.

The precursor for the catalyst production, an industrial waste rich in $CaCO_3$, was calcined at 850 ºC for 3 h in a muffle furnace before the catalytic testing to remove residual moisture and convert $CaCO_3$ into CaO, known for its catalytic activity in pyrolysis reactions.

The condensable species from the flash pyrolysis of microalga *Chlorella* sp. were analyzed using a Pyroprobe 5200 HP-R micro pyrolyzer (CDS Analytical, Oxford, United States) interfaced with a Varian 3900 gas chromatograph coupled to a Varian Saturn 2100T ion trap mass spectrometer (Agilent Technologies, Santa Clara, United States). The biomass (approximately 1 mg) was placed in a quartz capillary tube sealed at both ends with quartz wool and then positioned in a computer-controlled resistively heated element equipped with a sample holder. The thermal decomposition of the biomass was performed at 500 ºC with a heating rate of 10 °C ms^{-1} and a hold time of 20 s. Ultra-high purity nitrogen was provided at a 50 mL min^{-1} flow rate to ensure an inert atmosphere for flash pyrolysis. In catalytic pyrolysis, the condensable species were directed to a heated bed containing the catalyst at 500 °C, maintaining a biomass-to-catalyst mass ratio of 1:5. Evolved condensable species were directed into a sorbent bed and desorbed at 300 °C. The desorbed species were transferred through a heated line maintained at 300 °C to the GC inlet port using a helium carrier flow of 1 mL min^{-1}. The injector temperature was set at 300 °C, and the sample was injected with a split ratio of 1:50. The desorbed vapors were separated using a VF-5 MS fused silica capillary column (Agilent Technologies, Santa Clara, United States) with 30 m length, 0.25 mm diameter, and 0.25 μm film thickness. The GC oven heating program was initially held at 40 °C for 2 min, then ramped at 10 °C min^{-1} to 280 °C, with an isothermal hold of 10 min. Total ion chromatograms (TIC) were acquired for microalga *Chlorella* sp. in Py−GC/MS experiments, employing an electron ionization (EI) voltage of 70 eV and operating in full-scan mode to detect mass-to-charge (m/z) ratios ranging from 40 to 500. The product distribution of the condensable species was determined by performing peak identification with a probability-based matching algorithm and the NIST Mass Spectral Library. Library identifications with a probability match of 85% or higher were used to qualitatively compare the pyrolysis vapor composition between the catalyst-free and catalytic pyrolysis scenarios. Based on the relative peak areas, semi-quantitation was conducted utilizing the integrator from MS Workstation, an MS data analysis software.

Results and discussion

The average values for volatile matter, fixed carbon, and ash content on a dry basis in the proximate analysis of *Chlorella* sp. microalgae were reported as 61.3 wt.%, 14.8 wt.%, and 23.9 wt.%, respectively. García and colleagues (2014) characterized various biomass used commercially as solid fuels, finding ranges of 66.0 to 85.0 wt.% volatile matter, 11.2 to 30.5 wt.% fixed carbon, and 0.8 to 17.0 wt.% ash content. The *Chlorella* sp. microalgae show similarities to commercially used solid biomass fuels in terms of proximate composition, making it a promising candidate for biofuel production through thermochemical conversion technologies. According to the ultimate analysis, *Chlorella* sp. microalgae consisted of 50.3 wt.% carbon, 4.8 wt.% hydrogen, and 4.9 wt.% nitrogen (all on a dry basis). The oxygen content, determined via mass balance, was estimated at 40.0 wt.%. Commercially used solid biomass fuels show similar compositions to *Chlorella* sp. microalgae, with reported weight percentages for carbon (38.9–48.2 wt.%) and hydrogen (4.8–6.4 wt.%), according to literature (García et al., 2014). This insight highlights the value of Chlorella sp. microalgae as an energy resource. The *Chlorella* sp. microalgae exhibit an HHV of 21.9 MJ kg^{-1}, exceeding the 14.6 to 19.4 MJ kg^{-1} energy content previously reported for lignocellulosic materials used as biofuels in commercial-scale applications (García et al., 2014). Thus, physicochemical characterization confirms the potential of *Chlorella* sp.

microalgae as a promising raw material for producing energy-rich biofuels, justifying our efforts in converting this biomass into a hydrocarbon-rich bio-oil.

Figure 1 illustrates the total ion chromatogram of condensable volatile species produced from the flash pyrolysis of *Chlorella* sp. microalgae under catalyst-free and catalytic conditions. The predominant chemical class among the condensable volatile species was oxygen-containing compounds, constituting up to 40.1%. Phenols were identified as the predominant class among oxygenated compounds, accounting for 6.19% of the condensable volatile species. The thermal decomposition of the proteins is commonly mentioned as the source of phenolic compound formation (Marques et al., 2024). Oxygenated compounds, classified as esters, ketones, and furans, were also observed in the condensable volatile species, possibly released from the thermal decomposition of carbohydrates present in the composition of *Chlorella* sp. microalgae. As per the literature, oxygenated compounds such as esters, ketones, and furans are known to be generated during the thermal decomposition of carbohydrates (Almeida et al., 2017). Other oxygenated compounds, present in smaller quantities and classified as carboxylic acids, aldehydes, and alcohols, were also detected in the condensable volatile species. The thermal decomposition of lipids results in the production of carboxylic acids, aldehydes, and alcohols as oxygenated compounds (Almeida et al., 2017).

Fig. 1 − Pyrograms of condensable volatile species resulting from flash pyrolysis of *Chlorella* sp. microalgae under non-catalytic and catalytic conditions.

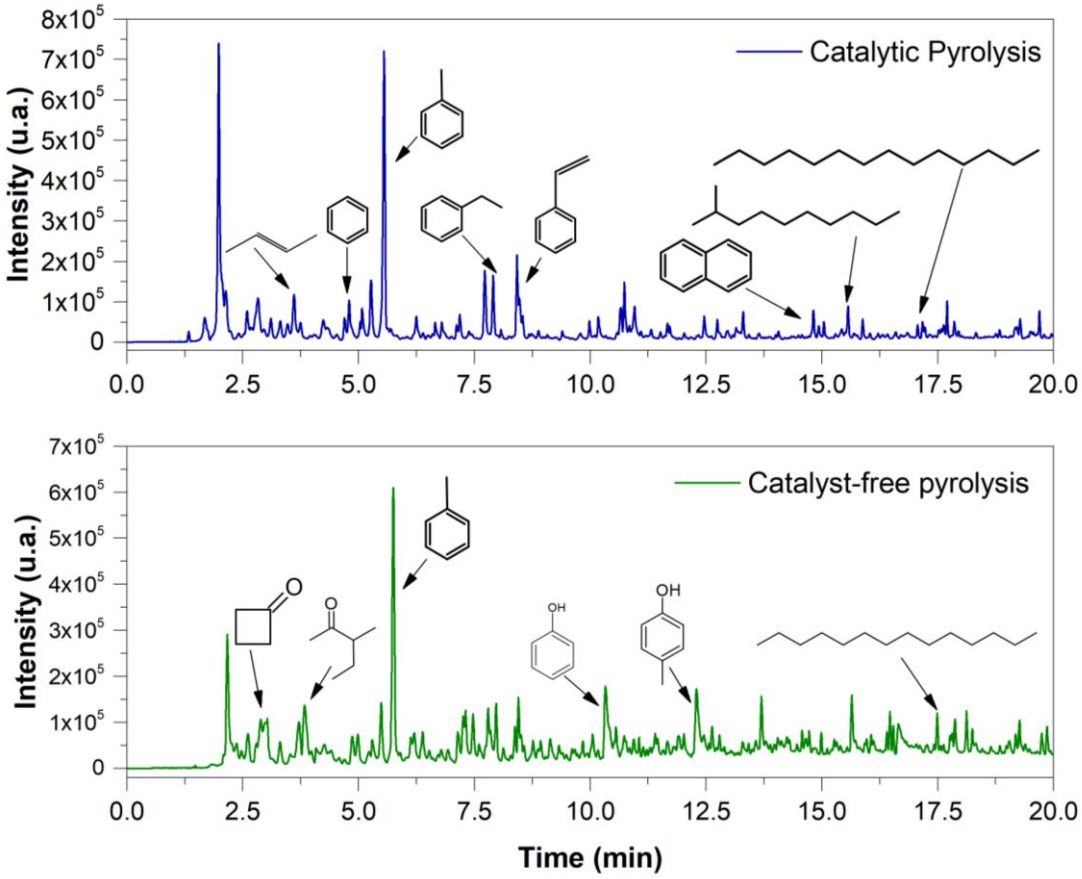
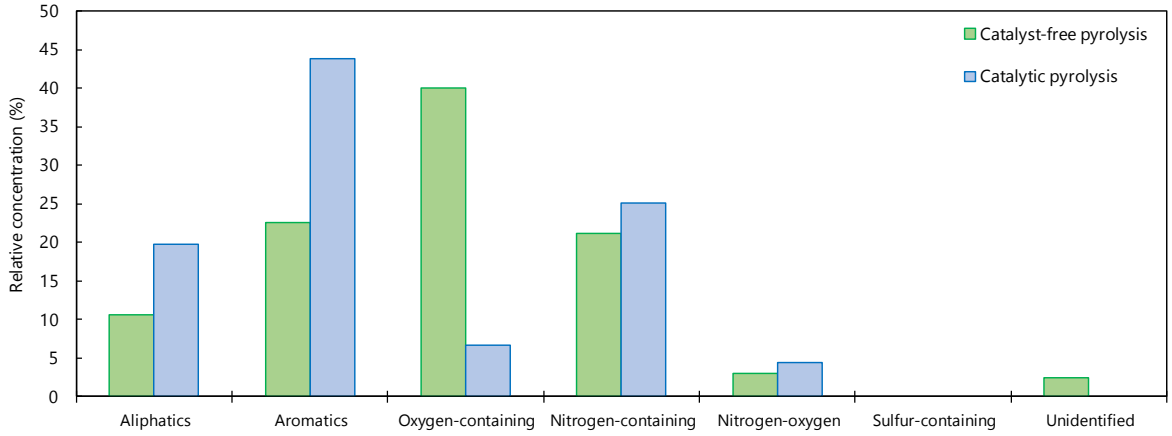


Figure 2 illustrates the organic compounds' classification of the condensable volatile products from catalyst-free and catalytic pyrolysis scenarios. After catalytic upgrading with CCKD, the condensable

volatile products showed significant deoxygenation (83.3%). This result is noteworthy because the high content of oxygenated compounds restricts the potential for direct use of bio-oil derived from the flash pyrolysis of *Chlorella* sp. microalgae as a renewable transportation fuel. A high concentration of oxygenated compounds generally leads to a high acidity and viscosity, which hinders the refining process of bio-oil and its direct utilization as a biofuel. When the CCKD was utilized, a 1.9-fold increase in the concentration of aromatic hydrocarbons was observed compared to the catalyst-free pyrolysis scenario. Similarly, a 1.9-fold increase in aliphatic hydrocarbons was also observed compared to the catalyst-free pyrolysis scenario. Thus, with a mass ratio of *Chlorella* sp. microalgae to CCKD of 1:5, the relative content of hydrocarbons reaches 63.4%. The low-cost catalyst employed in this study exhibits promising catalytic activity and can convert *Chlorella* sp. microalgae into a hydrocarbon-rich bio-oil, potentially suitable as a drop-in biofuel precursor.

Fig. 2 − Impact of the CCKD on the distribution of condensable volatile species resulting from flash pyrolysis of *Chlorella* sp. microalgae according to the chemical class.



The flash pyrolysis of *Chlorella* sp. microalgae, catalyzed by CCKD, demonstrated a high selectivity towards gasoline-equivalent hydrocarbons, with approximately 84% of hydrocarbons in the C_5–C_{12} range. The catalytic activity of CCKD is attributed to its CaO-rich composition, whose basic sites effectively promote deoxygenation and improve the hydrocarbon content. The basic active sites on the catalyst surface are proposed to react with condensable volatile products rich in oxygenated compounds, diffusing from the bulk to the catalyst surface, thus promoting deoxygenation, cracking, and aromatization. Within a circular economy context, it is noteworthy that using CCKD as a low-cost CaO-based catalyst represents a sustainable way of valorization for an industrial solid waste generated in significant quantities. Our findings encourage the use of pyrolysis of microalgal biomass over CCKD to produce a hydrocarbon-rich bio-oil as a sustainable precursor for low-carbon transportation fuel, aligning with global efforts toward energy transition and the decarbonization of the transportation sector.

Conclusions

Chlorella sp., cultivated using simulated flue gas from the cement industry as the carbon source, was catalytically pyrolyzed at 500 °C using a Py–GC/MS system to assess the capability of CCKD for oxygenated compound removal and hydrocarbon content enhancement. Based on the experimental results, our study expands the scientific knowledge and understanding regarding the catalytic pyrolysis of microalgae biomass using low-cost materials, revealing the following findings:

I. The CCKD catalyst exhibited selectivity in reducing oxygenated carbohydrate-derived compounds while simultaneously enhancing the content of aliphatic and aromatic hydrocarbons.
II. The CCKD, acting as a CaO-based catalyst, induced a nearly twofold increase in the relative concentration of aliphatic and aromatic hydrocarbons, all within the gasoline range (C_5 to C_{12}).
III. The CCKD catalyst also demonstrated high selectivity towards monoaromatics, coupled with low selectivity for PAHs, offering an advantage in enhancing catalyst longevity by mitigating PAH-related coke formation.
IV. The upgraded bio-oil can serve as a prospective source of renewable hydrocarbons, positioning it as an alternative precursor for low-carbon transportation fuel.

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