



UNIVERSIDADE FEDERAL DE UBERLÂNDIA
FAULDADE DE ENGENHARIA QUÍMICA
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA



**MICROALGAE *SCHIZOCHYTRIUM LIMACINUM* PYROLYSIS IN A TANDEM
CATALYTIC BED COMPOSED BY HYDROTALCITE PRECURSOR AND HZSM-5
ZEOLITE IN THREE DIFFERENT PROCESS CONFIGURATIONS (ANALYTICAL,
SOLAR AND MICROWAVE)**

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DUPLO COMPOSTO POR PRECURSOR TIPO HIDROTALCITA E ZEÓLITA HZSM-5 EM
TRÊS DIFERENTES CONFIGURAÇÕES DE PROCESSO (ANALÍTICA, SOLAR E POR
MICRO-ONDAS)*

Raíssa Aparecida da Silveira Rossi
Uberlândia
Fevereiro/2024

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Raíssa Aparecida da Silveira Rossi

Orientadores: Prof. Dr. Marcos Antonio de S. Barrozo
Prof. Dr. Luiz Gustavo Martins Vieira

Tese de Doutorado apresentada ao Programa de Pós-Graduação em Engenharia Química da Universidade Federal de Uberlândia como parte dos requisitos necessários à obtenção do título de Mestre em Engenharia Química na área de concentração em Processos Químicos.

Uberlândia
Fevereiro/2024

“... now this is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning.”

Winston Churchill

Ao meu marido, amor e companheiro, Rodolfo, que
está comigo em todos os ensejos que o acaso articula.

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ATA DE DEFESA - PÓS-GRADUAÇÃO

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ACRONYMS

APS - announced pledges scenario

ASTM - American Society for Testing and Materials

BECCS - bioenergy with carbon capture and storage

BET - Brunauer, Emmett e Teller (method and analysis)

BJH - Barret, Joyner, and Halenda (method)

CB_A - total catalysts/biomass ratio for analytical pyrolysis (dimensionless)

CB_M - total catalysts/biomass ratio for microwave-assisted pyrolysis (dimensionless)

CB_S - total catalysts/biomass ratio for solar pyrolysis (dimensionless)

C_A - catalysts' ratio $[NiHTC/(NiHTC+NiHZSM-5)]$ for analytical pyrolysis (dimensionless)

C_S - catalysts' ratio $[NiHTC/(NiHTC+NiHZSM-5)]$ for solar pyrolysis (dimensionless)

CSP - concentrated solar power

DHA - docosahexaenoic acid

D_P - pore diameter (nm)

EF_S - bio-oil emission factor for solar pyrolysis (g CO₂ eq/GJ)

$Energys$ - bio-oil energy content for solar pyrolysis (kJ)

ER_M - energy recovery efficiency for microwave-assisted pyrolysis (%)

ER_S - energy recovery efficiency for solar pyrolysis (%)

FTIR - Fourier transform infrared spectroscopy

GC - gas chromatograph

GC/MS - gas chromatograph and mass spectrometer

GHG - greenhouse gases

GY_M - gas yield for microwave-assisted pyrolysis (%)

GY_S - gas yield for solar pyrolysis (%)

H/C_{eff} - effective hydrogen-to-carbon ratio (dimensionless)

HHV - higher heating value

HHV_S - bio-oil higher heating value for solar pyrolysis (MJ/kg)

HHV_{Mgas} - gas higher heating value for microwave-assisted pyrolysis (MJ/kg)

HTC - hydrotalcite catalyst

Hydrocarbons - hydrocarbon content for solar pyrolysis (peak area %)

HZSM-5 - zeolite catalyst

IPCC - Intergovernmental Panel on Climate Change

JCPDS - Joint Committee on Powder Diffraction Standards

LDHs - layered double hydroxides

LY_M - liquid yield for microwave-assisted pyrolysis (%)

LY_S - liquid yield for solar pyrolysis (%)

Oxygenateds - oxygenated compound content for solar pyrolysis (peak area %)

PAHs - polycyclic aromatic hydrocarbons

Py-GC/MS - Analytical pyrolysis coupled with GC/MS

n_a - acid site density ($\mu\text{mol}/\text{m}^2$)

NiHTC - hydrotalcite impregnated with nickel

NiHZSM-5 - zeolite catalyst impregnated with nickel

NiHTC/SiC - hydrotalcite impregnated with nickel in a silicon carbide structure

NiHZSM-5/SiC - zeolite catalyst impregnated with nickel in a silicon carbide structure

Nitrogenateds - nitrogenated compound content for solar pyrolysis (peak area %)

NIST - National Institute of Standards and Technology

$nM_{overall}$ - overall energy efficiency for microwave-assisted pyrolysis (%)

NZE - net zero scenario

S_{BET} - BET-specific areas (m^2/g)

SEM - Scanning electron microscopy

SDGs - sustainable development goals

STEPS - stated policies scenario

SY_M - liquid yield for microwave-assisted pyrolysis (%)

SY_S - solid yield for solar pyrolysis (%)

T_A - temperature reaction for analytical pyrolysis tests ($^{\circ}\text{C}$)

TPD- NH_3 - temperature programmed desorption of ammonia

TGA – thermogravimetric analysis

T_S - temperature reaction for solar pyrolysis tests ($^{\circ}\text{C}$)

V_p - pore volume (cm^3/g)

U_M - upgrinding factor for microwave-assisted pyrolysis (dimensionless)

x_{1S} - coded levels for temperature reaction in solar pyrolysis tests

x_{2S} - coded levels for catalysts' ratio $[\text{NiHTC}/(\text{NiHTC}+\text{NiHZSM-5})]$ in solar pyrolysis tests

XRD - X-ray diffraction

XRF - X-ray fluorescence analysis

ABSTRACT

The growing concern over the environmental problems associated with fossil fuel consumption brings new opportunities and challenges for renewable energy development. Shifting to renewable energy will play a key role in transforming the energy industry to increase energy system flexibility, allowing it to absorb the energy consumption demand. The global exploration of these technologies will support the necessary decarbonization to preserve environmental health. Essential technologies such as thermochemical processes have become of significant interest due to the flexibility in operation, versatility of the technology, and adaptability to a wide variety of feedstocks and products. Pyrolysis for liquid generation has been developed in recent decades as a fast and flexible method to provide high yields of liquid products. The liquid fraction called bio-oil can be used in diverse chemical applications and as an efficient energy carrier, easily stored and transported, assisting the change in the global energy matrix. Nevertheless, the formation of oxygenated and nitrogenated compounds in microalgae pyrolysis bio-oil interferes with its use as a viable competitor against fossil fuels. Aiming to reduce these undesirable substances and improve aromatic hydrocarbon production, the catalytic pyrolysis of the microalgae *Schizochytrium limacinum* in a tandem catalytic bed was investigated. This study evaluated the effects of the reaction temperature and the double catalytic bed (NiHTC followed by NiHZSM-5) on the product distribution and bio-oil features in three distinct pyrolysis setups: (1) analytical; (2) solar; and (3) microwave. In the analytical pyrolysis, the tandem catalytic bed consisting of NiHTC followed by NiHZSM-5 demonstrated superior capabilities in deacidification and deoxygenation. This achievement is a promising indicator of the potential products that could be generated on a larger scale. With both catalysts calcined and subjected to reduction/passivation, the hydrocarbon production reached remarkable levels, standing at 89 and 92%, respectively, when the total catalyst-to-biomass ratio was set at 5:1. Under these optimized conditions, aromatic formation remained consistently within the range of 60 to 70%. Solar pyrolysis reached approximately 45 wt.% of liquid formation as regards the initial mass of microalgae and achieved about 75% of hydrocarbon generation, which is the product of interest. The bio-oil produced in the solar pyrolysis presented compounds highly desirable as long-chain hydrocarbons (aliphatic and aromatic). The formation of these hydrocarbons was more favored at the highest reaction temperature of 750°C, at NiHTC/(NiHTC+NiHZSM-5) of 0.50 and under a ratio of total catalyst to biomass of 4:1, a condition that also led to an aromatization of approximately 80% of the hydrocarbons. Just as hydrocarbon production benefited under these conditions, which led to an energy recovery efficiency (ER_s) of approximately 65%. These data represent about 95% less CO₂ eq emissions as regards fossil crude oil usage since microalgae are considered renewable biomass, and the heating power also comes from a renewable energy source. In the environmental aspect, this fact can be a great form of mitigating the emissions of CO₂ and earning carbon credit potential. Experimental results showed that *ex-situ* catalytic microwave-assisted pyrolysis produced satisfactory liquid yields, reaching approximately 57 wt.% in the finest test. The results showed that NiHTC/SiC favored deacidification and denitrification reactions, leading to a more significant generation of

intermediate compounds such as ketones and alcohols. These compounds were then converted into hydrocarbons by the acidic sites of the NiHZSM-5/SiC catalyst. A maximum hydrocarbon and benzene formation of 93 and 78%, respectively, were reached, and overall, the loss of the liquid yield can be compensated by its quality improvement. In addition, the regeneration and recycling of the catalytic bed were carried out successfully. After 7 cycles, the activity of the bed concerning the formation of hydrocarbons was not significantly affected. This study also provided essential data of the microwave pyrolysis efficiency such as energy recovery (94%), overall efficiency (25.5%), and upgrading factor (1.36), which is defined as the ratio of the sum of produced bio-oil, gas, and bio-char heating values over the heating value of the processed biomass feedstock. The satisfactory results indicated that the biomass energy was successfully stored as a liquid fuel.

Keywords: microwave, solar pyrolysis, catalysis, thermochemical process, bio-oil.

RESUMO

A crescente preocupação com os problemas ambientais associados ao consumo de combustíveis fósseis traz novas oportunidades e desafios para o desenvolvimento de energias renováveis. A pirólise de materiais orgânicos tem sido estudada como um método rápido e flexível para fornecer altos rendimentos de produtos líquidos. A fração líquida denominada bio-óleo pode ser utilizada em diversas aplicações químicas e como eficiente carreador de energia, que é facilmente armazenado e transportado, auxiliando na mudança da matriz energética mundial. No entanto, a formação de compostos oxigenados e nitrogenados no bio-óleo de pirólise de microalgas interfere em seu uso como um competidor viável contra os combustíveis fósseis. Com o objetivo de reduzir essas substâncias indesejáveis e melhorar a produção de hidrocarbonetos aromáticos, a pirólise catalítica da microalga *Schizochytrium limacinum* em leito catalítico duplo foi investigada. Este estudo avaliou os efeitos da temperatura de reação e do leito catalítico duplo (NiHTC seguido de NiHZSM-5) na distribuição do produto e nas características do bio-óleo em três configurações distintas de pirólise: (1) analítica; (2) solar; e (3) de micro-ondas. Na pirólise analítica, o leito catalítico duplo consistindo de NiHTC seguido por NiHZSM-5 demonstrou capacidades superiores em desacidificação e desoxigenação. Com ambos os catalisadores calcinados e submetidos à redução/passivação, a produção de hidrocarbonetos atingiu níveis notáveis, que permaneceram entre 89 e 92%, respectivamente, quando a relação catalisador total/biomassa foi fixada em 5:1. Sob estas condições otimizadas, a formação de aromáticos permaneceu consistentemente na faixa de 60% a 70%. A pirólise solar atingiu aproximadamente 45% de rendimento de líquido (em relação a massa inicial de microalga) e alcançou cerca de 75% de geração de hidrocarbonetos, que é o produto de interesse. Os bio-óleos produzidos na pirólise solar apresentaram compostos altamente desejáveis como hidrocarbonetos de cadeia longa (alifáticos e aromáticos). A formação desses hidrocarbonetos foi mais favorecida na temperatura máxima de reação de 750°C, em NiHTC/(NiHTC+NiHZSM-5) de 0,50 e sob uma proporção de catalisador total para biomassa de 4:1, condição que também levou a uma aromatização de aproximadamente 80% em relação aos hidrocarbonetos formados. Assim como a produção de hidrocarbonetos se beneficiou nessas condições, atingindo uma eficiência de recuperação de energia (ER_s) de aproximadamente 65%. Esses dados representam cerca de 95% menos emissões em CO₂ eq em relação ao consumo de derivados do petróleo, uma vez que a microalga e a energia solar utilizados no processo de pirólise são renováveis. No aspecto ambiental, esse fato pode ser uma ótima forma de mitigar as emissões de CO₂ e adquirir créditos de carbono. Os resultados experimentais mostraram que a pirólise catalítica *ex-situ* assistida por micro-ondas foi capaz de produzir rendimentos de líquido satisfatórios, atingindo 57%. Os resultados mostraram que NiHTC/SiC favoreceu reações de desacidificação e desnitrificação que levaram a uma maior geração de compostos intermediários como cetonas e álcoois. Esses compostos foram então convertidos em hidrocarbonetos pelos sítios ácidos do catalisador NiHZSM-5/SiC. Os rendimentos máximos de hidrocarbonetos e benzeno alcançados foram de 93 e 78%, respectivamente e, em geral, a perda do rendimento do bio-óleo

pode ser compensada pela melhoria em sua qualidade. Adicionalmente, a regeneração e reciclagem do leito catalítico foram realizadas com sucesso, sendo que, após 7 ciclos, o leito não teve sua atividade em relação a formação de hidrocarbonetos afetada de forma significativa. Este estudo também forneceu dados essenciais de eficiência para pirólise de micro-ondas, sendo a recuperação de energia de 94%, eficiência total da pirólise de 25,5% e fator de *upgrading* de 1,36. Os resultados satisfatórios indicaram que a energia da biomassa foi armazenada com sucesso como combustível líquido.

Palavras-chave: micro-ondas, pirólise solar, catálise, processo termoquímico, bio-óleo.

CHAPTER 1

1. INTRODUCTION

The magnitude and pace of climate change are strongly associated with the development of low-carbon emitting technologies (Akan, 2023). The emission intensity and its correlated impacts can only be overcome through sustainable actions involving all sectors and nations worldwide. The study and progress related to renewable energy should enhance knowledge and integrate multidisciplinary solutions to increase the feasibility of biofuels to shift the current state of the art (Potrč et al., 2021). The present environmental mobilization influences the financial resource spent in this research field and assists in creating innovative technical solutions which aim for biofuel upgrading that will allow them to be viable competitors to fossil fuels. Enabling renewable technologies to expand is necessary to implement, accelerate and sustain the adaptation in human systems and ecosystems to reduce greenhouse gas (GHG) emissions (Opeyemi, 2021; Usman et al., 2021). The most recent report of the Intergovernmental Panel on Climate Change (IPCC) revealed that global GHG emissions have reached their highest levels in history. On the other hand, the growth rate slowed to 1.3% between 2010 and 2020, compared to 2.1% in the previous decade (Pörtner et al., 2022).

The use of biomass has been considered one of the leading solutions to provide low-cost renewable energy in addition to decreasing GHG emissions and mitigating global warming. Biomass thermochemical conversion to substitute fossil fuels has widely expanded over the past decades aiming to meet global economic growth and ensure energy security (Proskurina et al., 2019). The worldwide forecast for biomass potential is 96 EJ in 2050 against 11 EJ obtained in 2020 (IEA, 2021). In 2018, biomass energy developed a key role in some countries, such as Brazil, India, and Germany, where biomass energy accounted for 31, 21, and 11% of their total energy use (GBS, 2020). The conversion of biomass into products with higher calorific value and, consequently, higher added value has the potential to provide a significant part of the expected renewable energy for the future as biofuels in the form of solid, gas, and liquid fuels (Bridgwater, 2018). Among several biomass conversion processes, fast catalytic pyrolysis has shown significant advances in bio-oil generation that can be employed as a fuel that offers the advantages of easy

storage and transport. However, despite all the progress, discoveries of new biomass sources and catalytic beds capable of upgrading pyrolysis products are still fundamental to reducing fossil fuel use and GHG emissions (Liu et al., 2022). The crude oil resulting from pyrolytic processes commonly presents undesirable characteristics, including high viscosity and acidity that account for the bio-oil chemical instability, which hinders its direct use and its miscibility in fossil fuels. These properties that adversely affect bio-oil quality arise most likely from its high oxygen/nitrogen contents (Rossi et al., 2021). Studies aimed at converting these compounds into hydrocarbons and increasing bio-oil energy density are significantly needed to generate products that would be viable competitors against fossil fuels.

Microalgae have emerged as a promising biomass energy crop for thermochemical conversions. They are highly efficient photosynthetic microorganisms that offer various advantages, including rapid growth, the ability to thrive in non-land cultivation, simple nutrient requirements, resilience in hostile environments, and significant CO₂ fixation capabilities. Microalgae are rich in oil, making them a valuable feedstock for pyrolysis, leading to the production of environmentally friendly bio-oil with low sulfur content. Recent studies indicate that microalgae pyrolysis generates bio-oil with superior characteristics compared to lignocellulosic biomass, as it can efficiently convert oxygenated compounds and polycyclic aromatic hydrocarbons (PAHs) into valuable products under optimized conditions (Babich et al., 2011; Aysu et al., 2017; Gao et al., 2017; Lee et al., 2020). Hence, the present study focused on assembling a distinct pyrolysis setup by selecting specific biomass. The *Schizochytrium limacinum* microalgae were chosen due to their chemical composition since microalgae species with a high content of carbohydrates and lipids have great potential for biofuel production because these compounds have higher energy content than proteins (Li et al., 2019; Aniza et al., 2021). Subsequently, a new catalytic bed composed of two catalysts (NiHTC followed by NiHZSM-5) was developed to improve the liquid product resulting from the *Schizochytrium limacinum* microalgae thermochemical conversion.

In addition to the analytical pyrolysis conducted to identify the potential compounds formed within this specific setup of the *Schizochytrium limacinum* microalgae and the tandem catalytic bed of NiHTC and NiHZSM-5, this study also encompassed pilot-scale experiments employing two distinct heating methodologies: solar energy and microwave-assisted pyrolysis. These setups can offer advantages compared to the conventional electrical heating system in

pyrolysis processes. For instance, solar heating offers advantages, including its eco-friendly energy source, minimal environmental footprint, creating temperature zones conducive to curtailing secondary reactions, and promoting enhanced liquid yield (Zeng et al., 2017; Sobek et al., 2020). Furthermore, microwave pyrolysis facilitates uniform internal heating of larger biomass particles with higher heating rates, which can reduce reaction time and contribute to employing a semi-continuous process (Ma et al., 2017; Zhang et al., 2015).

1.1. Objectives

The main objectives of this thesis are: (i) to perform the pyrolysis of the microalgae *Schizochytrium limacinum* in a double catalytic bed; (ii) to evaluate the effects of the reaction temperature and the double catalytic bed (NiHTC followed by NiHZSM-5) on the product distribution, and on bio-oil features in three distinct pyrolysis setups: (1) analytical; (2) solar; and (3) microwave.

Specifically, the objectives are:

- to characterize the biomass;
- to impregnate nickel in the catalysts to obtain metallic sites;
- to characterize the catalysts;
- to analyze the quantity and quality of the bio-oil resulting from the three distinct pyrolysis setups;
- to evaluate the effects of the reaction temperature;
- to evaluate the influence of the double catalytic bed on products distribution and bio-oil characteristics;
- to evaluate the effects of different ratios of total catalyst/biomass in products distribution and bio-oil characteristics;
- to estimate the biomass energy content/conversion through the process energy balance;
- to propose mechanisms for hydrocarbon formation.

1.2. Thesis structure

This Ph.D. thesis is divided into 9 chapters, as described below:

Chapter 1 comprises the introduction of this study.

Chapter 2 presents the literature review, comprising the theoretical basis for the thesis development.

Chapter 3 comprises the materials used, and the methodologies adopted for conducting analytical, solar, and assisted-microwave pyrolysis experiments.

Chapter 4 discusses the characterization of the *Schizochytrium limacinum* microalgae and the catalysts hydrotalcite and zeolite.

Chapter 5 discusses the results of analytical pyrolysis in the tandem catalytic bed composed of hydrotalcite and zeolite. Effects of the temperature, catalysts' ratios, catalysts synthesis, and pre-treatment are evaluated.

Chapter 6 discusses the results of solar pyrolysis in the tandem catalytic bed composed of hydrotalcite and zeolite. The influence of the variables on the distribution of the products. Subsequently, the bio-oil chemical composition and HHV were investigated.

Chapter 7 discusses the results of microwave-assisted pyrolysis in the tandem catalytic bed composed of NiHTC/SiC and NiHZSM-5/SiC. The reuse and regeneration of the catalysts are investigated, as well as the energy content of bio-oil fraction.

Chapter 8 presents the summarized conclusions of this study.

Chapter 9 gives suggestions for future work related to this present study.

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CHAPTER 2

2. LITERATURE REVIEW

In this chapter, the theoretical basis for the thesis development is presented.

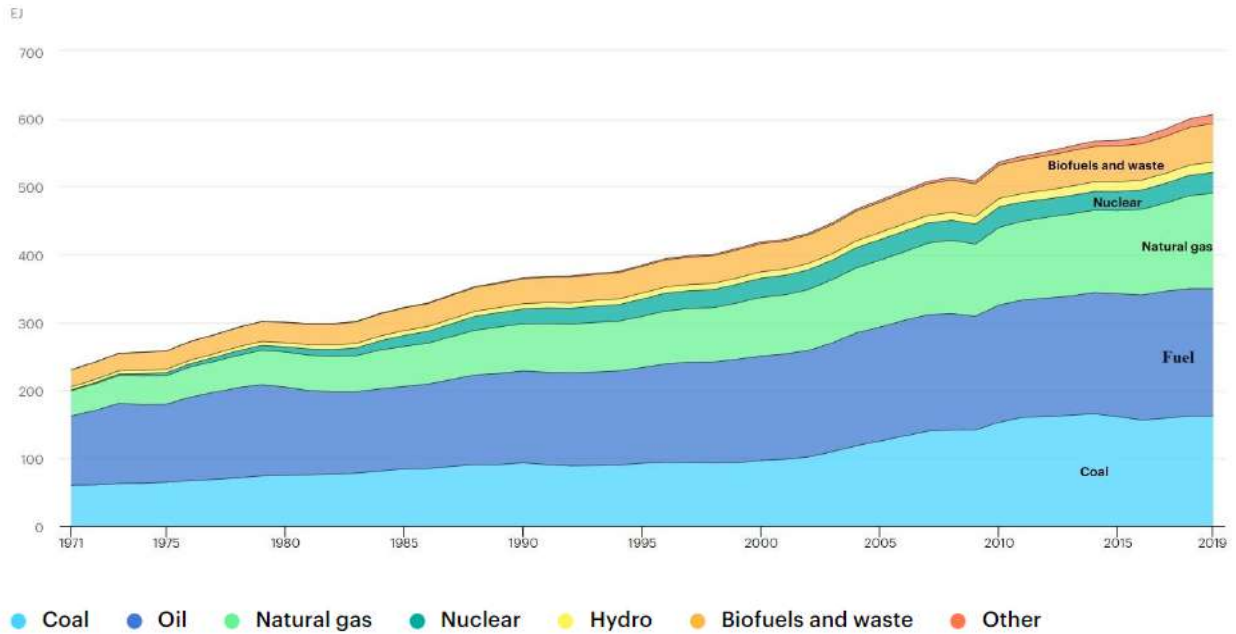
2.1. Renewable energy overview

The use of bioenergy has increased by ~7% on average per year between 2010 and 2021 and is a continuous upward trend. However, more efforts are needed to accelerate bioenergy deployment to achieve the Net Zero Scenario (NZE) by 2050. The concern in mitigating climate change is a great challenge that faces modern society and might increase geopolitical unrest as regards the roles that need to be developed by distinct nations involving their economy, development, and cultural peculiarities (Potrč et al., 2021). The current global energy system demands a reduction in the dependency on coal, oil, and gas through the deployment of renewable energy generation and improvement in energy efficiency worldwide (Yildizbasi, 2021). Figure 2.1 (a) shows the progressive growth in primary energy supply from 1971 to 2019. Notably, there has been a pronounced surge in renewable energy production from the 1970s to the present day, following the overall primary energy demand. Fig. 2.1 (b) and (c) present the difference between the global primary energy supply in 2018 and 2020. Despite some discernible progress, the data indicates a marginal increase of 1% in renewable energy generation. This demonstrates that renewable energy growth is still shorter than necessary to respond to today's energy crisis. The transport sector is one of the economic segments that lack the most, regarding renewable energy use. As indicated in Fig. 2.2, 91% of the global energy used in transport in 2019 came from fossil fuels, while renewable fuels accounted for only 3.6%. In 2020 the transport sector contributed to 7.6 GtCO₂, representing 14% of global emissions (EGR, 2022).

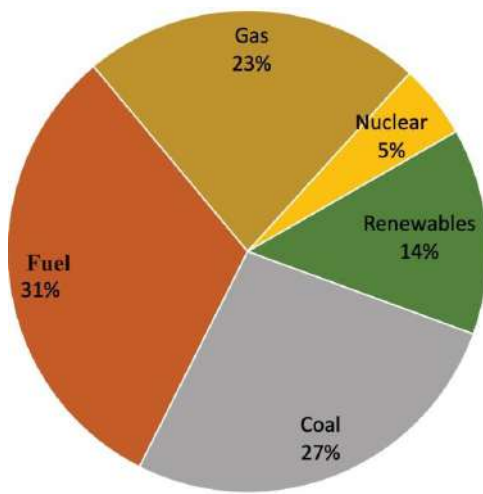
The global surface temperature is estimated to be between 1.5 to 4.8°C higher during the twenty-first century, depending on the GHG emission scenario (Pörtner et al., 2022). Thus, a fair, inclusive, and thriving energy transition that accounts for using renewable energy instead of fossil fuels may help achieve a low-GHG emission scenario (Anwar et al. 2021). The energy transition

to halt climate change involves the further development and deployment of zero-emissions technologies that would synchronize the scaling up of green energy technologies with the scaling back of fossil fuels. Consequently, progressive decarbonization is entirely dependent on the speed at which clean energy investment scales up (IEA, 2022).

a)



b)



c)

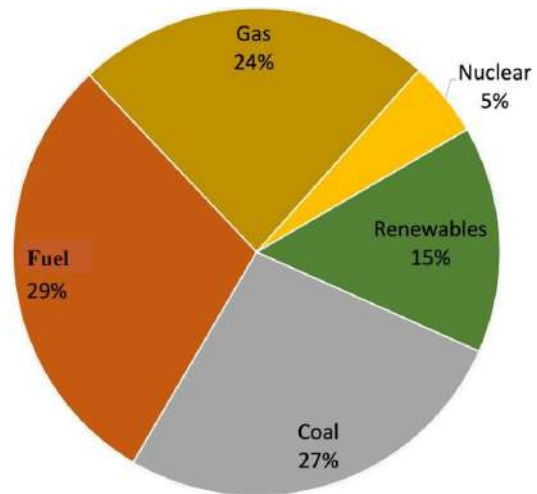


Fig. 2.1. Total primary energy supply globally from (a) 1971 to 2019, (b) in 2018, and (c) 2020 (IEA, 2019; GBS, 2020; GBS, 2022).

Renewable energy is obtained from natural and unlimited sources, accounting for low environmental impact. Advances in research and growing investment are essential elements to achieve a sustainable energy system and meet the Sustainable Development Goals (SDG) built by the United Nations (UN) (SDGR UN, 2022).

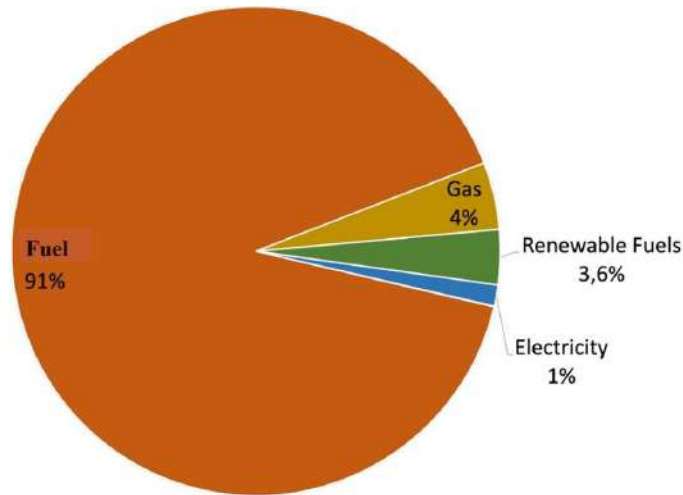


Fig. 2.2. Global energy use in transport in 2019 (GBS, 2022).

Fig. 2.3 summarizes the international financial investment and provisions to support efficiency and clean energy from 2021 to 2030. Many companies and organizations have established goals to decrease fossil fuel consumption. Ergo, they have been raising their investment in clean energy technologies. As shown in Fig. 2.3, for every USD 1 spent globally on fossil fuels, USD 2, USD 3, and USD 9 will be spent on clean energy supply plus efficiency and end-use in the Stated Policies Scenario (STEPS), Announced Pledges Scenario (APS), and Net Zero Emissions by 2050 (NZE) scenarios, respectively. Investments in green energy have a favorable political framework for their full implementation. In general, most global decision-makers are promoting an atmosphere of an international agreement to make renewable energy reliable, profitable, and economically competitive, which might lead to a low-carbon economy for sustainable future generations (Jahanger et al., 2022). The development and optimization of the production of clean and renewable fuels are necessary to lead the energy sector toward a sustainable future (Andrade et al., 2019) since alternative forms of clean energy production can bring social, economic, and environmental benefits to the population. The search for sustainable

alternatives can arise in several aspects, such as using clean energy sources (solar, wind, and geothermal energy) and biomass thermal conversion.

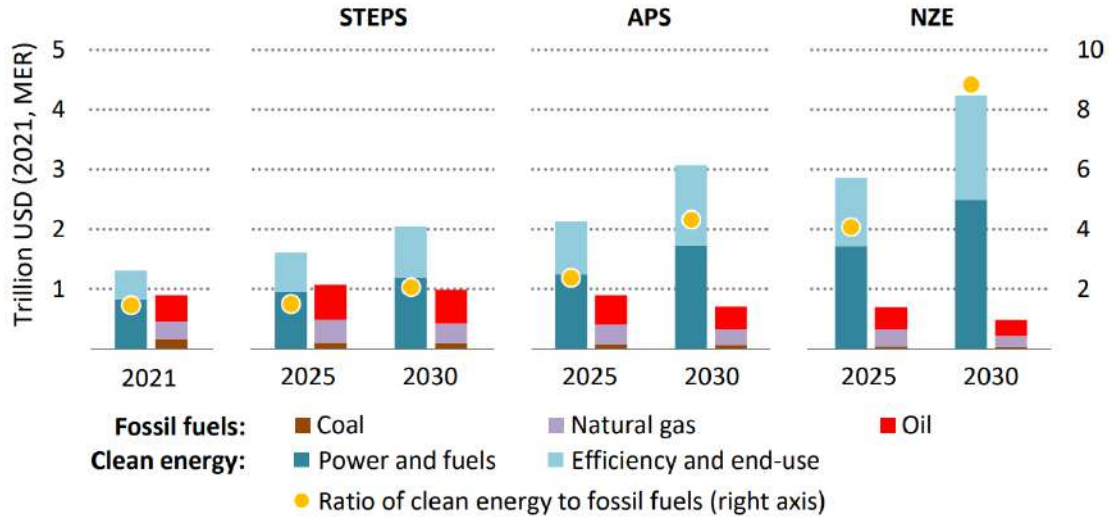


Fig. 2.3. Investment in clean energy and fossil fuels by scenario, 2025 and 2030 (IEA, 2022).

2.1.1. Solar energy

Solar energy systems have proved to be one of the best sources of free renewable energy to provide clean power and account for minimal environmental impact. The sun is a significant radiation source resulting from hydrogen fusion that occurs in its core, and it can provide $\sim 1.1 \times 10^{22}$ J per day. This energy can be converted in versatile ways such as heat, electricity, and solar fuels (Hayat et al., 2019). The use of solar energy has gained substantial attention worldwide, as indicated in Fig. 2.4, which shows the world's non-fossil energy supply (data and provision) by source. The increment in solar energy supply is estimated by 130 EJ/yr between 2020 and 2050, which will represent 14% more in the global share of primary energy supply (DNV, 2022). Brazil is an essential player as regards solar energy generation. The Brazilian territory is located in the world's intertropical region, which has a high incidence of solar radiation throughout the year. Figure 2.5 displays the 2019 solar atlas for global horizontal irradiation (GSA, 2019). Together with Africa and Oceania, South America, especially Brazil, presents excellent global horizontal irradiation, which might account for significant installed capacity for solar generators.

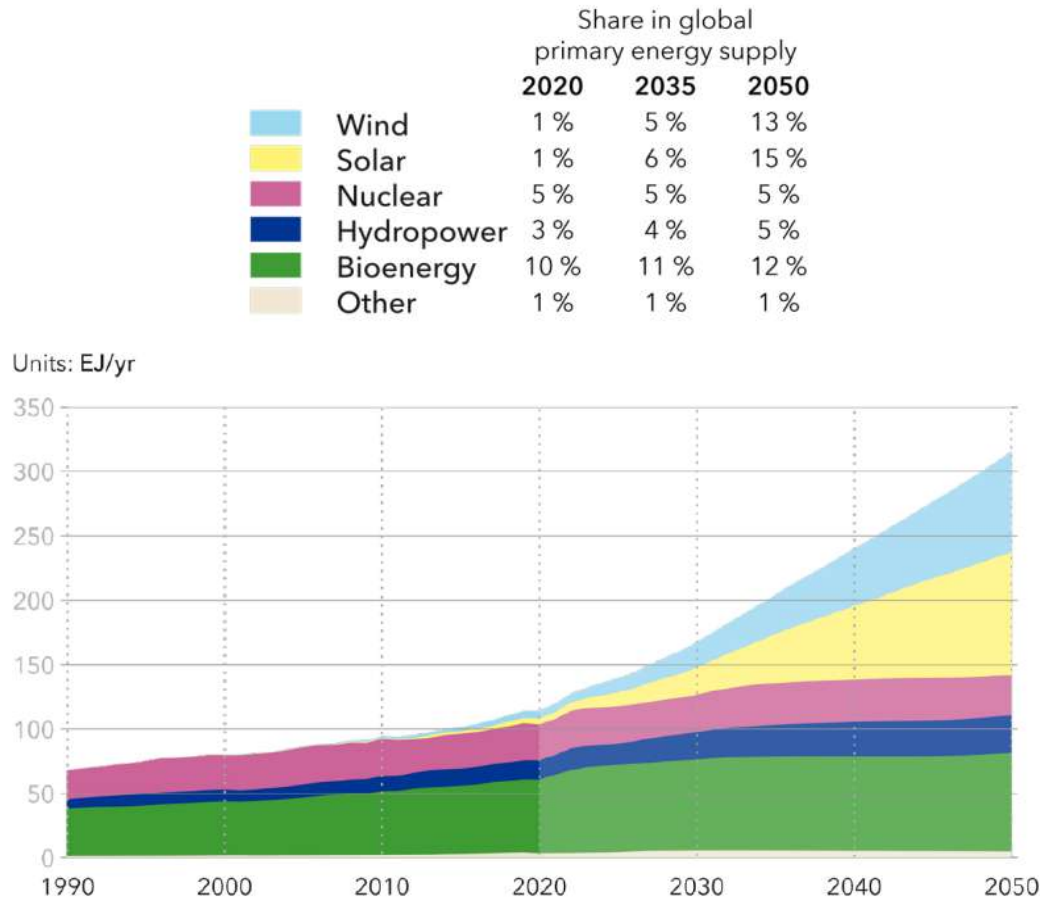


Fig. 2.4. World's non-fossil energy supply (data and provision) by source in EJ/yr (DNV, 2022).

According to the Brazilian Atlas of solar energy (GSA, 2019), the country receives, throughout the year, more than 3000 hours of sunlight, corresponding to a daily solar incidence that can range from 4.5 to 6.3 kWh/m². The region with the highest energy availability is the Northeast, with 5.9 kWh/m² of average radiation. Comparatively, Germany, the country that most explores photovoltaic energy globally, receives approximately 40% less sunlight in its region of most significant potential compared to the Brazilian incidence (IRENA, 2023). In this scenario, solar radiation is one of Brazil's promising renewable energy sources and can offer a significant advantage over conventional forms of energy production as regards GHG emissions. Brazil reached 8th in the global solar energy generation ranking in 2022. However, this represents less than 2% of the primary energy supply, meaning solar energy has room for continuous growth (OWD, 2021). Consequently, studies focused on enhancements for solar energy use and the

development of efficient systems are significantly needed. In this way, the regulatory aspects and economic viability must be increasingly improved so that this source can follow the pace, evolution, and demand needs of the energy market.

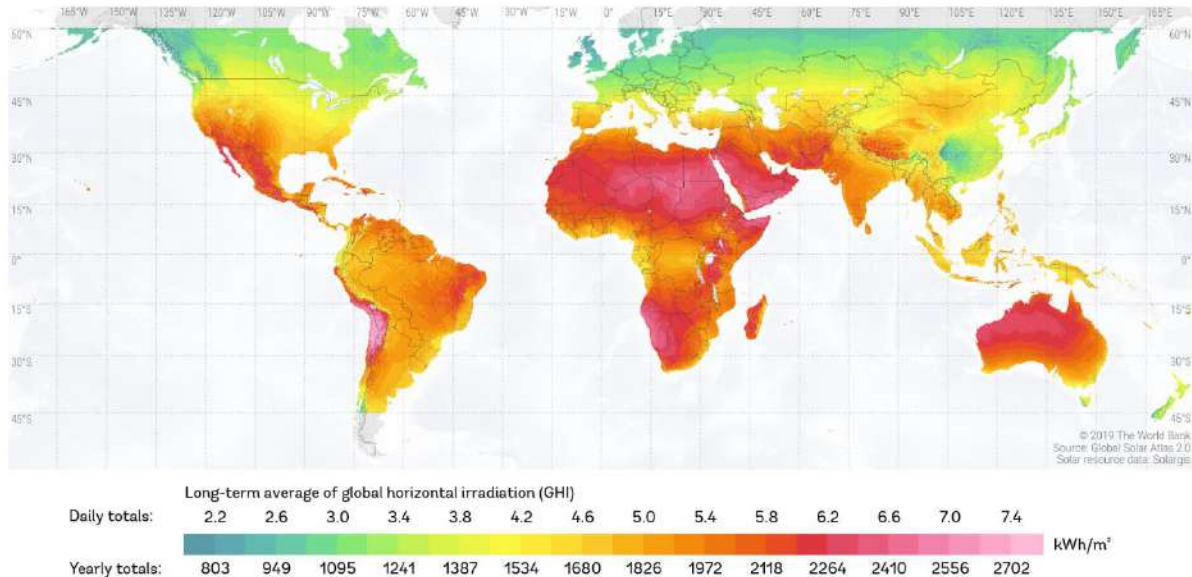


Fig. 2.5. Solar atlas for global horizontal irradiation (GSA, 2019).

2.1.2. Biomass energy

Biomass is organic matter that comprises, among others, crops, woody, manure, and organic waste. Among renewable sources, biomass plays a crucial role in supporting the development of one's economy allied with the energy transition from fossil fuels to green energy towards the environmentally sustainable growth that is currently needed (Liu et al., 2022). In other words, biomass energy can decarbonize the economy through its direct and indirect consumption. Bioenergy refers to the use of biomass for energy purposes, which implies its burning for electricity and heating generation or its conversion into biofuels for transportation (Danish et al., 2020). Bioenergy efficient use is decisive in achieving the Sustainable Development Goals (SDGs) proposed by the United Nations. Thus, biomass implementations and contributions must be sustainably managed to accomplish a near-zero-emission scenario (Destek et al., 2021).

Fig 2.6 compiles the global renewable heat production by source between the years 2000 and 2020. The data shows an upward trend as regards biomass use. In 2020, 96% of all renewable

heat produced worldwide was from biomass (Fig. 2.6), and its domestic supply was 57.5 EJ globally, being 86% from solid biomass sources such as wood chips and pellets. Liquid biofuels and municipal and industrial waste accounted for 7 and 6%, respectively (GBS, 2022). Regarding the global electricity generated from biomass usage, 69% of all biopower came from solid biomass sources, followed by 17% from municipal and industrial waste, which totalized 685 TWh of electricity in 2020, representing 9% of the total global electricity that was generated (3% more than the biopower generated in 2000) (GBS, 2022), as shown in Fig. 2.7. Overall, the use of biomass has been gradually increasing over the years. However, over 35% of the bioenergy used in 2021 was generated from the traditional use of biomass, including less efficient practices such as combustion. To achieve the UN Sustainable Development Goal 7 (Affordable and Clean Energy) is necessary to increase modern usage of biomass, such as its thermochemical conversion, to result in higher energy efficiency and, consequently, lower GHG emissions (IEA, 2022; Majeed et al., 2022).

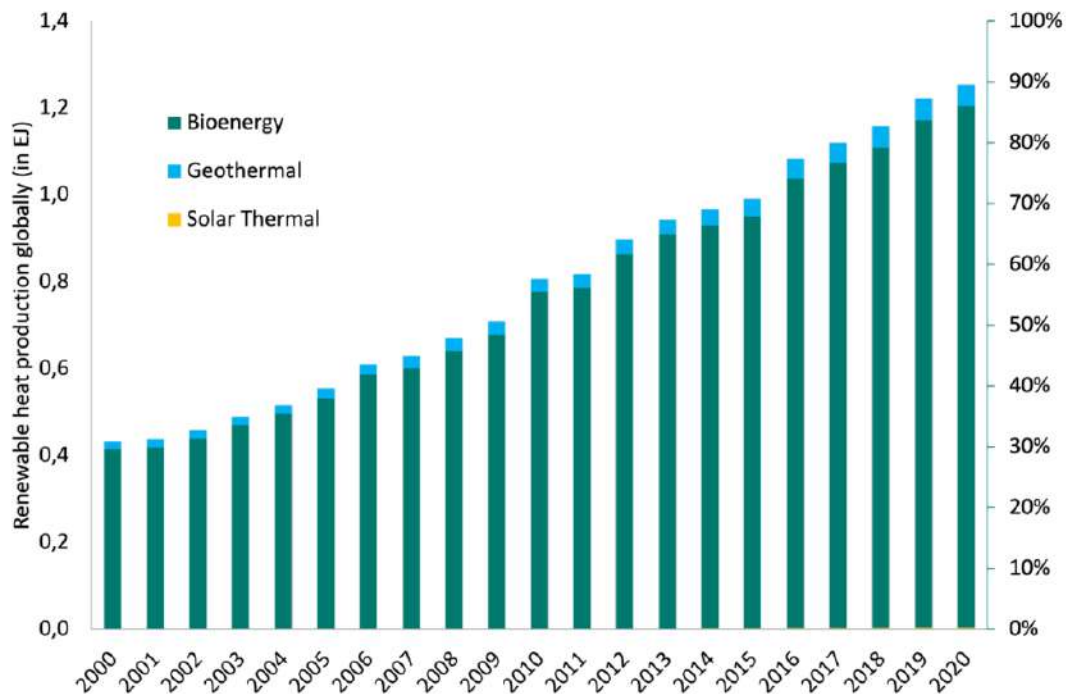


Fig. 2.6. Global renewable heat production by source (GBS, 2022).

In addition to thermochemical conversion, there is bioenergy with carbon capture and storage (BECCS), which can accomplish negative emissions by capturing and storing bioenergy

emissions that are already carbon neutral. In 2022, BECCS removed 2 Mt of CO₂ from the atmosphere. The provision for 2030 would be the removal of 250 Mt of CO₂ to offset emissions from sectors where abatement will be most difficult (GBS, 2022).

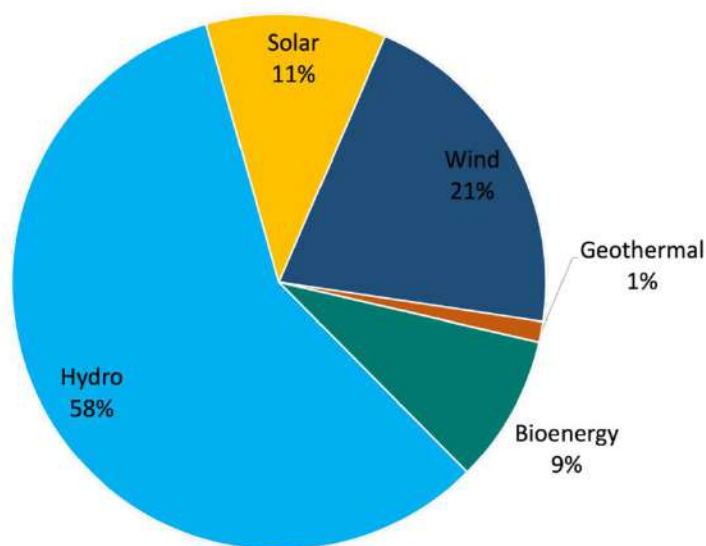


Fig. 2.7. Global renewable electricity production by source in 2020 (GBS, 2022).

2.2. Thermochemical processes of biomass

Biomass is an environment-friendly resource that supports a carbon-neutral economy. The search for increasing the share of renewables and enhancing the efficiency of biomass use through the development of effective clean energy systems will assist in improving energy access and demand, resulting in a minimum impact on nature (Koniuszy et al., 2020). Biomass can be converted to energy via thermal processes, which lately have gained attention due to promising findings regarding biomass degradation into a more useful energy carrier. Among the thermal processes, pyrolysis offers potentially higher efficiencies compared with combustion. The liquid fuel explicitly obtained from fast pyrolysis currently attracts the most interest since it can be easily stored and transported. In addition, on a small scale, pyrolytic biofuel can reach higher power generation efficiency when compared to other bio-energy systems, resulting in a more useful energy form (Gyamfi et al., 2021; Bridgwater, 2012). Figure 2.8 shows the steady increase in

biomass used in heat generation from 2000 to 2020. Figure 2.9 reveals a significant percentage of 90% of the global renewable energy used in transport in 2020 since biofuel is a sustainable option for the sector.

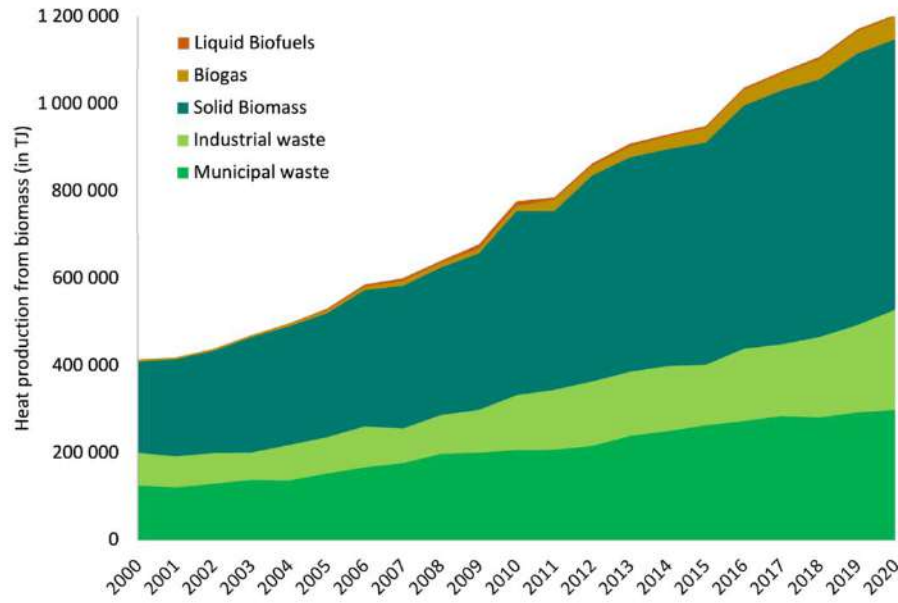


Fig. 2.8. Global Bioheat production (GBS, 2022).

However, despite the rise in biomass use in the energy sector, the production of biofuels remains below the necessary to reach net zero emissions (GBS, 2022). The traditional use of biomass needs to be switched at speed to its modern usage, which produces more efficient biofuels. In the NZE scenario, the conventional use of biomass will be reduced to neglectable values by 2030 and 2050 (Fig. 2.10) (IEA, 2022). Pyrolysis of biomass might be one of the solutions to increase processes that can handle several different fuels, either mixed or separately broadened product applications. The optimization of pyrolytic biofuel quality is a significant step to aggregate value and increase their share in the energy mix (Mahmood et al., 2019). Therefore, several studies have investigated new approaches to produce higher yields of biofuels with desirable characteristics (lower acidity, greater stability, and higher heating value) to allow them to be viable competitors to fossil fuels. Pyrolysis process design, operation parameters, and the raw material used in the system strongly affect the products' yield and composition (Zhang et al., 2019). Thermochemical routes are characterized by the thermal decomposition of organic matter to

produce biofuels. Carbonaceous raw materials, consisting of carbon and hydrogen, can be suitable reagents due to their power to store energy in liquid fuel form (Guedes et al., 2018).

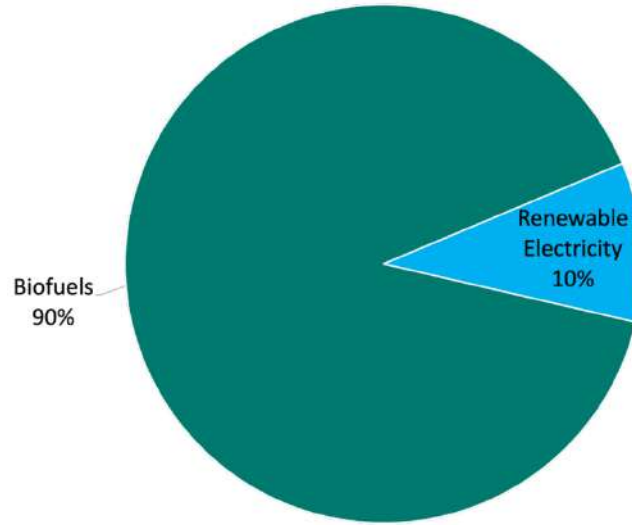


Fig. 2.9. Global renewable energy use in transport in 2020 (GBS, 2022).

Pyrolysis is the thermal decomposition of organic matter that occurs in the partial or total absence of oxygen at temperatures between 350 to 700°C and results in solid, liquid, and gaseous products. Research on fast pyrolysis of biomass has advanced significantly in recent years, and it is mainly used for liquid production. Fast pyrolysis technology can have relatively low-cost investments and high efficiency compared to other processes, especially on small scales (Choi et al., 2019; Bridgwater, 2006). The search for biomass options that can provide better quality in bio-oil is fundamental since the raw material's composition greatly influences biofuel characteristics.

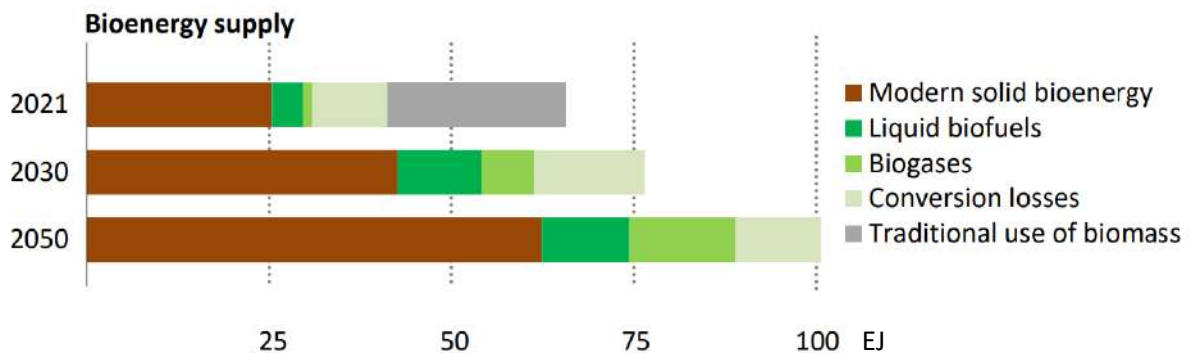


Fig. 2.10. Bioenergy supply production by source in the NZE Scenario, 2021-2050 (IEA, 2022).

A type of biomass energy crop that lately has gained focus in thermochemical conversions is microalgae. Microalgae are microscopic unicellular organisms generally found in marine and aquatic environments (Andrade et al., 2020; Rossi et al., 2021a). They are highly efficient photosynthetic microorganisms (prokaryotic or eukaryotic) and present advantages over other organic materials, such as high growth rates, cultures that thrive in non-land cultivation, and require simple nutrient requirements. Microalgae also can survive in hostile environments and account for high CO₂ fixation that mitigates GHG emissions (Lee et al., 2020a). In addition, they are rich in oil and have demonstrated outstanding potential as pyrolysis feedstock in generating energy-dense and valuable pyrolytic products such as bio-oil (Lee et al., 2020b). Usually, microalgae contain protein, lipids, and carbohydrates, which are suitable for thermal conversion. Fast pyrolysis of microalgae leads to high bio-oil recovery, a biofuel that is environmentally beneficial in terms of air pollution controls since it is absent in sulfur (Li et al., 2021). Recent studies showed that microalgae pyrolysis presented a bio-oil with better characteristics than those obtained from lignocellulosic biomass (Table 2.1) as their oxygenated compounds and polycyclic aromatic hydrocarbons (PAHs) released during the pyrolysis process can be converted into valuable products under optimized reaction circumstances. Table 2.1 compares the HHV of the bio-oil produced from different lignocellulosic biomasses and microalgae species.

Microalgae species with a high content of carbohydrates and lipids have great potential for biofuel production since these compounds have higher energy content than proteins (Li et al., 2019; Aniza et al., 2021). *Schizochytrium limacinum* (*S. limacinum*) (biomass used in this study and shown in Fig. 2.11) is a brown marine spherical unicellular microorganism (sized between 10-20 µm). It has been considered an important algae species in biofuel research due to its high oil content and low protein percentage of its composition (Johnson et al., 2009). Bindea et al. (2018) investigated the production of docosahexaenoic acid (DHA) production by optimizing this microalgae's culture conditions. Li et al. (2013) ascertained fast pyrolysis of *S. limacinum* in the absence of catalysts. Their results showed that the major compounds generated were tetradecanoic acid and hexadecanoic acid. The high quantity of organic acids generated from this microalgae specie can be converted into hydrocarbons using an adequate catalytic bed. These studies indicate that fast pyrolysis of appropriate algae can improve the yield and quality of the bio-oil.

Table 2.1. Comparison of HHV of lignocellulose materials and microalgae species.

Biomass	Class	Pyrolysis Parameter	Bio-oil HHV [MJ/kg]	Reference
<i>Chlorella</i>	Microalgae	Catalytic slow pyrolysis	32	Babich et al. (2011)
<i>Pavlova</i>	Microalgae	Catalytic fast pyrolysis	36	Aysu et al. (2017)
<i>Cynobacteria</i>	Microalgae	Catalytic slow pyrolysis	38	Gao et al. (2017)
<i>Nannochloropsis sp.</i>	Microalgae	Catalytic fast pyrolysis	37	Guo et al. (2015)
Wood	Lignocellulosic	Catalytic fast pyrolysis	19	Bridgwater et al. (2000)
Pine sawdust	Lignocellulosic	Catalytic fast pyrolysis	18	Nokkosmaki et al. (2000)
Larch wood	Lignocellulosic	Catalytic fast pyrolysis	22	Suzuki et al. (2009)
<i>Miscanthus giganteus</i>	Lignocellulosic	Catalytic fast pyrolysis	29	Yorgun et al. (2008)
Rice husk	Lignocellulosic	Catalytic fast pyrolysis	26	Zhou et al. (2013)

**Fig. 2.11.** *Schizochytrium limacinum* microalgae dry powder.

2.3. Analytical pyrolysis

Analytical pyrolysis (Py-GC/MS) is notoriously a powerful technique for the analysis at a molecular level of the chemical composition of pyrolysates. Py-GC/MS has been widely used in biomass research to characterize products, optimize reaction conditions, screen catalysts, and study

the process' reaction mechanisms (Nardella et al., 2021). Analytical pyrolysis is a practical technique that enables fast thermal decomposition in the absence of oxygen to characterize macromolecular samples and offers distinct advantages, such as high operational stability and reproducibility, permitting the performance of many experiments in a short period. In addition, no special sample treatment or extraction is needed, which avoids using aggressive chemicals in sample preparation. For this reason, Py-GC/MS can be used to quickly investigate the influence of raw materials and catalysts under different conditions, giving it a first sense of what can be expected in the degradation process (Kumagai et al., 2020a; Šimkovic et al., 2023). Analytical pyrolyzers or micro-pyrolyzers are equipped with controllable heating rates and analytical equipment with a wide detection range for organic compound characterization. The biomass is subjected to thermal treatment, and then the volatiles produced are identified using a gas chromatograph and mass spectrometer (GC/MS) (Coralli et al., 2023).

In a Py-GC/MS system, a micro-pyrolizer is connected directly to a GC/MS injector. A minor part of the volatiles is drawn into the column, carried by an inert gas, usually helium, to reduce background interferences. A mass spectrometer (MS) is often coupled with a gas chromatograph (GC) for qualitative analysis of pyrolytic products. The identifications are performed by a mass spectrum library (Nardella et al., 2022). The semi-quantitative data acquired from the spectrum library is used to perform principal component analysis, highlighting the differences in bio-oil composition. The method estimates the composition of the pyrolysis oils based on the chromatographic peak areas and the chemical formulas of the identified pyrolysis products (Santana Junior et al., 2019). Substantial progress has been made during the past few decades in developing analytical pyrolysis systems. Thus, various types of micro-pyrolyzers have been developed to perform biomass thermochemical conversion. Micro-furnace pyrolyzers, filament pyrolyzers, and Curie-point are the most widely used and differ from each other based on their heating mechanism. Its application has extended to biomass thermochemical technologies, including catalytic pyrolysis and gasification, to explore optimal reaction conditions (Li et al., 2022; Kumagai et al., 2020b).

Due to operational stability and nimbleness, analytical pyrolysis has been widely used to investigate several biomass/catalysts setups for thermochemical conversion research since the operating conditions such as temperatures, heating rates, reaction atmosphere, and pressure can be easily adjusted and controlled by a micro-pyrolyzer (Li et al., 2022). Santana Junior et al. (2019)

performed analytical hydropyrolysis from industrial Kraft lignin using ZSM-5. Their results showed a high formation of aromatic hydrocarbons, reaching 98% in selectivity for these compounds. Mariyam et al. (2022) investigated the pyrolytic behavior of waste biomass that generated bio-oil with carbon chains ranging from C2–C33 suitable for gasoline production. Yu et al. (2018) conducted analytical pyrolysis experiments of microalgae over oil shale. Their findings indicated that the high H/C ratio of the oil shale accelerated the production of hydrocarbons, which was beneficial in improving the quality of pyrolytic bio-oil.

Analytical pyrolysis is a robust tool to investigate the pyrolytic behavior, the composition of the pyrolysis oil, and the synergistic effects of different biomass/catalyst configurations. Py-GC/MS is used in this study to evaluate the composition of the pyrolytic vapors obtained from *Schizochytrium limacinum* microalgae under distinct temperatures and catalysts' ratios using a vertical-type micro-furnace pyrolyzer as shown in Fig. 2.12. Although analytical pyrolysis has been employed in several biomass conversion studies, evaluating *Schizochytrium limacinum* microalgae decomposition using a double catalytic bed is scarce.

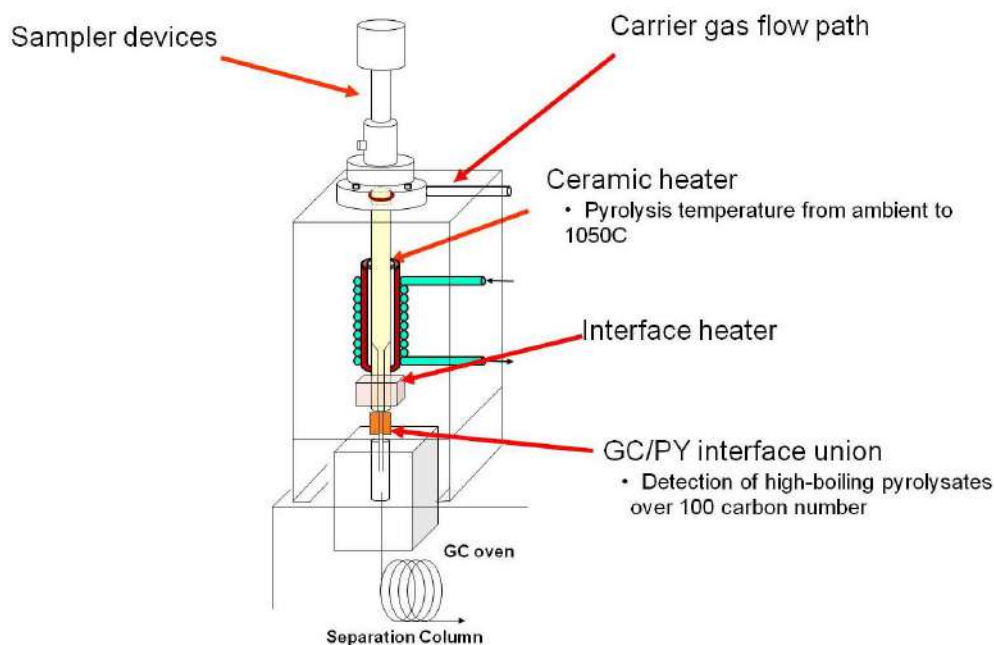


Fig. 2.12. Schematic drawing of the vertical-type micro-furnace pyrolyzer (Quantum Analytics, 2023).

2.4. Solar pyrolysis

Sun is an inexhaustible energy source capable of fulfilling a significant role in the global energy need. Solar energy can be converted into electricity through photovoltaic (PV) cells or used directly with concentrated solar power (CSP) technology (Dudziak et al., 2022). Solar collectors are usually classified into two categories: (1) non-concentrating collector that has the same intercepting and absorbing areas; and (2) sun-tracking concentrating solar collector that usually has a concave reflecting surface to intercept and focus the solar irradiation into a much smaller receiving area, resulting in an increased heat flux that achieves higher Carnot efficiency in their thermodynamic cycle once working under higher temperatures (Streicher, 2016). Solar radiation provides higher heating power densities when compared to conduction and convection due to the lack of contact between the energy source and matter. The conversion of radiated energy into heat takes place through absorption (Hayat et al., 2019). Concentrated solar technologies have a promising future because of their high capacity, efficiency, and energy storage capability.

Moreover, the advancement in solar energy use will help to enhance the pace toward an environment-friendly and sustainable future (Abro et al., 2019). To produce solar fuels, solar radiation is concentrated through optical devices (such as gutters, parabolic dishes, or Fresnel reflectors) that can achieve the high temperatures required for thermochemical conversion, harnessing the energy of sunlight to drive the synthesis of molecular fuels and chemical feedstocks (Rossi et al., 2021b). Figure 2.13 shows two types of concentrating solar collectors. For solar thermal applications, concentrating solar collector converts solar irradiation energy into thermal energy by absorbing solar irradiation as heat and then transferring it to its working material, such as biomass (Tian et al., 2013). A solar parabolic dish collector is a system that reflects the rays of incident sunlight at the reflector's focal point, where the reactor is fixed to absorb the heat. Solar pyrolysis, which uses emission-free solar heat, opens a new possibility for biomass degradation (Sobek et al., 2020a). Solar-thermal biomass conversion technology usually comprises: (1) a solar concentrator for heat acquisition; (2) a two-axis tracking mechanism that keeps the dish always normal to the incoming solar radiation, forcing its efficient utilization for pyrolysis purposes due to the increased radiation and utility of the sunlight acquired by and (3) the reactor as a radiation receiver of solar heat (Andrade et al., 2016).

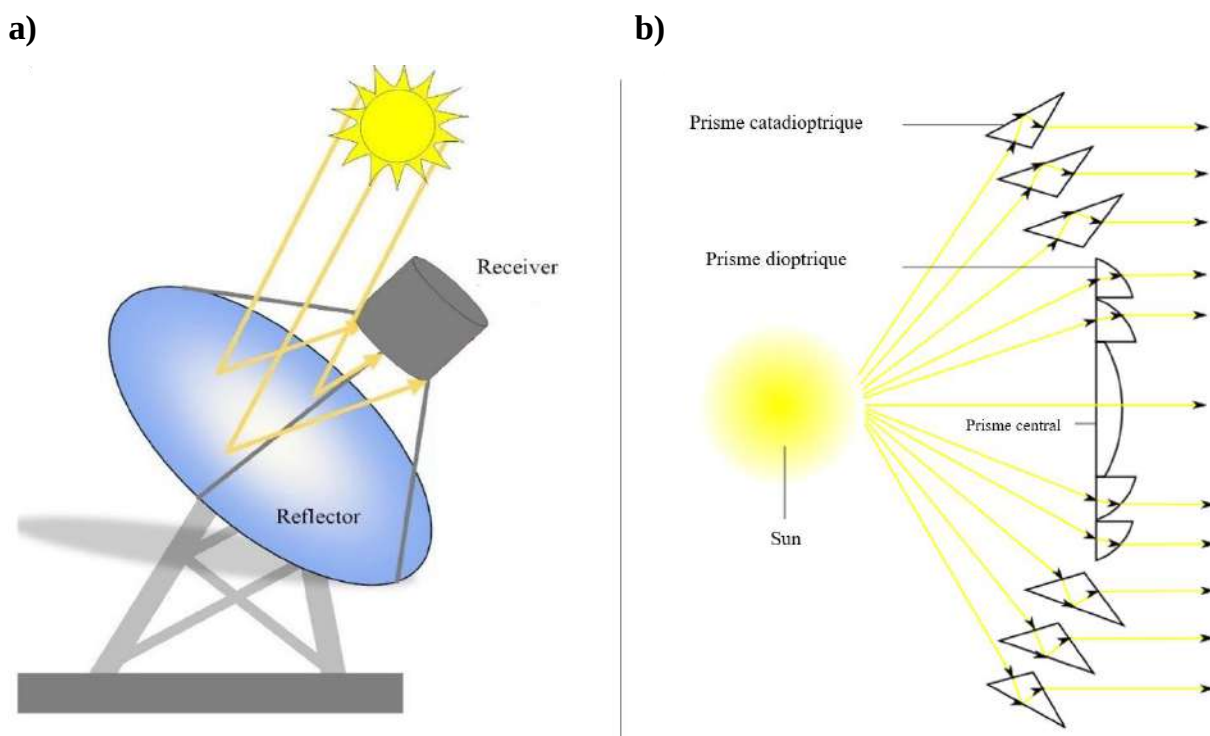


Fig. 2.13. Schematic drawing of concentrating solar collectors: (a) parabolic dish and (b) Fresnel reflector (adapted from Soomro et al., 2019).

Compared to conventional pyrolysis, solar pyrolysis has advantages such as high temperatures and heating rates and more agile systems at start-up and shutdown. It has the potential to produce higher calorific value products with lower CO₂ emission compared with conventional pyrolysis, in addition to minimizing the intrinsic intermittency of some renewable energies (solar and wind, for example) (Chintala, 2018). Studies indicate that direct solar irradiation in the pyrolysis reactor causes an effect of two temperatures: a hot zone of volatiles (heated by the sun's rays) and a cold zone (circulating vapors); this effect causes a faster cooling of the gases that can minimize secondary reactions, which is advantageous for liquid production (Zeng et al., 2017; Sobek et al., 2020b). In the thermochemical conversion of biomass, reaction conditions, such as temperatures, heating rates, atmospheres, pressures, and layouts, can be adjusted depending on different target products (Hou et al., 2022). Biomass and solar energy can be converted into transportable solar fuels as biomass energy is upgraded through solar energy, providing pyrolysis reaction enthalpy transferred into products (Zeng et al., 2017).

2.5. Microwave-assisted pyrolysis

Assisted-microwave pyrolysis relies on the ability of the biomass to absorb microwave energy efficiently, taking advantage of microwave dielectric heating phenomena such as dipolar polarization and ionic conduction mechanisms (Gabriel et al., 1998). The in-core volumetric heating by the direct interaction of electromagnetic irradiation reaching the biomass molecules allows for rapid temperatures above the boiling point. Such temperature profiles could be difficult to reproduce using standard conductive heating methods. Effective microwave heating is dependent on material dielectric properties, i.e., dielectric constant (ϵ') and dielectric loss factor (ϵ''), which describe the ability of materials to couple with the applied electromagnetic field (Kappe et al., 2013). When a microwave goes through a particular dielectric material, the dipole molecule in the dielectric will make high frequency reciprocating motion in the electromagnetic field, resulting in internal friction heat, which causes the material temperature to rise. This process transforms microwave energy into heat energy through power dissipation (Ke et al., 2019). Due to the substances' different dielectric properties, their microwave absorption abilities are distinct. A material with a higher dielectric constant typically absorbs more microwave energy. Solid particles absorb most of the energy in a microwave, resulting in mass and energy transfer between solid and gaseous phases (Luo et al., 2021). The temperature of the solid phase rises with the continuous input of the microwave. Then water evaporation and volatile matter formation occur, simultaneously with the heating transfer into the gas phase. With the increase in temperature, some volatiles and fixed carbon begin to degrade (Robinson et al., 2022). With the absorption of microwave energy, the intensity of the electric field decreases. However, this attenuation can be neglected because the equivalent size of the material is considerably smaller than the penetration depth of the microwave (Ramirez et al., 2020).

For microwave heating of low-loss materials for pyrolysis applications, a microwave absorber is usually necessary to catalyze dielectric heating in the bulk material. Many microwave absorbers, including carbonaceous material, have been reported in the literature. Microwave-assisted pyrolysis is an emerging research area with applications in thermal converting feedstocks such as biomass, coal, and plastics (Ellison et al., 2020). Integrating microwave heating into pyrolysis has recently drawn attention due to its advantages compared to conventional electrical

heating methods, including higher heating efficiency and shorter reaction time (Borges et al., 2014). This method also provides uniform internal heating of large biomass particles, which reduces energy losses in the system, suppressing the need for reactor fluidization, which diminishes ash particles in the bio-oil. Furthermore, studies suggest that this is a highly scalable technology suitable for distributed conversion of bulk biomasses and has already been successfully applied to biomass pyrolysis (Zhang et al., 2018). Recently, a novel concept of microwave-assisted pyrolysis utilizing microwave absorbents has been developed. Using these absorbents with higher values of dielectric loss factor than biomass feedstocks can significantly improve the heating rate of the system (Wu et al., 2023). With minimal energy input through microwave irradiation, the reactor's temperature is steady when the solid residue is dropped directly onto the heated absorbent. Thus, the biomass is simultaneously heated through direct microwave irradiation and thermal conduction from the hot microwave's absorbents. This fact leads to a rise in the heating rate that could reduce the reaction time, assisting in obtaining higher yields and quality of bio-oil in addition to making a semi-continuously process feasible (Ma et al., 2017; Zhang et al., 2015).

2.6. Catalytic pyrolysis

Catalytic pyrolysis is a promising way to upgrade pyrolytic volatiles. Catalysts can be present in the thermochemical process in both *in-situ* and *ex-situ* configurations, as shown in Fig. 2.14. In the *in-situ* setup, the catalyst is mixed with the biomass in the same reactor in a more straightforward arrangement. However, the catalyst can hinder heat and mass transfers during feedstock degradation (Guo et al., 2020). The *ex-situ* configuration allocates the catalyst in a secondary reactor; this setup can produce high-quality biofuels with lower catalyst consumption and less coke formation, thus avoiding rapid catalyst deactivation and increasing its useful life. In addition, unlike in the *in-situ* process, catalysts can be recovered through regeneration after being used in *ex-situ* catalysis (Wan et al., 2014).

Bio-oil composition is complex. It might contain several nitrogenated and oxygenated compounds, including acids, aldehydes, ketones, phenols, nitriles, and amines, which can hinder its high-value application (Ansah et al., 2018). Using the appropriate catalyst can enhance the specific reaction pathways and promote the formation of desirable products, effectively improving bio-oil quality. Catalytic pyrolysis can assist hydrocarbon generation, mainly through

denitrification and deoxygenation reactions, which eliminate NH_3 , H_2O , CO_2 , and CO . The catalyst selection can be a satisfactory alternative to eliminate undesirable compounds for pyrolytic biofuel upgrading (Dai et al., 2019). Catalytic pyrolysis can significantly reduce the energy demand for breaking down chemical bonds. Thus, catalytic cracking effectively converts biomass into biofuels at lower temperatures, increasing conversion efficiency. This process can have a remarkable future in bio-oil generation. Recent studies suggest catalytic pyrolysis is an appropriate method to improve the liquid fraction produced from microalgae, reaching lower levels of undesirable compounds (Xu et al., 2020).

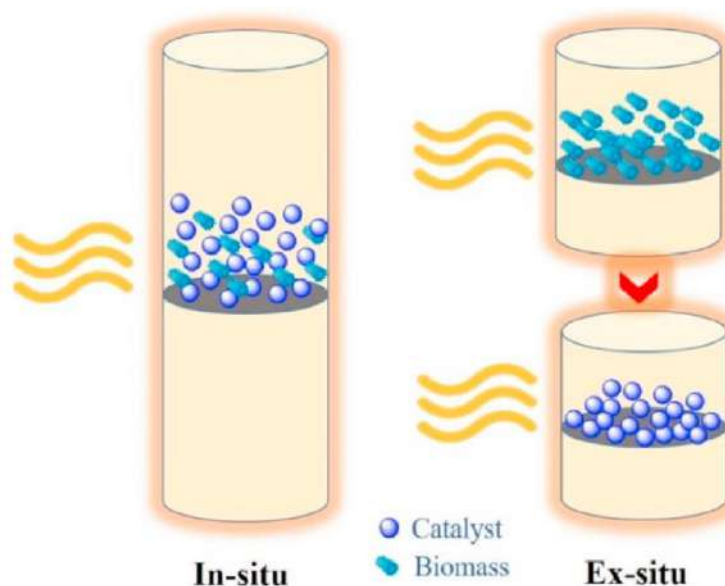


Fig. 2.14. Schematic drawing of *in-situ* and *ex-situ* catalytic pyrolysis (Li et al., 2021).

2.6.1. Catalysts

Several catalysts of different natures, such as metal oxide, acid, carbon-based, and metal catalysts, have been investigated to improve biofuels' quality. A satisfactory catalyst should be developed/studied based on standards such as conversion efficiency, suitable selectivity for desirable products, resistance to deactivation, mechanical strength, and low-cost synthesis (Fan et al., 2018). Different catalysts can perform on distinct routes and promote the removal of nitrogenous and oxygenated compounds through cracking and reforming reactions. Improving catalysts' properties is critical to overcoming some barriers, such as coke formation, deactivation,

and high costs. Zeolites are often used because of their topology and acidic strength, which can increase the hydrocarbon amount present in pyrolytic bio-oil (Ding et al., 2018). On the other hand, recently, studies using mixed oxides derived from hydrotalcite have emerged. Hydrotalcites are double hydroxides arranged in sheets derived from brucite (MgOH) layers. This type of catalyst has been highlighted in research due to its properties, such as large surface area and structure stability, its acid-base characteristics, and the low cost of synthesis (Barbosa et al., 2021).

The catalyst design can affect the selectivity of the product formation. The incorporation of a transition metal such as nickel (Ni) moderates the acid sites and leads to less coke formation, besides creating additional transport channels that assist hydrocarbon formation through the cracking of heavy fractions (Zainan et al., 2018; Jafarian et al., 2018). Recent studies suggest that heterogeneous catalytic pyrolysis from microalgae is an appropriate method to generate bio-oils that contain high-added value compounds, achieving higher yields and lower levels of oxygenated compounds. The improvement in oxygen removal assists the bio-oil stability and enhances energy density. A proper catalyst application might change the chain of reactions resulting in the bio-oil upgrade (Oh et al., 2016). Several researchers have examined the catalytic pyrolysis of microalgae materials. However, studies involving double catalytic bed in pyrolysis remain insufficient. To our knowledge, no studies have been reported using a tandem catalytic bed of metal-loaded hydrotalcite and zeolite. Hence research in developing new catalysts for microalgae thermochemical processes is needed. In the attempt to increase hydrocarbon generation and consequently provide high-energy outputs, hydrotalcite (HTC) can achieve good deacidification, while zeolite (HZSM-5) assists in the deoxygenation and aromatization reactions (Wiyantoko et al., 2015; Díez et al., 2003).

2.6.1.1. Hydrotalcite

Hydrotalcite is a double hydroxide clay arranged in lamellar layers and used as a catalyst precursor due to its structural properties. They are derived from layers of brucite (MgOH) and have the formula $[M_{(1-x)}^{2+} M_x^{3+}(\text{OH})_2] \cdot [A^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} occupy the six-coordinate octahedral interstitial sites for hydroxyl groups forming brucite-like compounds in sheets that stack up to create a layered structure (Andrade et al., 2018). Figure 2.15 shows the lamellar and interlayer compositions of hydrotalcite. Hydrotalcite has good potential to be applied as a catalyst due to its

large surface area and stability in its structure, its acid-base characteristics, its capacity to transport bioactive molecules, and the low cost of synthesis. Hydrotalcite has been used in applications such as ion exchangers, adsorbents, and CO₂ capture (Navarro et al., 2018).

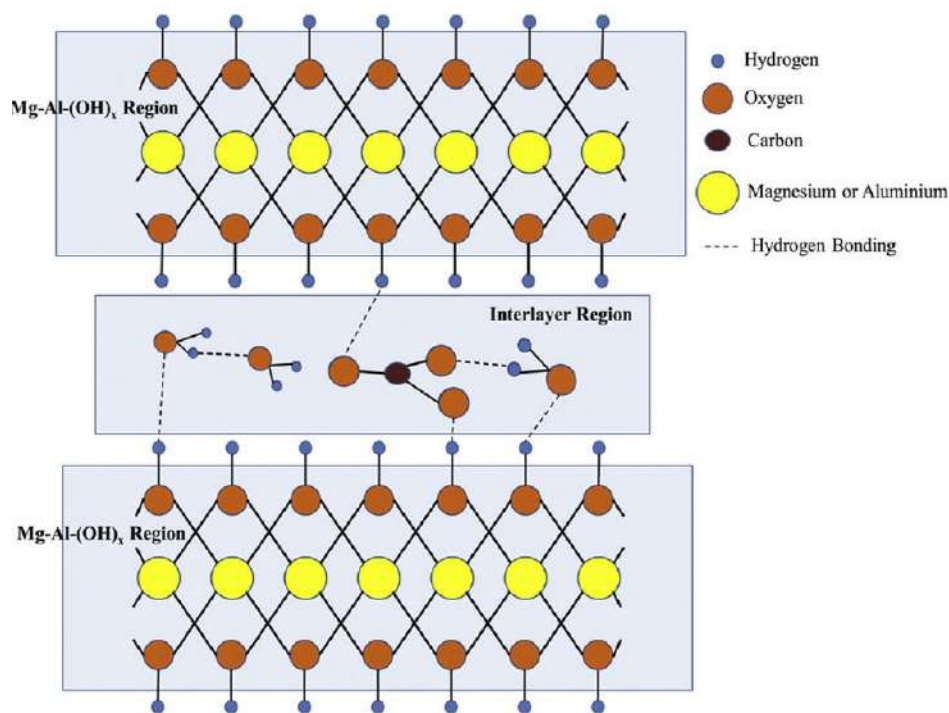


Fig. 2.15. Schematic drawing of Mg-Al hydrotalcite structure (Sikander et al., 2017).

The dual character of its oxides of magnesium and aluminum is constituted after the calcination process, which is a method to promote the thermal and structural stability of the catalyst (Sikander et al., 2017). The Mg/Al ratio affects the catalyst acid-base functions since the Al⁺³ and Mg⁺² ions are responsible for the acidic and basic characteristics, respectively. This dual character is most likely to favor the nitrogen removal from the bio-oil via Hofmann elimination (Prado et al., 2017). Hydrotalcite acid and base functions work together to remove nitrogen. In the Hofmann elimination mechanism, the -NH- of a heterocyclic nitrogenous molecule is protonated by the acid site forming a radical amino -NH₂-, while the basic site attracts the β-H. Then, the bond C-N is broken down, and the nitrogen is removed (Andrade et al., 2018; Prado et al., 2017). Díez et al. (2003) reported 0.59 and 1.02 μmol/m² for basic and acidic sites, respectively for a Mg/Al ratio of 3:1. The bio-oil nitrogenous compounds could not be removed using only zeolites since their acidic

character can be deactivated when highly basic nitrogenous compounds are associated with their acidic sites (Yu et al., 2021).

2.6.1.2. Zeolite

Zeolites are solid catalysts with a high internal surface area due to the microporous framework, which can promote shape-selective catalysis (Li et al., 2017). They are crystalline, three-dimensional microporous aluminosilicates, as shown in Figure 2.16. Crystallized zeolites have ordered micropores comparable to the reactant molecules in pore size, resulting in a large specific surface area, typically ranging from 400 to 800 m²/g. This high surface area allows large amounts of reactants to chemisorb onto its surface to undergo a reaction. Compared with other porous materials, they exhibit high hydrothermal stability (Munthali et al., 2014).

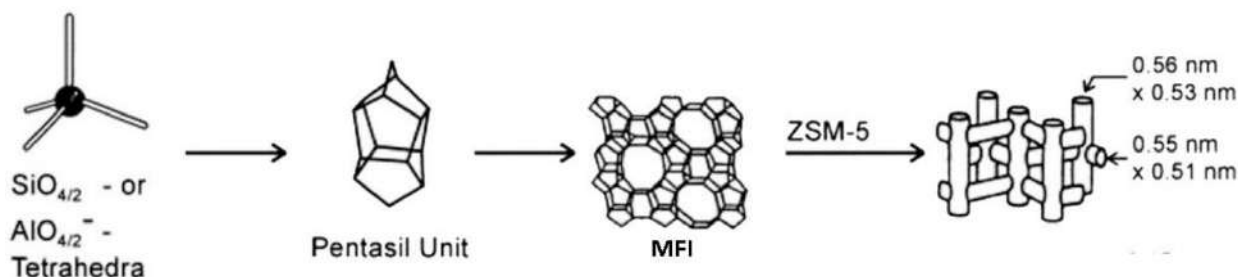


Fig. 2.16. Schematic representation of different building blocks of zeolite ZSM-5 (Daramola et al., 2012).

Among several catalysts, zeolites have gained wide attention for direct thermochemical conversion of biomass into hydrocarbons. This type of catalyst has shown an excellent catalytic performance in deoxygenation and aromatization due to their selectivity for aromatic compounds (Dai et al., 2018). The catalytic performance of zeolites is closely related to their crystallographic structure and acidity. As a result of its moderate pore openings, internal pore space and steric hindrance, HZSM-5 has been proven to be one of the most effective catalysts for hydrocarbons generation via catalytic pyrolysis of biomass (Dai et al., 2020). The large tri-glyceride molecules are subjected to deoxygenation in zeolite's catalytic cracking processes. The oxygenated compounds can be converted into several types of hydrocarbons according to various reaction pathways determined by the catalysts' properties and operating conditions. Among the different

products that can be obtained, light olefins and aromatic hydrocarbons are particularly interesting due to their applications in producing raw chemicals and fuels (Kristiani et al., 2017). Zeolite HZSM-5 is well known as an efficient catalyst for converting petroleum-based fuels. However, coke formation due to the acidic sites is one of the challenges that need to be overcome regarding zeolite catalysts (Musa et al., 2018; Dai et al., 2020).

2.6.1.3. Nickel impregnation

One option to hinder coke formation during catalytic pyrolysis is to moderate the acid sites in the catalysts by incorporating transition metals such as nickel (Ni), cobalt (Co), gallium (Ga), palladium (Pd), copper (Cu), iron (Fe), and molybdenum (Mo) to produce a metal-loaded catalyst (Iliopoulou et al., 2012). Metal modification can be an effective methodology to hinder catalyst deactivation caused by coke on its surface, improve the selectivity for aromatics, and enhance catalytic biomass pyrolysis performance. The incorporation of transition metals into catalysts can have a significant influence on bio-oil chemical compositions, assisting the rise in aromatics contents (Zainan et al., 2018). In recent years, Ni-based bifunctional catalysts supported on silica-alumina zeolites have achieved satisfactory performance in the hydrodeoxygenation of lipids by integrating the hydrogenation function of the metal and the acid function of the supports, creating new intermediate acid sites. Previous studies have shown that these transition metals can reduce coke formation and increase hydrocarbon production by decreasing the oxygen content in bio-oil (Kristiani et al., 2017). Liang et al. (2017) reported that Ni-ZSM-5 improved the selectivity for hydrocarbons since Ni is an active metal and can be utilized to promote the pyrolysis vapors deoxygenation and olefin oligomerization reactions, boosting the selectivity of aromatics, and limiting coking formation and deposition. Although several studies have been conducted on biomass pyrolysis using metal-loaded catalysts, there are few studies on microalgae pyrolysis using metal-loaded catalysts. Hence, more research is required to develop new catalysts and further fine-tuning for this process. The present work is an effort in this direction.

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CHAPTER 3

3. MATERIALS AND METHODS

This chapter presents the materials used and the methodologies adopted for conducting analytical, solar, and assisted-microwave pyrolysis experiments.

3.1. Biomass characterization

The biomass used as raw material in the analytical, solar, and assisted-microwave pyrolysis studies was the microalgae *Schizochytrium limacinum*, acquired as a thin (60-80 Mesh, i.e., the average microalgae particle diameter remained between 0.250 and 0.177 mm) and dehydrated powder from the company Xian Le Sen Biotechnology CO, LTD (China).

3.1.1. Proximate analysis of the microalgae *Schizochytrium limacinum*

Immediate analysis was performed according to the American Society for Testing and Materials (ASTM) standards. All analyzes were performed in triplicate.

Moisture

The microalgae moisture content was determined based on the ASTM E871-82 (2019) standard. Approximately 2.0 ± 0.1 g of the microalgae *Schizochytrium limacinum* was placed in a Petri dish in an oven at a temperature of 105°C. After 2 h, the sample was removed from the oven, and after natural cooling in a desiccator, it was weighed again. This procedure was repeated until the difference between sequentially considered masses reached less than 0.2%. The moisture content was determined according to Equation 3.1.

$$\text{Moisture} = \frac{m_i - m_f}{m_i - m_p} 100\% \quad (3.1)$$

where m_i corresponds to the initial mass of the set (sample + Petri dish), m_f to the final mass and m_p is the mass of the Petri dish.

Volatile matter

The volatile content was determined according to the ASTM E872-82 (2019) standard. Approximately 1.0 ± 0.1 g of the sample was weighed and placed inside an already-weighted crucible with a lid. The set was placed in a muffle at a temperature of 950°C , remaining for 7 min. After natural cooling in a desiccator, the mass of the set was weighed again. The volatile content was calculated according to Equations 3.2 and 3.3.

$$\text{Weight loss} = \frac{m_i - m_f}{m_i - m_c} 100\% \quad (3.2)$$

$$\text{Volatile matter} = \text{Weight loss} - \text{Moisture} \quad (3.3)$$

where m_i corresponds to the initial mass of the set (sample + crucible), m_f is the final mass, and m_c is the crucible mass.

Ash content

The ash content was determined according to the ASTM E1534-93 (2013) standard. In an already-weighted crucible, 2.0 ± 0.1 g of microalgae were added. The sample was placed in a muffle at a temperature of 700°C for 4 h. After natural cooling in a desiccator, the set was weighed, and the ash content was calculated according to Equation 3.4.

$$\text{Ash content} = \frac{m_f - m_c}{m_i - m_c} 100\% \quad (3.4)$$

where m_i corresponds to the initial mass of the set (sample + crucible), m_f to the final mass (ash + crucible), and m_c is the mass of the crucible.

Fixed carbon

Fixed carbon content was determined by the difference from previous volatile and ash analyses (Equation 3.5), according to the ASTM Standard D3172 (2014).

$$\text{Fixed carbon} = 100\% - (\text{Volatile matter} + \text{Ash content}) \quad (3.5)$$

3.1.2. Elemental analysis and higher heating value (HHV) of the microalgae *Schizochytrium limacinum*

Elemental analysis (CHNS/O) was performed using a Perkin Elmer analyzer - CHNS 2400 at the Multiuser Laboratory of the Institute of Chemistry at UFU. The analysis is based on the traditional Pregl-Dumas method. The samples are combusted in a pure oxygen environment. In the presence of excess oxygen and combustion reagents, samples are combusted entirely and reduced to the elemental gases CO_2 , H_2O , N_2 , and SO_2 . The resultant gases are separated by a chromatography column and subsequently measured by a thermal conductivity detector (The PerkinElmer® 2400 Series II CHNS/O Elemental Analyzer). Approximately 1.5 mg of sample was used, the oven temperature was maintained at 975°C , and the chromatogram runs time at 420 s. In the identification and quantification of the contents (in percentage) of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S), an external calibration curve was used (calibration standard: Cystine). All analyzes were performed in triplicate. The oxygen content was calculated by the difference according to Equation 3.6 (Dewayanto et al., 2014).

$$\text{Oxygen content} = 100\% - (\text{C} + \text{H} + \text{N} + \text{S} + \text{Ash}) \quad (3.6)$$

The higher heating value (HHV) was obtained through analysis in a calorimetric bomb (IKA C 2000) according to the ASTM D240-09 (2009) standard. Approximately 1.5 g of sample was used, and combustion occurred at a pressure of 30 bar. The triplicates were performed by the private laboratory Labornutri Análises Bromatológicas.

3.1.3. Chemical composition analysis of the microalgae *Schizochytrium limacinum*

Protein

The total protein content in percentage was determined by the Kjeldahl method according to the rules of the Association of Official Analytical Chemists (A.O.A.C, 1997) (Etheridge et al., 1998). The sample of approximately 0.25 g of microalgae was added to sulfuric acid in a glass tube and then placed in a digester block. After all the sample digestion had taken place, the analytical procedures were performed with the subsequent steps of distillation to recover the ammonia, and titration with hydrochloric acid. The determination of the protein content was carried out indirectly, based on the organic nitrogen content found, which was multiplied by the conversion factor of 6.25 according to Equations 3.7 and 3.8.

$$\text{Nitrogen content} = \frac{1.4 C_{HCl} (V_{HCl} - V_{blank}) f_{HCl}}{m_{sample}} 100\% \quad (3.7)$$

$$\text{Protein content} = 6.25 (\text{Nitrogen content}) 100\% \quad (3.8)$$

where C_{HCl} is the molar concentration of HCl, f_{HCl} is the correction factor for hydrochloric acid, V_{HCl} is the volume spent in the titration of the sample (mL), V_{blank} is the volume consumed in the titration of the blank (mL), and the m_{sample} is the mass of the sample (g).

Lipid

The lipid analysis was performed according to D'oca et al. (2011). Initially, 1 g of microalgae was weighed and added to 40 mL of hexane. This solution was subjected to ultrasound

for 20 min at room temperature to facilitate cell lysis, which is the rupture of the cell's plasma membrane and the release of material from the inside to the outside of the cell. The sample was centrifuged at 2000 rpm for 20 min to separate the organic phase. The organic phase was weighed after evaporating the hexane. The lipid content was calculated according to Equation 3.9.

$$\text{Lipid content} = \frac{m_{\text{organic phase}}}{m_{\text{sample}}} 100\% \quad (3.9)$$

where $m_{\text{organic phase}}$ is the mass of the organic phase and m_{sample} is the mass of the sample (g).

Carbohydrate

The carbohydrate content was determined by mass balance, according to Equation 3.10, as described in Jafarian et al. (2018).

$$\text{Carbohydrate content} = 100\% - (\text{Protein} + \text{Lipid} + \text{Ash}) \quad (3.10)$$

3.1.1. Lignocellulosic composition of the microalgae *Schizochytrium limacinum*

The chemical composition of *S. Limacinum* was assessed to determine the cellulose, hemicellulose, and lignin content. These analyses were performed in duplicate using the methodology outlined by Morais et al. (2010). The chemical composition assessments were conducted at the private laboratory LaborNutri Bromatological Analysis - Uberlândia.

3.1.2. Thermogravimetric analysis (TGA) of the microalgae *Schizochytrium limacinum*

The thermal decomposition behavior of the microalgae used as biomass in the pyrolysis experiments was evaluated by TGA/DTG analysis, carried out in a thermogravimetric analyzer (Shimadzu TGA-50) located at the Laboratory of the Nucleus of Physical-Chemical Processes (NUFISQ) of FEQUI/ UFU. TGA is a technique in which, upon heating a material, measures a

sample's weight (ASTM E1131-20, 2020). Approximately 10 mg of catalyst was heated from 30 to 900°C at a fixed rate of 10°C min⁻¹ under a helium atmosphere (He).

3.1.3. Fourier transform infrared spectroscopy (FTIR) analysis of the microalgae *Schizochytrium limacinum*

To identify the functional groups present in the microalgae *Schizochytrium limacinum*, Fourier transform infrared spectroscopy (FTIR) analysis was carried out in an infrared spectrometer model Equinox 55 from Bruker, located at the Multiuser Laboratory of the Institute of Chemistry of the Federal University of Uberlândia (IQ/UFU). FTIR is a technique that originated in the 1800s. The British-German astronomer Sir William Herschel discovered that different light colors had different temperatures, now called infrared light (IR). In the early 1900s, William Weber Coblentz found that IR light interacts with matter and created the first IR spectra. The spectrometer came to market in the 1940s. IR spectroscopy was continuously improved throughout the 1900s with FTIR, which can check all the wavelengths of IR light at once using an interferometer (Bruker Guide to Infrared Spectroscopy, 2023). Potassium bromide (KBr) pellets were prepared at a mass ratio of 1/100 (sample/KBr) in a hydraulic press. These pellets passed through IR light using the interferometer (Chen et al., 2014). The wavelength used was from 400 to 4500 cm⁻¹, with 32 scans at a resolution of 4 cm⁻¹. The FTIR spectra is preprocessed by calculating the first derivative followed by vector normalization of the spectra (Helm et al., 1995; Janbu et al., 2008).

3.1.4. X-ray fluorescence analysis (XRF) of the microalgae *Schizochytrium limacinum*

The minerals present in the biomass were quantified by X-ray fluorescence (XRF). Pastilles were prepared at a mass ratio of 10/1 (sample/wax) in a hydraulic press. The equipment used in this analysis was an X-ray fluorescence model S8 Tiger Bruker, located in the Multiuser Laboratory in Renewable Energy at the Faculty of Chemical Engineering at the Federal University of Uberlândia (FEQUI/UFU). XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. The Quant-Express method (Bruker AXS) calculates, according to the manufacturer, the concentration (mass fraction) of each element utilizing parameters stored for more than 500

reference samples covering the most typical samples for XRF: oils, aqueous solutions, rocks, metals, chemicals, and polymers (S8 Tiger Bruker AXS, 2009).

3.1.5. Scanning electron microscopy (SEM) analysis of the microalgae *Schizochytrium limacinum*

The morphology of the microalgae was investigated using a scanning electron microscope model EVO MA 10 Zeiss, located at the Multiuser Laboratory of Scanning Electron Microscopy at FEQUI/UFU. SEM analysis is based on a focused beam of electrons that scan the sample, which interacts with the atoms in the sample to provide three-dimensional surface topography (Lam et al., 2023). The samples were sputter coated with a 20 nm layer of gold. Gold is used for its high electron density, which increases electron scatter to give high contrast in dark spots. Thus, promoting the emission of secondary electrons so that the specimen conducts evenly and provides a homogeneous surface for analysis and imaging (Bogner et al., 2007). The analysis was performed using an electronic acceleration of 5 kV, and the images were acquired with a magnification between 1 and 5 Kx.

3.2. Catalysts: Synthesis and Characterization

3.2.1. Synthesis

Hydrotalcite-like precursor

The hydrotalcite-like catalytic precursor $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$ was synthesized in a molar ratio of 3:1 (Mg/Al) so that its acidic character was approximately twice as great as its basic one (Díez et al., 2003). The synthesis methodology used (Cavani et al., 1991) was the co-precipitation of metallic nitrates at constant pH (maintained at 10.0 ± 0.2). To synthesize the catalyst, two primary solutions were prepared: 100 mL of a mixture of magnesium $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and aluminum $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ nitrates (mol ratio of 3:1 of Mg/ Al) and 200 mL of sodium carbonate $[\text{Na}_2\text{CO}_3]$ at a 0.2 mol/L concentration. The solution containing the two nitrates was dripped into the carbonate solution. Simultaneously, the pH was controlled by adding a NaOH solution (4 mol/L). After mustering the solutions, the mixture was stirred for 18 h

at 650 rpm. After this time of solution aging, the suspension was filtered with heated distilled water (approximately 80°C) until its pH reached 7.0. The cake remaining from the filtration process was dried in an oven (105°C) for 16 h and then macerated and sieved (80 mesh). The average diameter of the catalyst particles remained between 0.119 and 0.177 mm. Before the nickel impregnation process to obtain metallic sites, the catalyst was calcined at 550°C in a constant flow of synthetic air for 4 h so that the nitrates could decompose into oxides. The heating rate used was 1°C min⁻¹, so the exposure of the catalyst to the gas was slow, a precaution taken due to the presence of nitrates, which are explosive materials.

Synthetic Hydrotalcite

The synthetic hydrotalcite [Mg₆Al₂(OH)₁₆CO₃·4H₂O] was purchased from the company Sigma-Aldrich. The powdered catalyst was purchased with an Mg/Al molar ratio of 4:1. It presented an X-Ray diffraction that conforms to its structure, and the particle size distribution is lower than 5 µm. Analogously to the hydrotalcite-type catalytic precursor, before the metallic impregnation of nickel, the synthetic hydrotalcite catalyst was subjected to a calcination process in a muffle furnace at a temperature of 550°C (heating rate of 5°C min⁻¹) in a constant flow of synthetic air for 4 h.

Zeolite HZSM-5

The HZSM-5 zeolite catalyst (CBV 8014) was purchased from the British company Zeolyst International. The powdered catalyst was purchased in ammoniacal form with a SiO₂/Al₂O₃ molar ratio of 80. Analogously to the hydrotalcite-type catalysts, before the metallic impregnation of nickel, the HZSM-5 catalyst was subjected to a calcination process in a muffle furnace at a temperature of 550°C in a constant flow of synthetic air for 4 h at a heating rate of 5°C min⁻¹.

Nickel impregnation

To obtain metallic sites in the two catalysts was done through the wetness impregnation technique (according to Hori et al., 1998) using nickel nitrate [Ni(NO₃)₂·6H₂O]. To impregnate 10% of nickel (Ni) in each catalyst, approximately 5.50 g of nickel nitrate was diluted with 3.00 g

of distilled water. The nickel solution was slowly added to each catalyst and homogenized. After being well homogenized, the catalysts were dried in an oven (105°C), macerated, and again calcined in a muffle at 550°C in a constant flow of synthetic air for 4 h at a heating rate of 5°C min⁻¹. The calcination treatment assists in forming oxides and stabilizing the catalysts, which were then stored in their most stable form. The catalysts impregnated with nickel were named NiHTC and NiHZSM-5 and used in analytical, solar, and assisted-microwave pyrolysis processes. The impregnation technique was chosen because it is a simple procedure that would allow the production of greater amounts of catalysts required in the solar and microwave units. The increase in metal load can raise catalytic cracking and hinder coke formation due to the moderation of the catalysts' acid sites (Maia et al., 2010). However, metallic impregnation can be responsible for forming large metallic particles in the catalyst support. These large particles become unattractive since they decrease the catalysts' specific surface area. Thus, the amount of 10 wt.% of nickel was chosen, a percentage that is widely used in the literature (Bouchy et al., 2000; Parsafard et al., 2017; Li et al., 2017).

Catalysts loading in structured SiC foam

Silicon carbide foam disks are sponge-like interconnecting structures that can be applied as catalyst support. The SiC foams (Fig. 3.1) used in this study had a pore size of 20 ppi (pores per inch) and a dimension of $\Phi 50 \times 20$ mm and were purchased from Tongda Carbide Co., Ltd.



Fig. 3.1. SiC foam used in the catalytic bed during the assisted-microwave pyrolysis experiments.

After the nickel impregnation, for the assisted-microwave catalytic pyrolysis, structured NiHTC/SiC and NiZSM-5/SiC catalysts were prepared using a dip coating method. Each catalyst was mixed thoroughly with deionized water in a mass ratio of 1:5 to form a slurry. The SiC foam cylinders were dipped into the slurry, and each SiC foam acquired around 0.5 g of catalyst per deepening. Then, the SiC foams were dried at 105°C for 2 h. Higher catalyst loading ratios were achieved by repeating the dipping and drying cycle multiple times. The experiments were carried out with SiC-structured catalysts, and to study the catalyst placement, tests were performed with the powder catalysts (without the SiC foams).

3.2.2. Catalysts' characterization

3.2.2.1. X-ray diffraction (XRD) analysis of hydrotalcite and zeolite catalysts

X-ray diffraction analyses were carried out to identify the crystalline structure of the catalysts *in natura* and after the nickel impregnation and calcination processes. They were carried out in the RIGAKU Miniflex model equipment at the Multiuser Laboratory of the Chemistry Institute of the Federal University of Uberlândia (IQ/UFU). Samples of both catalysts were placed and subjected to CuK α radiation ($\lambda = 1.540 \text{ \AA}$) and a goniometer speed of 2θ per minute. Diffraction patterns were recorded at $5^\circ \leq 2\theta \leq 90^\circ$ range. The X-rays are collimated and directed onto the powder samples. When an X-ray beam hits a sample and is diffracted, we can measure the distances between the planes of the atoms that constitute the sample by applying Bragg's Law (Maroliya, 2012). The X-ray scan provides a unique "fingerprint" of the mineral or minerals present in the sample that is interpreted by comparison with standard reference patterns [such as the powder diffraction file from the International Center for Diffraction Data (ICDD)], allowing the material identification (Ruffell et al., 2004).

3.2.2.2. Nitrogen adsorption analysis (specific surface area and texture properties) of hydrotalcite and zeolite catalysts

The adsorption of N₂ at 77 K is based on a model of physisorption and originally involved the measurement of gas volumes, before and after adsorption. Different N₂ partial pressure values were used to build the adsorption and desorption curves. The detailed methodology can be found

in Sing (2001). The analysis was carried out in a surface area and porosity analyzer (ASAP) located at the Multiusuários do Pontal Laboratory (LEMUP) of the Federal University of Uberlândia, being applied for the characterization of the specific area (S_{BET}), as well as of properties of texture [total pore volume (V_p) and pore diameter (D_p)] of both catalysts. The Brunauer, Emmett, and Teller (BET) method determined the specific surface area, and the Barret, Joyner, and Halenda (BJH) method was used to obtain the pore size and volume distribution (Sinha et al., 2019; Villarroel-Rocha et al., 2014).

3.2.2.3. Temperature programmed desorption of ammonia analysis (TPD-NH₃)

To characterize the acidity properties of the catalysts, temperature-programmed desorption of ammonia analysis (TPD- NH₃) was performed according to Zhou et al. (2022). The analysis was conducted in a furnace, coupled with an online gas analyzer (QGA, hidden Analytical). Catalyst samples were calcined at 550°C to remove any moisture content. Around 0.1 g of sample was loaded into a quartz U-tube placed inside a furnace at 50°C, and then the tube was purged using a mixture of N₂ (99%) and NH₃ (1%) gases at a constant flow rate of 100 mL/min until saturation. After the adsorption step, the samples were purged with pure N₂ for 2 h to remove the bound ammonia from the catalyst physically. Finally, the furnace temperature was raised from 50 to 550°C at a heating rate of 5°C/min, and the desorbed ammonia concentration was measured every 15 s by the electron multipliers detector of the QGA mass spectrometry gas analyzer.

3.2.2.4. Thermogravimetric analysis (TGA) of hydrotalcite and zeolite catalysts

The thermal decomposition behavior of hydrotalcite (HTC) and zeolite (HZSM-5) catalysts was evaluated by TGA/DTG analysis, carried out in a thermogravimetric analyzer (Shimadzu TGA-50) located at the Laboratory of the Nucleus of Physical-Chemical Processes (NUFISQ) from FEQUI/UFU. TGA is a technique in which, upon heating a material, measures a sample's weight (ASTM E1131-20, 2020). Approximately 10 mg of catalyst was heated from 30 to 900°C at a fixed rate of 10°C min⁻¹ under a helium (He) atmosphere to verify its stability.

3.2.2.5. Fourier transform infrared spectroscopy (FTIR) of hydrotalcite and zeolite catalysts

To identify the functional groups present in the catalysts, Fourier transform infrared spectroscopy (FTIR) analysis was carried out in an Agilent Cary 630 FTIR spectrometer located at the Pontal Multiuser Laboratory (LEMUP) at the Federal University of Uberlândia. To identify the functional groups present in the microalgae *Schizochytrium limacinum*, Fourier transform infrared spectroscopy (FTIR) analysis was carried out in an infrared spectrometer model Equinox 55 from Bruker, located at the Multiuser Laboratory of the Institute of Chemistry of the Federal University of Uberlândia (IQ/UFU). FTIR is a technique that originated in the 1800s. The British-German astronomer Sir William Herschel discovered that different light colors had different temperatures, now called infrared light (IR). In the early 1900s, William Weber Coblentz found that IR light interacts with matter and created the first IR spectra. The spectrometer came to market in the 1940s. IR spectroscopy was continuously improved throughout the 1900s with FTIR, which can check all the wavelengths of IR light at once using an interferometer (Bruker Guide to Infrared Spectroscopy, 2023). The wavelength used was from 500 to 4500 cm^{-1} , with 32 scans at a resolution of 4 cm^{-1} . The FTIR spectra is preprocessed by calculating the first derivative followed by vector normalization of the spectra (Helm et al., 1995; Janbu et al., 2008).

3.2.2.6. X-ray fluorescence analysis (XRF) of the hydrotalcite and zeolite catalysts

The minerals present in the catalysts were quantified by X-ray fluorescence (XRF). Pastilles were prepared at a mass ratio of 10/1 (sample/wax) in a hydraulic press. The equipment used in this analysis was an X-ray fluorescence model S8 Tiger Bruker, located in the Multiuser Laboratory in Renewable Energy at the Faculty of Chemical Engineering at the Federal University of Uberlândia (FEQUI/UFU). XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. The Quant-Express method (Bruker AXS) calculates, according to the manufacturer, the concentration (mass fraction) of each element utilizing parameters stored for more than 500 reference samples covering the most typical samples for XRF: oils, aqueous solutions, rocks, metals, chemicals, and polymers (S8 Tiger Bruker AXS, 2009).

3.2.2.7. Scanning electron microscopy (SEM) of hydrotalcite and zeolite catalysts

The morphology of the catalysts was investigated using a scanning electron microscope model EVO MA 10 Zeiss, located at the Multiuser Laboratory of Scanning Electron Microscopy at FEQUI/UFU. SEM analysis is based on a focused beam of electrons that scan the sample, which interacts with the atoms in the sample to provide three-dimensional surface topography (Lam et al., 2023). The samples were sputter coated with a 20 nm layer of gold. Gold is used for its high electron density, which increases electron scatter to give high contrast in dark spots. Thus, promoting the emission of secondary electrons so that the specimen conducts evenly and provides a homogeneous surface for analysis and imaging (Bogner et al., 2007). The analysis was performed using an electronic acceleration of 5 kV, and the images were acquired with a magnification between 1 and 5 Kx.

3.3. Analytical pyrolysis (micro pyrolysis) using a double catalytic bed

The analytical pyrolysis tests of the microalgae *Schizochytrium limacinum* were carried out in a Frontier Lab micro pyrolyzer (EGA/PY-3030D) coupled to a gas chromatograph with mass spectrometry (Shimadzu GC/MS-QP2020 NX). For each experimental run performed in the micro pyrolyzer, the microalgae *Schizochytrium limacinum* was weighed (1.00 ± 0.01 mg) and placed in a metallic crucible (diameter = 4 mm and length = 8 mm). Then, the NiHTC and NiHZSM-5 catalysts were placed sequentially on the biomass; all separated using quartz wool. The catalysts' ratios are presented in Tables 3.2 and 3.3. The crucible was then placed in the micro pyrolyzer and heated to the desired temperature by a resistance. The interface between the micro pyrolyzer and the GC/MS was maintained at 250°C. Ultrapure helium (99.999%) was used as inert gas for pyrolysis and carrier gas for the volatiles. Pyrolytic vapors were introduced into the GC/MS along with the helium gas through a heating tube maintained at 280°C. The method programmed into the equipment was the Blasi method with solvent cut (Andrade, 2018). The vapors were separated by an Rtx 1701 GC 195 capillary column (length = 60 m, I.D. = 0.25 mm, film thickness = 0.25 μ m). The column gas flow rate was 1 mL/min, while the injector split ratio was 1:450. An initial oven temperature of 45°C was held for 4 min, and then a heating rate of 3°C/min was implemented to reach an oven temperature of 235°C, which was held for 8 min. The injector and interface

temperatures were 250 and 235°C, respectively. Each experimental run was repeated at least twice to get results with a relative standard deviation inferior to 5%. The average data were used. The ion chromatogram obtained was identified using the library database of the National Institute of Standards and Technology (NIST 14). The most abundant 60 components with a similarity index greater than 80% were selected and then categorized according to carbon number and chemical group. To determine the distribution of compounds in the pyrolysis products, a semi-quantitative study was made employing the area of the chromatographic peaks, a method widely adopted by several researchers in the field (Lee et al., 2022; Moogi et al., 2022; Prabhakara et al., 2022). These values estimate how much of a measured substance is present (Domínguez et al., 2003).

3.3.1. Experimental design for the analytical pyrolysis

3.3.1.1. Effects of the reaction temperature, tandem catalytic bed (NiHTC and NiHZSM-5), and total catalysts to biomass ratio on analytical pyrolysis

In this study, we conducted analytical pyrolysis experiments to assess reaction temperature (T_A) and the combination of NiHTC and NiHZSM-5 in a tandem catalytic bed. The effects of different reaction temperatures, distinct ratios of NiHTC to NiHZSM-5 (C_A), along with different total catalyst-to-biomass (CB_A) ratios were evaluated. Tables 3.1 to 3.3 provide detailed information on the experiments conducted in this context.

Table 3.1. Non-catalytic analytical pyrolysis tests' conditions.

T_A [°C]
450
550
650

Following the examination of the catalytic experiments as detailed in Table 3.2 and the determination of the ideal conditions that resulted in a notable increase in hydrocarbon production, we conducted further tests to investigate the impact of the total catalyst-to-biomass (CB_A) mass ratio within the dual catalytic bed, as presented in Table 3.3. In this phase, NiHTC to NiHZSM-5 (C_A) ratio was maintained at 1:1.

Table 3.2. Catalytic analytical pyrolysis tests' conditions.

T_A [°C]	C_A	CB_A
450	0:1	1:1
550	0:1	1:1
650	0:1	1:1
450	1:0	1:1
550	1:0	1:1
650	1:0	1:1
450	1:1	1:1
550	1:1	1:1
650	1:1	1:1

Table 3.3. Experimental conditions for the total catalyst/biomass ratio.

T_A [°C]	C_A	CB_A
650	1:1	0.5:1
650	1:1	1:1
650	1:1	5:1

3.3.1.2. Effects of the NiHTC catalyst synthesis method on the tandem catalytic bed in analytical pyrolysis

After assessing the influence of the catalyst-to-biomass mass ratio (CB_A) within the dual catalytic bed, as illustrated in Tables 3.2 and 3.3, and identifying the best experimental condition to obtain pyrolytic products with more significant quantities of desirable compounds, we proceeded to investigate the effects of the synthesis method employed for the NiHTC catalyst within the dual catalytic bed during analytical pyrolysis, as outlined in Table 3.4. In this phase, the tests were performed at 650°C and the NiHTC to NiHZSM-5 (C_A) ratio was maintained at 1:1.

In this phase, HTC-type catalytic precursors with varying Ni mass contents, synthesized through the precipitation of magnesium, aluminum, and nickel nitrate-based solutions (Ferreira, 2016), were employed. The series prepared by Ferreira (2016) was composed of four catalysts, varying the Ni content from 23.5 to 47.5% by weight, to observe the possible insertion and dispersion of greater amounts of nickel in the catalysts' structures. Notably, nickel nitrate was employed as part of the synthesis solution rather than used in the impregnation process. A

comparative analysis of the results obtained from analytical pyrolysis using different NiHTC synthesis methods was conducted.

Table 3.4. Experimental conditions for NiHTC catalysts synthesized by precipitation.

T_A [°C]	C_A	CB_A	Ni content by precipitation in HTC [wt. %]*
650	1:1	1:1	47.5
650	1:1	1:1	37.3
650	1:1	1:1	23.5
650	1:1	5:1	47.5
650	1:1	5:1	37.3
650	1:1	5:1	23.5

*Data from FERREIRA (2016).

3.3.1.3. Effects of the pre-treatment (reduction and passivation) of NiHTC and NiHZSM-5 catalysts in the tandem catalytic bed in analytical pyrolysis

To study the effect of the pre-treatment on the catalysts NiHTC and NiHZSM-5, after nickel impregnation, the catalysts samples were dried in the oven overnight at 110°C and then reduced at 550°C for 4 h with a heating rate of 2°C/min under a H₂ flow (60 mL/min). After reduction, the samples were cooled at about -10°C and passivated under a 5% O₂/Ar mixture flow (60 mL/min) for 30 min (Moura, 2022). Table 3.5 presents the experimental conditions carried out at this stage. In this phase, the tests were performed at 650°C and the NiHTC to NiHZSM-5 (C_A) ratio was maintained at 1:1. The nickel content was 10 wt.% by impregnation.

Table 3.5. Experimental conditions for NiHTC and HZSM-5 catalysts reduced and passivated.

T_A [°C]	C_A	CB_A	Pre-treatment
650	1:1	1:1	Reduc./Passiv.
650	1:1	5:1	Reduc./Passiv.

3.4. Solar pyrolysis using a double catalytic bed

To perform the solar pyrolysis experiments, a concave parabolic mirror was coupled to an automated system that allowed the tracking of orbs and stars on two axes, represented in Fig. 3.2. The concave mirror could concentrate sunlight and reflect it onto a focal point where the reactor

was positioned to be then heated to the desired temperature, which strongly depended on the chosen radiation to perform the experimental runs. The reaction temperature was measured with a thermocouple type K positioned at the base of the reactor. The reactor, measuring 4.4 cm in diameter, was made of transparent quartz, a material with high transmittance (0.94), which allowed rapid heat distribution.

Table 3.6 provides data from the location (Uberlândia County) where the experiments were conducted, as well as the characteristics of the parabolic dish and the reactor. The respective characterizations (parabolic dish and reactor) can be found in Andrade et al. (2018a). The experimental runs were carried out in batches, with approximately 1.5 g of the microalgae *Schizochytrium limacinum* being degraded in each test for 7 min. As this was an *ex-situ* configuration, the reactor was followed by a heated fixed double catalytic bed (NiHTC followed by NiHZSM-5). The total amount of catalyst (NiHTC + NiHZSM-5) used in each experimental run was equal to the amount of biomass (1.5 g). Nitrogen (purity of 99.999%) at a flow rate of approximately 150 mL/min was used as sweeping gas to carry the pyrolysis vapors. After passing through the fixed bed of NiHTC and NiHZSM-5, the pyrolytic vapors went to the condensation system that consisted of two cold traps. Non-condensable vapors were released into the atmosphere.

The yields of solid (SY_S) remaining in the reactor and of liquid (LY_S) collected in the condensation system were determined by gravimetry, while the yield of the gaseous phase (GY_S) was calculated by difference. The initial microalgae mass was used as the basis for the calculation, as shown by Equations 3.11, 3.12, and 3.13. Figure 3.3 shows, in detail, the reactor heating dynamics during the pyrolysis tests carried out in two radiation ranges: $550 \pm 25 \text{ W/m}^2$ and $850 \pm 15 \text{ W/m}^2$.

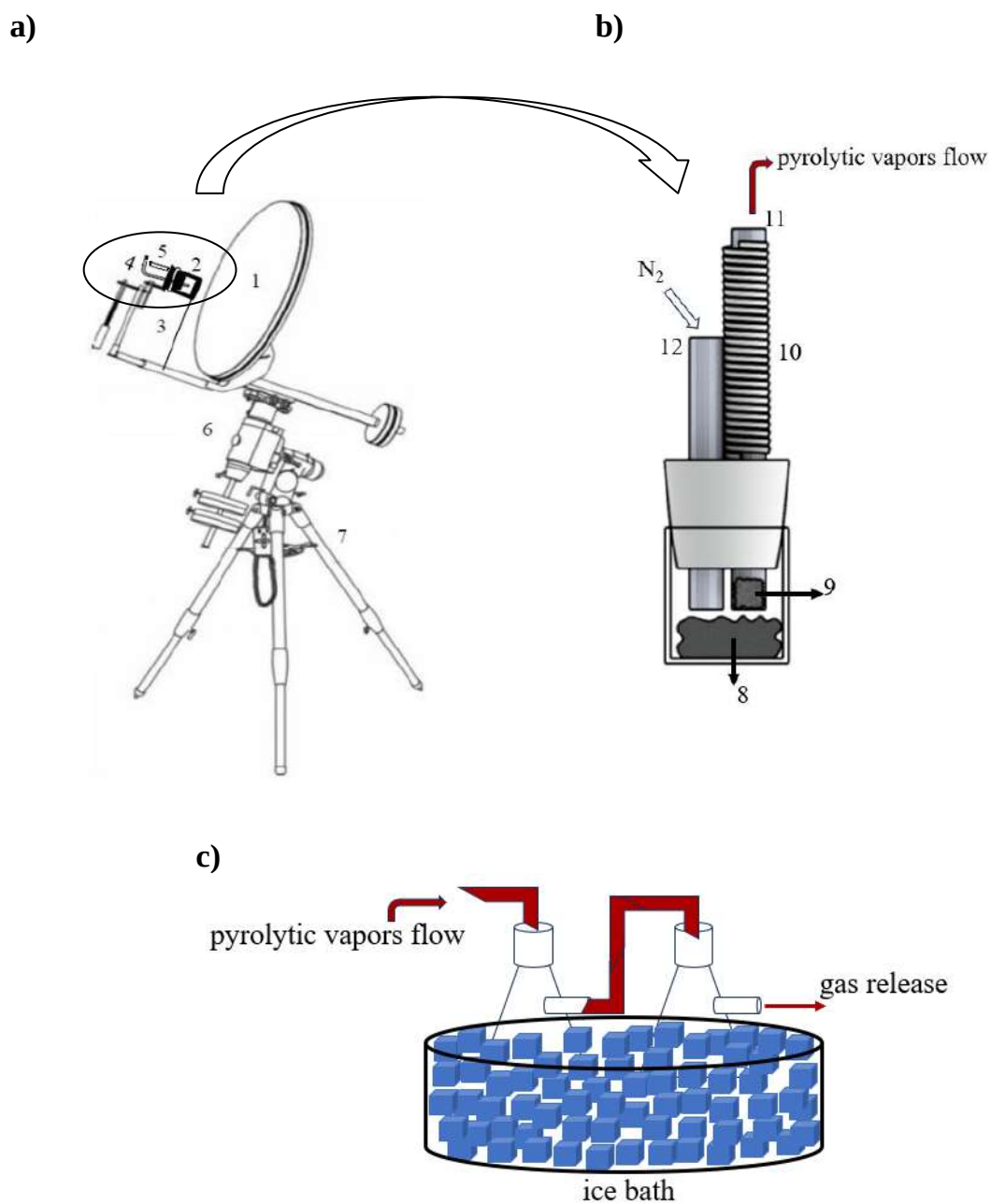
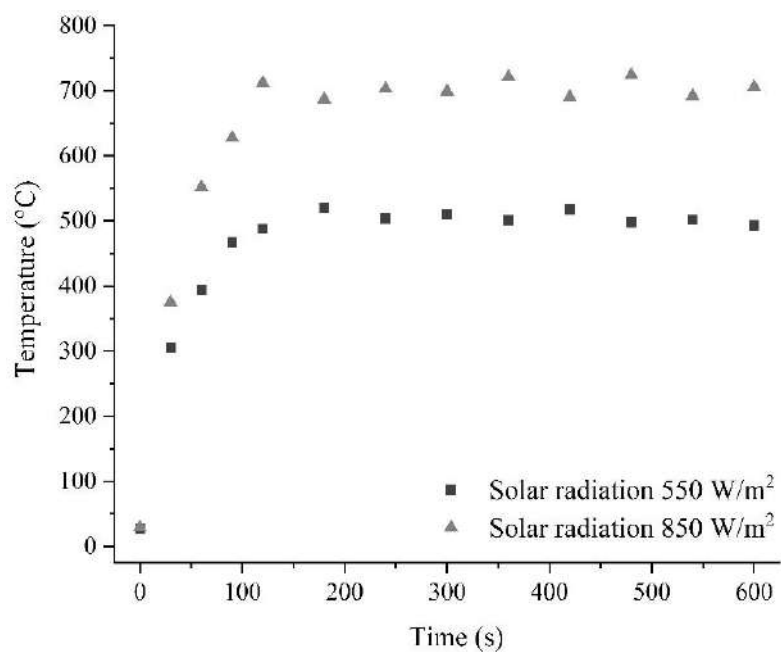


Fig. 3.2. Schematic representations of the (a) solar unit (adapted from Andrade et al., 2018b), (b) the pyrolysis reactor and fixed catalytic bed, and (c) condensation system.

Table 3.6. Solar concentrator and reactor parameters.

Solar concentrator (parabolic dish)	
Edge Angle (ϕ)	60°
Focal distance (f)	25.34 cm
Diameter (d)	60.96 cm
Depth (h)	7.2 cm
Reactor	
Height	50 mm
Thickness	2 mm
External diameter	44 mm
Focal Temperature Estimate	821°C
Specific Heat	1045 J/kg°C
Density (ρ)	2650 kg/m ³
Uberlândia site	
Latitude	18°55'09"S
Longitude	48°23'31"W

Source: adapted from Andrade et al. (2018a).

**Fig. 3.3.** Reactor heating rate for solar pyrolysis.

$$SY_s = \frac{\text{Mass of bio-char}}{\text{initial microalgae mass}} 100\% \quad (3.11)$$

$$LY_s = \frac{\text{mass of bio-oil}}{\text{initial microalgae mass}} 100\% \quad (3.12)$$

$$GY_s = 100\% - (SY_s + LY_s) \quad (3.13)$$

3.4.1. Experimental design for the solar pyrolysis

3.4.1.1. Effects of the temperature and the dual catalytic bed on catalytic solar pyrolysis

The experimental conditions for solar pyrolysis were chosen using a hybrid design in which the reaction temperature variable (T_s) was studied at two levels (2^2), selected from preliminary tests that indicated that the solar radiation range of $550 \pm 15 \text{ W/m}^2$ would achieve an average temperature of $550 \pm 20^\circ\text{C}$. In contrast, the radiation range of $850 \pm 25 \text{ W/m}^2$ would reach $750 \pm 25^\circ\text{C}$. As these were experiments using sunlight, which was not controlled, fluctuations occurred during heating. For this reason, it was decided that the temperature variable, called x_{1s} , would have only two levels (one colder and one warmer). Hypothesis tests ensured that the experimental runs performed at a temperature of 550°C differed from those performed at a temperature of 750°C . And, despite the current fluctuations at each level studied, statistically, it could be affirmed that there was no difference in the values of solar radiation and temperature. The solar experiments were conducted during the same annual season (April to May) at two distinct intervals: at 9:30 a.m. and 12:00 p.m., aiming to achieve irradiance levels of 550 and 850 W/m^2 , respectively. This approach ensured that any fluctuations in incident radiation and temperature remained minimal. For the catalysts mass ratio variable, called x_{2s} , NiHTC/(NiHTC+NiHZSM-5) (C_s), it was decided that five levels (5^2) would be studied to evaluate the effects of the double catalytic bed of NiHTC and NiHZSM-5. Tables 3.7 and 3.8 show the solar test conditions for non-catalytic and catalytic configurations, respectively.

The treatment of experimental data was performed using Regression Techniques and Response Surfaces. The effects of independent variables were calculated, and the significant parameters were determined by analysis of variance (ANOVA). Non-significant coefficients (p-value > 0.05) were eliminated, and the prediction equations were adjusted. Table 3.8 shows the levels of the independent variables, whose Equations 3.14 and 3.15 present the respective coding of the variables. Equations were proposed for the solid (SY_S), liquid (LY_S), and gas (GY_S) yields, as well as for the composition (oxygenated, nitrogenated and hydrocarbons) and generated energy/test (kJ) of the bio-oil as a function of the independent variables. The adequacy of the adjusted equations was evaluated based on the coefficient of determination (R^2) values. Based on the liquid yield, hydrocarbon generation, and HHV values, calculations were performed to evaluate the experimental conditions that favored the energy efficiency of the process.

Table 3.7. Non-catalytic solar pyrolysis tests' conditions.

Test	T_s [°C]	x_{1s}
1S	550	-1
2S	750	+1

Table 3.8. Experimental design matrix for catalytic solar pyrolysis.

Tests	T_s [°C]	x_{1s}	C_s		x_{2s}
			NiHTC:NiHZSM-5	NiHTC/(NiHTC+NiHZSM-5)	
3S	550	-1	0:1	0	-1
4S	750	+1	0:1	0	-1
5S	550	-1	1:2	0.33	0
6S	750	+1	1:2	0.33	0
7S	550	-1	1:1	0.50	0.5
8S	750	+1	1:1	0.50	0.5
9S	550	-1	2:1	0.67	+1
10S	750	+1	2:1	0.67	+1
11S	550	-1	1:0	1.00	+2
12S	750	+1	1:0	1.00	+2

$$x_{1s} = \frac{T_s(^{\circ}\text{C}) - 650}{100} \quad (3.14)$$

$$x_{2s} = \frac{C_s - 0.33}{0.33} \quad (3.15)$$

Bio-oil multi-response optimization: yield and HHV

Applying bio-oil as a second-generation biofuel requires some features, such as high liquid yield and high-quality chemical compounds (Yildiz et al., 2016). Therefore, it is essential to understand the relationship between the factors that influences the products and determines the optimal operating conditions considering the liquid yield and product quality. Given this importance, a multiple-response optimization study was carried out using the desirability function (Derringer et al., 1980) to simultaneously maximize the liquid yield (LY_s) and HHV (HHV_s). In this technique, both responses (LY_s and HHV_s) are transformed into dimensionless parameters ranging from 0 to 1, where 0 corresponds to the lowest level of desirability, and 1 is the most desirable condition (Ronix et al., 2017). The same weight was assigned to net yield (LY_s) and HHV (HHV_s) responses. Thus, the predicted values for the variables were obtained under the need to carry out a new experimental phase to analyze the effects of the total catalyst/biomass ratio.

3.4.1.2. Effects of the total catalyst/biomass ratio in the catalytic solar pyrolysis

After analyzing the hybrid design (Table 3.9) and identifying the optimal conditions through multiple-response optimization study, additional tests were performed to determine the effects of the total catalysts/biomass ratio (CB_s) in the double catalytic bed of solar pyrolysis (Table 3.4).

Table 3.9. Experimental conditions to evaluate the total catalyst/biomass ratio effects in solar pyrolysis.

Tests	T_s [°C]	C_s	CB_s
13S	750	0.5 or 1:1	0.5:1
14S	750	0.5 or 1:1	2:1
15S	750	0.5 or 1:1	4:1

3.4.2. Characterization of solar pyrolysis products

3.4.2.1. Gas chromatography and mass spectrometry (GC/MS) of the bio-oil

The bio-oil obtained from the catalytic solar pyrolysis experiments was diluted in ethanol. Its composition was determined using a chromatograph coupled to a mass spectrometer QP2010 Plus - Shimadzu (GC/MS), using a capillary column Rtx-1701 (60m × 0.25mm × 0.25µm). The method programmed into the equipment was the Blasi method with solvent cut (Andrade, 2018). Helium gas at a 1 mL/min flow rate was used to carry the vapors. The split ratio used was 1:5. The oven temperature was initially maintained at 45°C for 4 min and then increased to 235°C at 3°C min⁻¹. During the analysis, the injector temperature was maintained at 250°C and the interface at 235°C. The analyses were conducted at the Laboratory of Catalytic Processes at FEQUI/UFU. Compounds were identified using the NIST 08 mass spectral data library with a similarity index greater than 80%. The most abundant 60 components were classified into hydrocarbons, ketones, carboxylic acids, alcohols/phenols, and amines/nitriles. As in the analytical pyrolysis, a semi-quantitative examination of the compound distribution within the pyrolysis products was conducted. This investigation utilized the chromatographic peak areas, a widely embraced methodology within the research community (Lee et al., 2022; Moogi et al., 2022; Prabhakara et al., 2022). These values provide estimates of the relative amounts of the analyzed substances, as elucidated by Domínguez et al. (2003).

3.4.2.2. Water content in the bio-oil

The water content present in the bio-oil was determined using the Karl Fisher KF-1000 (Analyzer) titration equipment. The methodology used was based on the ASTM E203-96 standard. The analyzes were performed in triplicates.

3.4.2.3. Elemental analysis, higher heating value (HHV)

Elemental analysis (CHNS/O) was performed using a Perkin Elmer analyzer - CHNS 2400 at the Multiuser Laboratory of the Institute of Chemistry at UFU. The analysis is based on the traditional Pregl-Dumas method. The samples are combusted in a pure oxygen environment. In the

presence of excess oxygen and combustion reagents, samples are combusted entirely and reduced to the elemental gases CO_2 , H_2O , N_2 , and SO_2 . The resultant gases are separated by a chromatography column and subsequently measured by a thermal conductivity detector (The PerkinElmer® 2400 Series II CHNS/O Elemental Analyzer). Approximately 1.5 mg of sample was used, the oven temperature was maintained at 975°C , and the chromatogram runs time at 420 s. In the identification and quantification of the contents (in percentage) of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S), an external calibration curve was used (calibration standard: Cystine). All analyzes were performed in triplicate. The oxygen content was calculated by the difference according to Equation 3.6 (Naik et al., 2010). The higher heating value of the bio-oil (MJ/kg) was calculated according to Sheng et al. (2005) from the values found through the elemental composition, Equation 3.16.

$$HHV_s = -1.3675 + 0.3137 C + 0.7009 H + 0.0318 O \quad (3.16)$$

3.4.3. Energy contents and efficiency of solar pyrolysis process

The energy contents and efficiency of the catalytic solar pyrolysis were investigated and detailed in this study. The energy recovery (ER_s) is based on a standard thermochemical balance (Smith et al., 2007) (Equation 3.17). The bio-oil emission factor (EF_s) was calculated as the ratio of the energy carried by the biofuels produced in solar pyrolysis to the energy contained in the microalgae *Schizochytrium limacinum* throughout Equation 3.18. An emission factor is used to calculate the GHG emissions related to the direct use of a given source/fuel type (Innovation Center for U.S., 2019).

$$ER_s = \frac{m_{oil} HHV_{oil}}{m_{biomass} HHV_{biomass}} 100\% \quad (3.17)$$

where: m_{oil} and $m_{biomass}$ are the mass of bio-oil and microalgae; HHV_{oil} and $HHV_{biomass}$ are the higher heating values of bio-oil and microalgae (MJ/kg), respectively.

$$EF_s = \frac{(2009 \ m_{biomass} \ HHV_{biomass})}{m_{oil} \ HHV_{oil}} \quad (3.18)$$

where EF_s is the emission factor; m_{oil} , and $m_{biomass}$ are the mass of bio-oil and microalgae (kg); HHV_{oil} , and $HHV_{biomass}$ are the high heat values of bio-oil and microalgae (MJ/kg); 2009 is the emission factor related to the direct usage of general renewable biomasses (g CO₂ eq/GJ) (EPA, 2018).

3.5. Microwave-assisted catalytic fast pyrolysis (MACFP) using a double catalytic bed

The microwave-assisted catalytic fast pyrolysis (MACFP) experiments were performed in a microwave oven (Makewave Corporation, China) with a power of 800 W at a frequency of 2450 MHz. The schematic diagram is shown in Fig. 3.4 [Zhou et al. (2022)]. The experimental setup includes several components designed to carry out the experiment effectively. It comprises a biomass feeder to supply the biomass material by gravity at a rate of approximately 1.5 g of microalgae per min, a microwave oven for energy input, a quartz reactor to contain the reaction, and an absorbent bed made of SiC balls that serve as microwave susceptors, absorbing and converting microwave radiation into heat. The absorbent bed temperature varied at the same pyrolysis reaction temperature.

Additionally, there is a dual catalyst fixed catalyst bed to facilitate the desired reaction, a thermocouple (K-type) to measure and control the temperature of the absorbent bed, a condenser to condense any vaporized substances, a liquid collection flask to collect the condensed liquid, a rotameter to measure fluid flow rate, and a gas sampling bag for collecting gas samples. The pyrolytic vapors were swept using N₂. The system was under 150 mL/min of N₂ for 10 min prior to the microwave heating to maintain the whole system in an inert atmosphere. Before performing the tests, 800 g of SiC particles with a particle size of 0.5 cm were put in the quartz reactor to behave as an absorbent bed. The reactor was then placed in the cavity of the microwave oven. At the bottom of the quartz outlet connector, the NiHTC/SiC and the NiHZSM-5/SiC (in this order) catalysts were placed in a fixed heated bed (500°C), which was used for upgrading the primary pyrolytic vapors.

After each test, the condensable components (liquid fraction) were collected into the flask, and the gas product was trapped in a sampling bag, both for subsequent analysis. The liquid fraction was weighed and determined by gravimetry, while the gas flow rate was measured using a rotameter. The percentage yield of each product [solid yield (SY_M); liquid yield (LY_M); gas yield (GY_M)] was determined as follows using the initial microalgae mass of 10 g [Eq. (3.19), (3.20), and (3.21)].

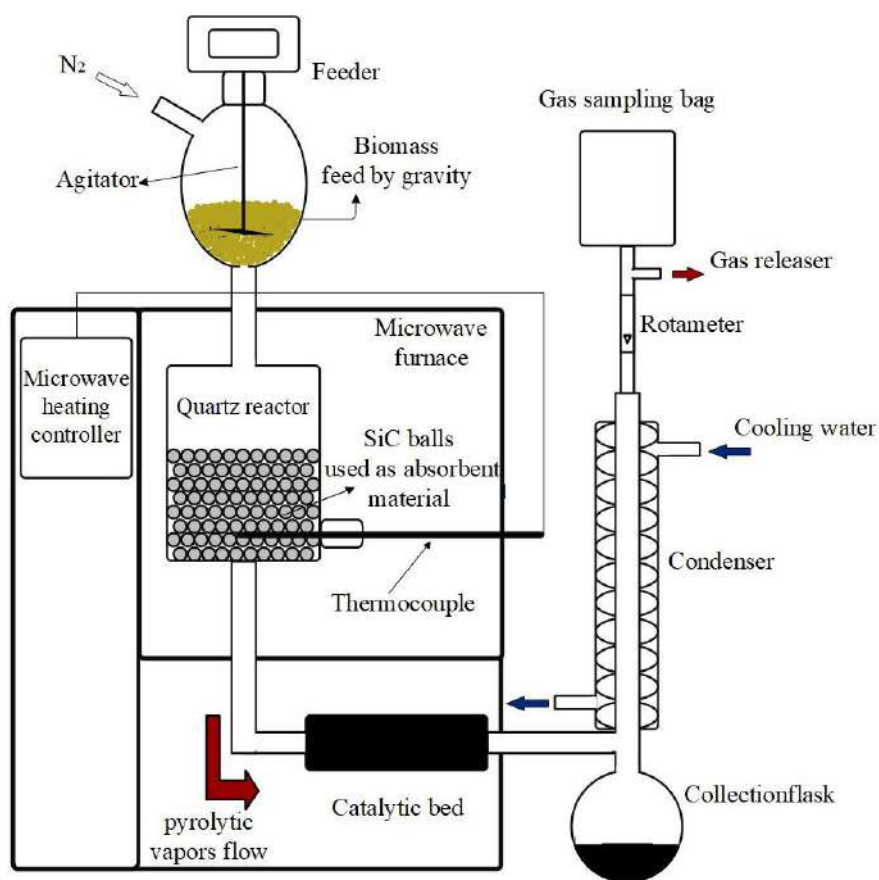


Fig. 3.4. Schematic diagram of the microwave catalytic pyrolysis system (Adapted from Zhou et al., 2022).

$$GY_M = \frac{Q t \sum \frac{x_i M_i}{V_{i 300K}^{1atm}}}{\text{microalgae mass fed}} 100\% \quad (3.19)$$

where x_i and M_i are the volume percentage and molecular weight of a gas component (g/mol) in the produced gas, respectively; Q is the gas flow rate exiting the reactor (mL/min); t is the reaction time (min); and V_i is the molar volume (mL/mol) at 300 K under atmospheric pressure of each gas component.

$$LY_M = \frac{\text{bio - oil mass}}{\text{microalgae mass fed}} 100\% \quad (3.20)$$

$$SY_M = 100\% - (GY_M + LY_M) \quad (3.21)$$

Microwave-assisted pyrolysis of the microalgae *Schizochytrium limacinum* without the presence of the tandem catalytic bed was carried out at three different temperatures (400, 500, and 600°C. After these tests, the pyrolysis temperature was established at 500°C to obtain a maximum yield of condensable organic products. To evaluate the effects of the tandem catalytic bed of NiHTC/SiC and NiHZSM-5/SiC, distinct ratios of NiHTC/SiC:NiHZSM-5/SiC (C_M) as well as the total catalyst:biomass (CB_M) were used. The loading total catalyst:biomass ratio ranged from 0.25:1 to 1:1 in this study. Tables 3.10 and 3.11 provide detailed information on the experiments conducted using microwave-assisted pyrolysis.

Table 3.10. Non-catalytic microwave-assisted pyrolysis tests' conditions.

T_M [°C]
400
500
600

Table 3.11. Catalytic microwave-assisted pyrolysis tests' conditions.

T_M [°C]	C_M	CB_M
500	0:1	0.5:1
500	1:0	0.5:1
500	1:1	0.5:1
500	1:1	0.25:1
500	1:1	1:1

To study the effect of reuse and regeneration on their catalytic activity, spent composite catalysts were employed in two distinct ways using the parameters of the optimized condition (temperature of 500°C, and the NiHTC/SiC:HZSM-5/SiC (C_M) and the CB_M ratios fixed at 1:1). Firstly, a batch of 7 consecutive experimental runs was performed using the spent catalysts without any treatment between the pyrolysis tests. Secondly, another batch of 7 experimental runs was completed. Still, this time, the spent catalysts were regenerated between each test by calcination in air atmosphere at 550°C overnight in an external muffle after each regenerated test.

3.5.1. Characterization of assisted-microwave pyrolysis products

3.5.1.1. Gas and bio-oil composition

The gas and bio-oil chemical compositions were analyzed according to Zhou et al. (2021) by a GC-TCD system (Varian Micro-GC CP 4900), equipped with a capillary column of 5 m length and an internal diameter of 2.10 mm. Argon flow rate and detector temperature were set to 30 mL/min and 200°C, respectively. Identification was done using the acquired calibration curves. Composition of the bio-oil was characterized using GC/MS (Agilent 7890-5975C) with a HP-5 MS capillary column, according to Dai et al. (2019). The oven temperature was held at 50°C for 2 min followed by a heating ramp to 260°C at 5°C/min and then was held for another 5 min. The injector was set at a temperature of 290°C and an injector size of 1 μ L with a split ratio of 1:10. The relative content of each component in the bio-oil product was estimated as the peak area percentage in the chromatogram. Compounds were identified based on retention time data using the National Institute of Standards and Technology (NIST library 08). The most abundant 60 components with a similarity index greater than 80% were selected for detailed analysis and then categorized according to carbon number and chemical group. As in the analytical and solar pyrolysis processes, a semi-quantitative analysis was conducted to assess the distribution of compounds in the resulting pyrolysis products. This investigation made use of the chromatographic peak areas. These values offer estimates of the relative quantities of the substances under analysis (Domínguez et al., 2003).

3.5.1.2. Gas and bio-oil higher heating values and assisted-microwave pyrolysis efficiency

The higher heating value (HHV, MJ/kg) of the condensable fraction was determined by the oxygen bomb calorimeter (1341 Parr Calorimeter) according to the ASTM D240-09 (2009) standard. Approximately 0.5 g of bio-oil was used, and combustion occurred at a pressure of 20 bar. The higher heating value (HHV, MJ/kg) of the gas was calculated according to the following formula:

$$HHV_{M_{gas}} = \sum y_i HHV_i \quad (3.22)$$

where y_i is the mass percentage of the respective gas component, and HHV_i is its higher heating value (MJ/kg).

The energy contents and efficiencies of the microwave pyrolysis process were investigated and detailed in this study. The energy recovery (ER_M) and overall energy efficiency ($\eta M_{overall}$) were based on a standard thermochemical balance (Smith et al., 2007) (Equations 3.23 and 3.24). The upgrading factor (U_M), which is defined as the ratio of the sum of produced bio-oil, gas, and bio-char heating values over the heating value of the processed biomass feedstock, was calculated as the ratio of the energy carried by the biofuels produced in MACFP to the energy contained in the microalgae *Schizochytrium limacinum* throughout Equation 3.25.

$$ER_M = \frac{m_{oil} HHV_{oil}}{m_{biomass} HHV_{biomass}} 100\% \quad (3.23)$$

where: m_{oil} and $m_{biomass}$ are the mass of bio-oil and microalgae; HHV_{oil} and $HHV_{biomass}$ are the high heat values of bio-oil and microalgae (MJ/kg), respectively.

$$\eta M_{overall} = \frac{m_{oil} HHV_{oil}}{m_{biomass} HHV_{biomass} + B} 100\% \quad (3.24)$$

where $\eta M_{overall}$ is the overall energy efficiency (%); m_{oil} and $m_{biomass}$ are the mass of bio-oil and microalgae (kg); B is the electricity consumption (MJ) of the microwave oven during the pyrolysis time of 10 min; HHV_{oil} and $HHV_{biomass}$ are the high heat values of bio-oil and microalgae (MJ/kg).

$$U_M = \frac{\sum m_i HHV_i}{m_{biomass} HHV_{biomass}} 100\% \quad (3.25)$$

where U_M is the upgrading factor; m_i and HHV_i are the mass (kg) and the higher heating value (MJ/kg) of the pyrolysis products i (bio-oil, gas, and char); $m_{biomass}$ and $HHV_{biomass}$ are the mass (kg) the higher heating value (MJ/kg) of the microalgae (MJ/kg).

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CHAPTER 4

4. BIOMASS AND CATALYSTS CHARACTERIZATION

This chapter presents and discusses the characterization of the *Schizochytrium limacinum* microalgae and the catalysts hydrotalcite and zeolite, which were used in the pyrolysis experiments.

4.1. *Schizochytrium limacinum* microalgae characterization: results and discussion

4.1.1. HHV, proximate, elemental, and chemical composition analyses

The results from proximate, elemental, and chemical composition analyses, together with the higher heating value and the granulometry of the microalgae *Schizochytrium limacinum* are presented in Table 4.1. Moisture content is a crucial biomass feature in the pyrolysis process. Three percent of moisture content can be considered adequate for biomass employed in thermochemical operations. Usually, for pyrolysis, the biomass is dehydrated to reach more significant energy efficiency during thermal degradation (Chen et al., 2014). *Schizochytrium limacinum* microalgae presented low fixed carbon and high volatile content. The volatiles are related to the material mass fraction that can be volatilized during thermal degradation. Since bio-oil is the product of interest, a high volatile content is desirable for biomasses employed in pyrolysis processes. The investigated microalgae in this study presented 88.7%, considered a satisfactory value for liquid generation (Hao et al., 2021).

The HHV found for the *Schizochytrium limacinum* microalgae was 23.7 MJ/kg (wet basis). The low ash content contributes to increasing the higher heating values since the ashes do not participate in the material thermal degradation (Fakayode et al., 2020). Wagenen et al. (2012) studied *Nannochloropsis salina* microalgae. The HHV and ash content for the *Nannochloropsis salina* was 25.4 MJ/kg and 2.5, respectively. Microalgae species with a high content of carbohydrates and lipids have great potential for biofuel production since these compounds have higher energy content than proteins (Li et al., 2019; Aniza et al., 2021). Considering the high lipid and carbohydrate content and low nitrogen percentage, *Schizochytrium limacinum* microalgae strains present significant potential for biofuel production. Usually, microalgae contain protein,

lipids, and carbohydrates. These chemical components are found to be decomposed in the sequence of carbohydrates, proteins, and lipids, and quantifying these three main components is essential since they influence the pyrolysis products composition (Li et al., 2013).

Table 4.1. *Schizochytrium limacinum* microalgae characterization.

<i>Schizochytrium limacinum</i>	
Proximate analysis (wt.%)	
Moisture	3.0 ± 0.8
Volatile matter	88.7 ± 0.5
Ash	9.2 ± 0.3
Fixed Carbon*	2.1
Elemental analysis (wt.%)	
C	56.31
H	8.46
N	2.71
S	1.81
O*	21.52
Higher heating value (HHV)	
23.74 ± 0.18 MJ/kg	
Granulometry (mm)	
Average particle diameter	0.250 - 0.177
Chemical composition (%)	
Proteins	14.5 ± 0.7
Lipids	52.4 ± 0.1
Carbohydrates	21.8 ± 0.2
Lignocellulosic composition (%)	
Cellulose	4.2 ± 0.2
Hemicellulose	8.2 ± 0.2
Lignin	2.3 ± 0.1

*By difference

The percentage of proteins found for *Schizochytrium limacinum* microalgae was 14.5%. Proteins are composed of amino acids, organic compounds that contain nitrogen, most likely responsible for forming undesirable nitrogenous compounds during pyrolysis (Barbosa et al., 2021). The low protein content found in the *Schizochytrium limacinum*, compared to values in other microalgae, makes this microalga a more appropriate biomass for pyrolysis. Andrade et al. (2020) studied the pyrolysis of two microalgae, *Chlamydomonas reinhardtii* and *Spirulina platenses*,

which presented 71 and 53% protein contents, respectively. Their generation of nitrogenated compounds ranged from 15 to 50%, hindering hydrocarbon formation. Coherently with the low protein content, the N content of 2.71% in the elemental analysis was also low. In contrast, Machado et al. (2022) studied processing methods on microalgae cells, finding protein contents of 51–58 % for *Chlorella vulgaris*, 46–63 for *Arthrospira platensis*, and 60–71 for *Arthrospira maxima*. The monosaccharide structure of carbohydrates results in oxygen-containing composites, and the thermal decomposition process of triglycerides, which are the main lipid component, can release carboxylic acids and generate hydrocarbons (Wang et al., 2017a). In this study, the lipid and carbohydrate compounds represented 52.4 and 21.8% of the microalgae chemical composition, respectively. These data can be correlated to the relatively high C content (56.3%) and low O content of 21.5%.

Regarding the lignocellulosic composition, cellulose and hemicellulose together reached around 12%, representing approximately 55% of the carbohydrate content. Cellulose is the main component of the plant cell wall. It is a high molecular weight polysaccharide that consists of a long linear chain of repeated D-glucose units (~10,000) linked by glycosidic bonds. Hemicellulose is a mixture of several polymerized monosaccharides (Hameed et al., 2019; Wang et al., 2017b). Hemicelluloses have branches with short side chains along the main polymer chain, consisting of different sugars such as glucose, mannose, galactose, xylose arabinose, and glucuronic acid (Mohan et al., 2006). These carbohydrates can lead to oxygen-containing compounds (Wang et al., 2017a). On the other hand, as expected, the lignin content of *S. limacinum* was less than 2.5%, which is consistent with what is observed in the algal cell wall, which is reported to contain very low or almost no lignin content (Ilyas et al., 2021). Lignin has a highly branched polyphenolic structure. Its chains are distributed in all directions and form a three-dimensional macromolecular structure, acting as a binder for the agglomeration of fibrous cellulosic components, providing structural support and impermeability to produce an impenetrable barrier in the plant cell wall. Due to the relatively simple structure of microalgae, in contrast to, for example, trees, their lignin content is notably low (Hameed et al., 2019; Wang et al., 2017b). This low lignin content of the algae can be advantageous due to the less complex pretreatments required before thermochemical degradation (Ilyas et al., 2021).

From a chemistry perspective, biomasses with lower O/C wt. ratios generate bio-oil with improved quality (van der Stelt et al., 2011). Barbosa et al. (2021) and Babich et al. (2011) studied

Chlamydomonas reinhardtii and *Chlorella* microalgae and obtained O/C wt. ratios of 0.66 and 0.59, respectively, against 0.38 found in this study. The chemical composition results were the main reason this material was chosen to be pyrolyzed in this study. Regarding the effective hydrogen-to-carbon ratio (H/C_{eff}), expressed by Equation 4.1, there is a strong correlation between the H/C_{eff} ratio of feedstock and the content of hydrocarbons. Furthermore, the content of hydrocarbons could be promoted by increasing the H/C_{eff} ratio in feedstock since it is crucial to have a greater range of H since, in most thermal degradation processes, the oxygen is removed as water (Chen et al., 1986). Thus, hydrogen is lost from the bio-oil, which can lead to the formation of polycyclic aromatic hydrocarbons (PAHs), which are cancerogenic products (Rannug et al., 2002). Zhang et al. (2015) demonstrated that higher H/C_{eff} resulted in more aromatic and olefin products and less coke, reporting that materials with $H/C_{eff} > 1$ can achieve higher aromatic hydrocarbon content. Accordingly, the biomass choice for pyrolysis should consider the hydrogen content in biomass. The *Schizochytrium limacinum* showed a H/C_{eff} of 1.08, a value slightly higher than 1. However, there is still room for H improvement that can be done by co-pyrolysis of this microalgae with hydrogen-rich materials or hydro-pyrolysis.

$$H/C_{eff} = (H - 2O - 3N - 2S) / C \quad (4.1)$$

where H, O, N, S, and C are the molar percentages of hydrogen, oxygen, nitrogen, sulfur, and carbon in feedstock, respectively.

Analyzing the O/C and H/C wt. ratios provides crucial insights into the potential use of biomass for fuel production, as these ratios gauge the energy released during the bond breakdown. A higher oxygen content tends to diminish the calorific value, as carbon-oxygen and carbon-hydrogen bonds possess lower energy than carbon-carbon bonds (Trif-Tordai et al., 2011). The impact of these relationships on the calorific value of solid fuels can be elucidated through the Van Krevelen diagram, which correlates H/C wt. and O/C wt. parameters (Keiller et al., 2019). In Figure 4.1, the Van Krevelen diagram, as adapted by Keiller et al. (2019), includes data for the microalgae *S. limacinum*, allowing for a comparison with information available in the literature for other materials. Figure 4.1 reveals that *S. limacinum* microalgae fall close to the intersection peat and biomass quadrant, displaying an intermediate O/C ratio when contrasted with other solid fuels

like bituminous coal and lignocellulosic biomass. Specifically, *S. limacinum* shows H/C and O/C (wt.) ratios of 0.15 and 0.38, consistent with the experimentally determined higher calorific value of 23.74 MJ/kg. For instance, anthracite, situated in the lower-left corner of the diagram, boasts the lowest oxygen content and a calorific value of approximately 30 MJ/kg (García et al., 2014). In contrast, lignocellulosic biomasses generally occupy the upper-right section of the diagram, exhibiting lower higher heating values (HHVs), as outlined in Table 2.1. This demonstrates the factors behind the superior quality of bio-oils typically obtained from microalgae compared to those from lignocellulosic biomasses (Lee et al., 2020c).

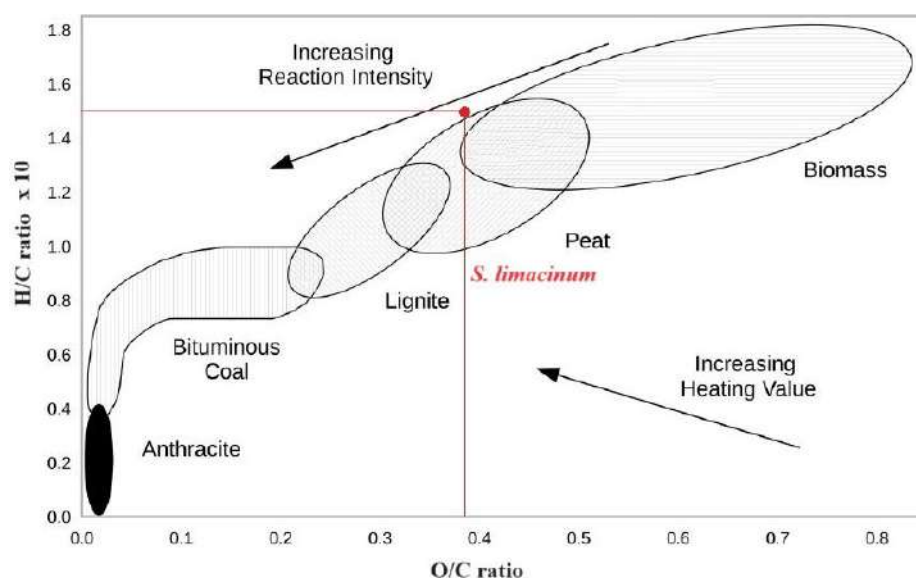


Fig. 4.1. Van Krevelen diagram (adapted Keiller et al., 2019), including the *S. limacinum* microalgae H/C and O/C ratios expressed in wt.

4.1.2. Thermogravimetric analysis (TGA) of the microalgae *Schizochytrium limacinum*

TGA results shows the *Schizochytrium limacinum* microalgae decomposition from 25 to ~900°C at a heating rate of 10°C/min. Fig. 4.2 presents the TGA and DTG curves from the biomass thermal conversion. Understanding the feedstock decomposition can assist in selecting the adequate temperature for thermal degradation, which will affect the liquid yield the three main microalgae chemical components decomposed in the sequence of carbohydrates, proteins, and lipids (Li et al., 2013; Li et al., 2019). As it can be seen in Figure 4.2, the sample weight started to decrease at ~50°C when moisture and highly volatile compounds were released. At approximately

200°C, there was an 11% weight loss, most likely due to the carbohydrate decomposition. The protein decomposition occurred around 300°C when the weight loss lowered by 10% more. A significant decrease of 40% in weight loss occurred at approximately 400°C and can be accounted for the lipid decomposition that mainly occurs between 400 and 500°C. Figure 4.2 shows that another 25% weight loss occurred at ~500°C, which suggests the material's complete decomposition.

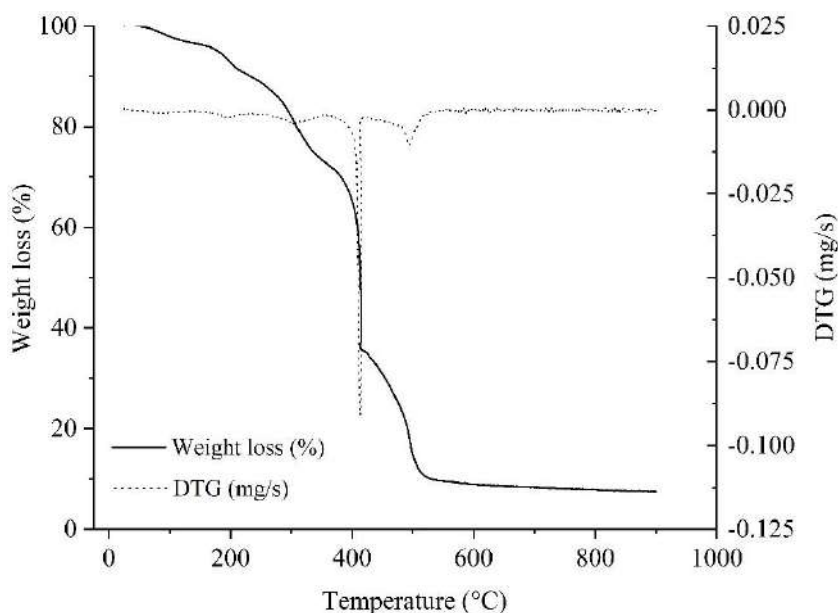


Fig. 4.2. TGA analysis expressed as weight loss (%) and its derivative DTG as a function of temperature for *Schizochytrium limacinum*.

4.1.3. FTIR, XRF and SEM analyzes of the *Schizochytrium limacinum* microalgae

The infrared spectra obtained for dry in natura biomass are shown in Figure 4.3. The absorbance corresponding to the chemical bonds of the microalgae *Schizochytrium limacinum* presented the functional groups' characteristics of lipids, proteins, and carbohydrates. The wide band between 3500 and 3100 cm^{-1} is assigned to O-H stretching vibrations, indicating carbohydrates in the biomass (Aboulkas et al., 2017). The C-H bonds, corresponding to methyl and methylene groups, which indicate the lipids' presence, mainly appear in the region between 2960-2850 cm^{-1} (Maliutina et al., 2018). Proteins are represented by amide I (C=O), a bond that produces a strong absorption band in the 1750–1745 cm^{-1} region range (Marcilla et al., 2009), and amide II

(N-H and C-N) peaks that are present in the 1550–1650 cm^{-1} region (Zainan et al., 2015). The C-O stretching band in the 1200–900 cm^{-1} region might indicate the presence of either carbohydrates or proteins (Yang et al., 2007).

The FTIR analysis reveals the presence of organic bonds consistent with the constituents found in microalgae, namely: (a) lipids/triglycerides, which are primarily composed of ester chains; (b) carbohydrates, which are constituted of monosaccharides that are aldehydes and ketones, and (c) proteins, which consist of amino acids, which are essentially amines with carboxylic acids. This analysis confirms the specific bonds that need to suffer cleavage during both pyrolysis and the path of the pyrolytic vapors through a catalytic bed. Consequently, to eliminate undesired compounds containing oxygen and nitrogen, it is primarily essential to break down the N-H, -OH, and =O bonds. These cleavages result in the release of the O and N atoms in the form of CO, CO₂, H₂O, and NH₃.

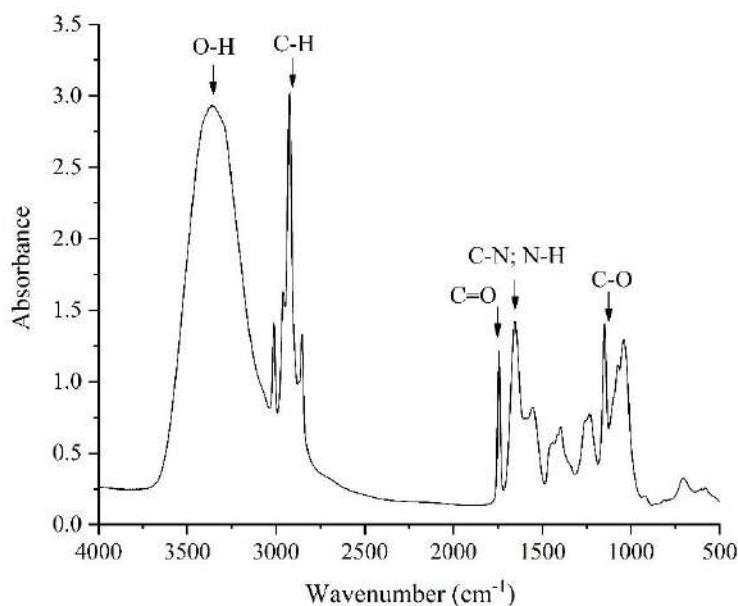


Fig. 4.3. FTIR spectrum for *Schizochytrium limacinum* microalgae.

The XRF results are presented in Table 4.2, which shows the elements found in the *Schizochytrium limacinum* microalgae. This data holds significance as it provides insights into biomass contamination, a factor that can negatively impact pyrolysis reactions and hinder the generation of desired products.

The presence of some inorganic elements, such as alkali (potassium) and alkaline earth (calcium and magnesium) metals, can assist the hydrocarbon formation during thermal degradation. Thus, the content of these elements in the biomass may indicate greater reactivity (Chagas et al., 2016). Nickel and zinc metals accounted for only a small part of the biomass and sum up to 24 ppm. Non-metal elements such as silicon and phosphorus, which tend to lessen reactivity during the thermal conversion (Eom et al., 2012), remained below 1%. Overall, the *Schizochytrium limacinum* microalgae presented low non-metal content of 2.89%, which could hinder thermal degradation. Andrade et al. (2018b) performed XRF analyses of *Spirulina platensis* e *Chlamydomonas reinhardtii* microalgae, finding non-metal contents of 4.71 and 11.42%, respectively.

Table 4.2. XRF results of *Schizochytrium limacinum* microalgae.

Element	Content
Na	1.50%
K	0.62%
Mg	0.26%
Ca	2.48%
Fe	88 ppm
Ni	11 ppm
Zn	13 ppm
Mo	31 ppm
Pd	30 ppm
Al	0.03%
Si	0.97%
P	0.36%
S	1.21%
Cl	0.35%

Figure 4.4 shows the image obtained by scanning electron microscopy (SEM) for the *Schizochytrium limacinum* microalgae. The heterotrophic microalgae, morphologically, exhibits spherical cellular, usually with diameters between 7-15 μm . Its spherical shape characterizes it as a homogeneous biomass (Honda et al., 1998). The authors suggest that its homogeneity may favor the degradation process during the heat transfer in the thermal conversion. Recent research on this microalga is to produce docosahexaenoic acid (DHA) and biofuel production (Bindea et al., 2018; Johnson et al., 2009).

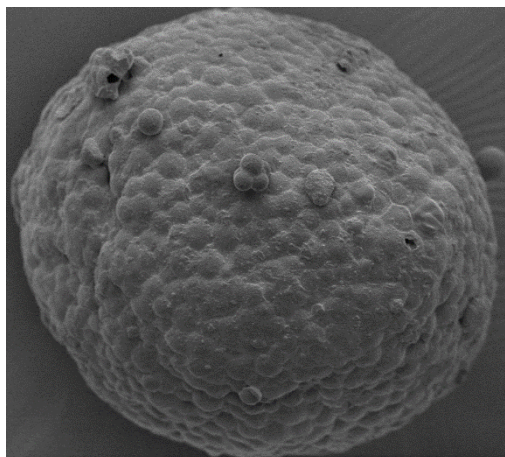


Fig. 4.4. Microscopic image of the *Schizochytrium limacinum* microalgae (1.5 Kx of magnification, scanning electron microscope EVO MA 10 Zeiss, Laboratory of Scanning Electron Microscopy at FEQUI/UFU).

4.2. Catalysts hydrotalcite and zeolite H-ZSM-5: results and discussion

4.2.1. X-ray diffraction (XRD) analysis of hydrotalcite and zeolite catalysts

Hydrotalcite

Figure 4.5 shows the X-ray diffraction (XRD) patterns of the HTC catalysts, before calcination, after calcination, and for NiHTC after calcination. The XRD pattern of HTC before calcination showed typical peaks of layered double hydroxides (LDHs) structures (Wiyantoko et al., 2015), which consist of symmetric and sharp peaks with high intensity at low 2θ angle and asymmetric and broad peaks at high 2θ angle. This behavior is typical of the double-layer hydroxide in which the isomorphic substitution of Mg^{2+} by Al^{3+} in the brucite layers occurs (Mokhtar et al., 2012).

The XRD diffractogram of HTC before calcination show a well-crystallized structure with high homogeneity in the carbonate form, with characteristic peaks at 11.5, 23.1, 34.5, 39.0, 46.5, 60.8, and 63.9°, which correspond to the (0 0 3), (0 0 6), (0 0 9), (0 1 5), (0 1 8), (1 1 0), and (1 1

3) planes (according to the Joint Committee on Powder Diffraction Standards, JCPDS #70-2151) (Kim et al., 2016; Wang et al., 2020).

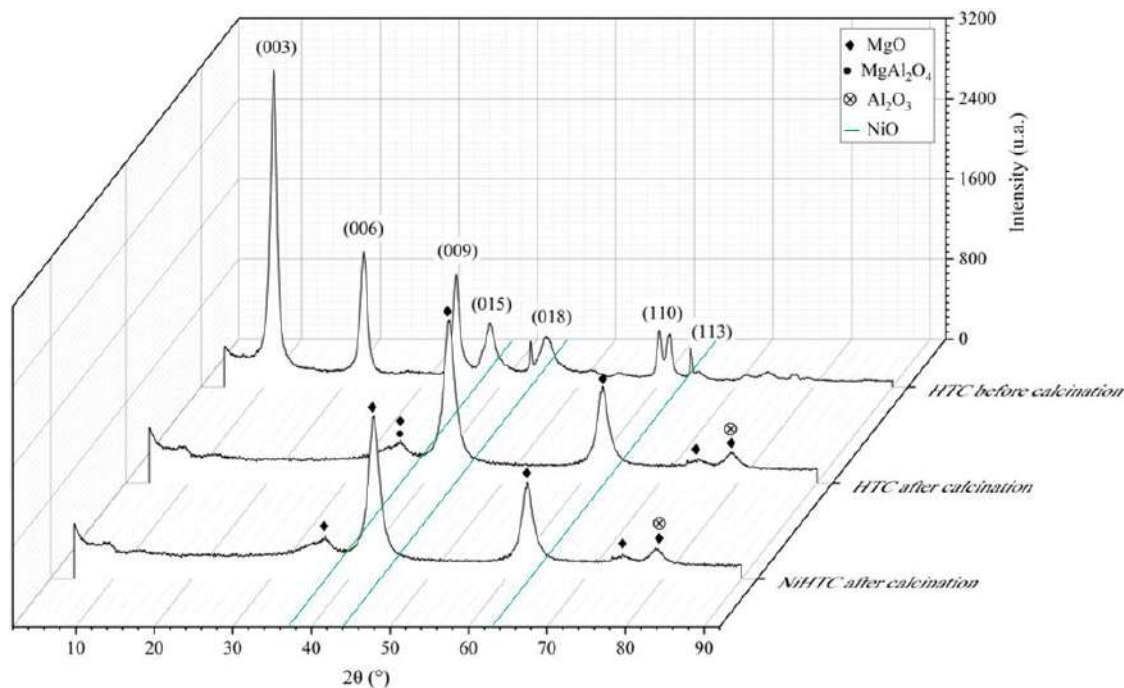


Fig. 4.5. X-ray diffraction (XRD) patterns of the HTC catalysts, before calcination, after calcination, and NiHTC after calcination.

The typical phases of the hydrotalcite disappeared after calcination at 550°C, and according to the ICSD database (Inorganic Crystal Structure Database), the 2θ peaks demonstrate the formation of the mixed oxides derived from hydrotalcite (Rodrigues et al., 2003). The characteristic peaks at 43, 63, and 77.5° correspond to a MgO-like phase. In contrast, the peaks of MgAl_2O_4 and Al_2O_3 (overlapped by the diffraction peak of MgO) were minimal, indicating that Al^{3+} cations were dispersed in the structure of MgO without forming spinel species (Navarro et al., 2018). Regarding the NiHTC (10 wt.% Ni) after calcination, no significant differences were observed in the XRD patterns. The Ni impregnation did not alter the HTC crystal structure. In addition, no patterns specific to NiO (37, 44 and 63°) crystalline alone were detected from the XRD spectra (Hotovy et al., 2004). This result indicated that NiO might be highly dispersed on the surface of HTC.

As revealed by the X-ray diffraction (DRX) analysis, the synthesized mixed hydrotalcite oxides exhibit a combination of acidic and basic sites. Furthermore, upon impregnation with nickel,

these catalysts also present metallic sites. Hydrotalcite's acidic and basic properties work in tandem to eliminate nitrogen, possibly through the Hofmann mechanism (Andrade et al., 2018). In addition, the basic sites found within lamellar mixed hydroxides, such as hydrotalcite, are characterized by positively charged layers, making them adept at adsorbing inorganic anions, notably -OH (Goh et al., 2008). It is important to note that bifunctional catalysts like hydrotalcite, which incorporate both metals and metal oxides, demonstrate significant capabilities in promoting deoxygenation and carbon-carbon coupling reactions. Combining transition metals into these bifunctional catalysts results in the creation of numerous Lewis acid sites, thereby enhancing selectivity towards benzene, toluene, and xylene. Likewise, the presence of metal oxides generates Lewis acid sites, elevating the catalytic activity of bifunctional catalysts (Liu et al., 2020). These reactions that might be promoted by the HTC catalysts are valuable to enhance pyrolytic bio-oil since they can assist in oxygen and nitrogen removal.

Zeolite

Fig. 4.6 shows the X-ray diffraction results for pure HZSM-5 before and after calcination at 550°C and for the 10 wt.% Ni impregnated sample (NiHZSM-5) after calcination. The X-ray diffraction patterns for the pure and metal zeolite samples presented the characteristic mordenite structure according to JCPDS (#44-0002) data (Parsafard et al., 2017). The main five peaks in the 2θ region (two between 7 and 10° and three diffraction peaks at around 23 - 25°) corresponding to (010), (020), (501), (151), and (303) indicated the formation of a well-crystalline structure of HZSM-5 molecular sieves (Lima et al., 2019). The XRD pattern of the modified zeolite (NiHZSM-5) indicates that the structure of the zeolites remained intact after the Ni loading, which, analogously to the HTC results, illustrates that NiO might be highly dispersed on the surface of the zeolite catalyst (Musa et al., 2018). The cubic NiO (100), NiO (200), and (220) reflections at 37 , 44 , and 63° , respectively, were not observed in the XRD spectra (Hotovy et al., 2004).

As scrutinized for the HTC catalyst, the distinctive peaks observed in the HZSM-5 material confirm its adherence to the supplier's specified standards. This catalyst, featuring both acidic and metallic sites following wetness impregnation, plays a crucial role in the catalytic pyrolysis process, aiding in removing oxygenated compounds and promoting aromatization. Additionally, it serves to mitigate the formation of coke while simultaneously enhancing the catalytic cracking

process, ultimately facilitating the generation of hydrocarbons (Lashchinskaya et al., 2023; Zhao et al., 2013).

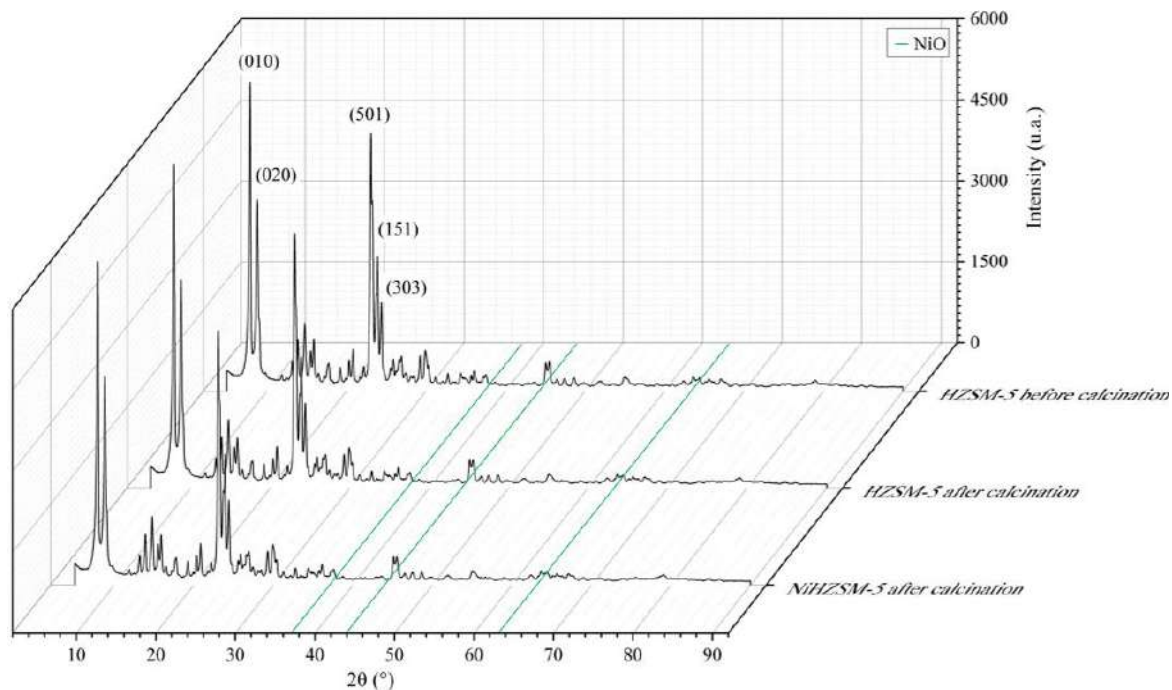


Fig. 4.6. X-ray diffraction (XRD) patterns of the HZSM-5 catalysts, before calcination, after calcination, and NiHZSM-5 after calcination.

4.2.2. Nitrogen adsorption analysis (specific surface area and texture properties) and Thermo Scientific temperature-programmed desorption of ammonia (TPD-NH₃) of hydrotalcite and zeolite catalysts

The acidity of catalysts samples acquired from TPD-NH₃, the BET surface areas and texture properties derived from the N₂ adsorption-desorption isotherms for the calcined hydrotalcite and zeolite catalysts before and after nickel impregnation are recorded in Table 4.3. The BET surface areas (S_{BET}) of 188 and 419 m²/g for the HTC and HZSM-5, respectively, are in close agreement with their characteristics observed in other studies (Navarro et al., 2018; Jafarian et al., 2018). The moderate specific area is characteristic of the hydrotalcite-type precursors and favors its action during pyrolysis. Conversely, zeolites are known to have higher BET-specific areas that favor their action during pyrolysis. Wang et al. (2020) studied Mg-Al mixed oxide derived from hydrotalcite and found a pore volume (V_p) of 0.72 cm³ and a pore diameter (D_p) of 16.50 nm, similar values to

those found in the present work. The formation of mesopores (2 to 50 nm) may be related to the elimination of carbonate ions (in the form of CO₂), which results in craters appearance in the lamellar structure and the formation of pores (Rodrigues et al., 2003; Arias et al., 2021).

Table 4.3. Catalysts' textural and acidity properties.

Catalyst	S_{BET} [m ² /g]	V_p [cm ³ /g]	D_p [nm]	Acid site density (n_a) [μmol/m ²]
HTC after calcination	188	0.85	15.35	1.13
NiHTC after calcination	186	0.70	8.23	0.81
HZSM-5 after calcination	419	0.26	2.79	2.08
NiHZSM-5 after calcination	390	0.24	2.88	1.76

Regarding the HTC acidity, the number of acid sites on the Mg-Al mixed oxides is determined by their Mg/Al ratio. The acid site density (n_a) of 1.13 μmol/m² is consistent with the Mg/Al molar ratio of 3:1 since the catalyst acidity increases with the Al content increment (Prinetto et al., 2000). Analyzing the NiHTC, no significant difference was found in the S_{BET} and V_p values, which implies that the nickel was highly dispersed on the support. On the other hand, the pore diameter and acid site density showed a downward trend, as expected. The author suggest that the metallic sites added to the HTC catalyst through the nickel impregnation might cover some of the catalyst's pores, which could lessen the pore diameter. In addition, incorporating transition metals, such as nickel, reduced the catalyst's acidity by integrating the metal's hydrogenation function and the supports' acid function, creating new intermediate acid sites (Zainan et al., 2018).

As regards the zeolite, Azreena et al. (2021) also characterized HZSM-5. Their findings are in agreement with the results of this present study and revealed the presence of microporous and high acidity, presenting V_p , D_p , and n_a values of 0.29 cm³/g, 3.30 nm, and 2.29 μmol/m². Differently from the NiHTC behavior, when comparing the pure HZSM-5 and NiHZSM-5, the catalyst impregnated with Ni revealed no significant change in the V_p and D_p values. Still, it caused a slight decrease in the catalyst surface area, indicating that Ni was deposited in the zeolite pores (Liang et al., 2017). The NiHZSM-5 also had its acidity diminished by approximately 15% due to the incorporation of the transition metal.

4.2.3. Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and X-ray fluorescence (XRF), and scanning electron microscopy (SEM) analyzes of hydrotalcite and zeolite catalysts

Thermogravimetric curves (TGA/DTG) for NiHTC and NiHZSM-5 shown in Figures 4.7 (a) and (b) indicate minimal variations of mass loss (approximately 10% for both samples). This fact can be explained by the loss of moisture possibly acquired by the catalyst during storage. The curve shows only one stage of mass loss, remaining constant afterward, demonstrating the catalysts' thermal and structural stability, reaffirming that the impregnation processes followed by calcination were satisfactory.

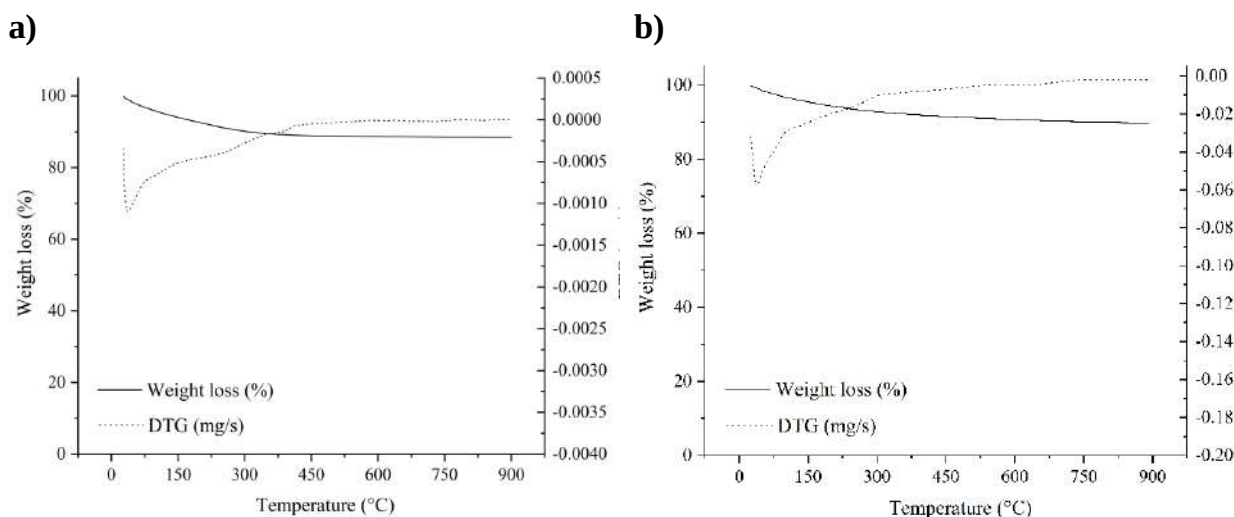


Fig. 4.7. TGA/DTG curves of (a) NiHTC and (b) NiHZSM-5 performed at a heating rate of 10°C/min under a helium atmosphere.

Figure 4.8 illustrates the infrared spectra for NiHTC and NiHZSM-5 in the 4000-400 cm^{-1} region. In fig. 4.8 (a), the broad peak between 3600-3200 cm^{-1} characterizes the H bond vibrations regarding the O-H groups most likely situated in the layers of brucite $[\text{Mg}(\text{OH})_2]$ present in the hydrotalcite catalyst (Abelló et al., 2007; Shekoohi et al., 2017). The band located between 1600-1700 cm^{-1} represents -OH bonds but is related to the water molecules between the layers in double hydroxides (LDHs) structures (Wiyantoko et al., 2015). The peaks at wavenumbers between 1300-1450 cm^{-1} correspond to the presence of carbonate anions (CO_3^{2-}) in the interlamellar spaces of hydrotalcite (Setshedi et al., 2012). Finally, the peaks found in 1375 and 815 cm^{-1} regions represent

the presence of nitrates (NO_3^{2-}), also located in the interlamellar layers (Mokhtar et al., 2012; Wiyantoko et al., 2015). The infrared spectrum showed the main typical peaks of hydrotalcite, similar to those reported by previous research studies (Wang et al., 2020; Di Cosimo et al., 1998). Figure 4.8 (b) shows the infrared spectra for NiHZSM-5, indicating well-known zeolite characteristics and is in accordance with other research studies (Veiga et al., 2017; Yu et al., 2021).

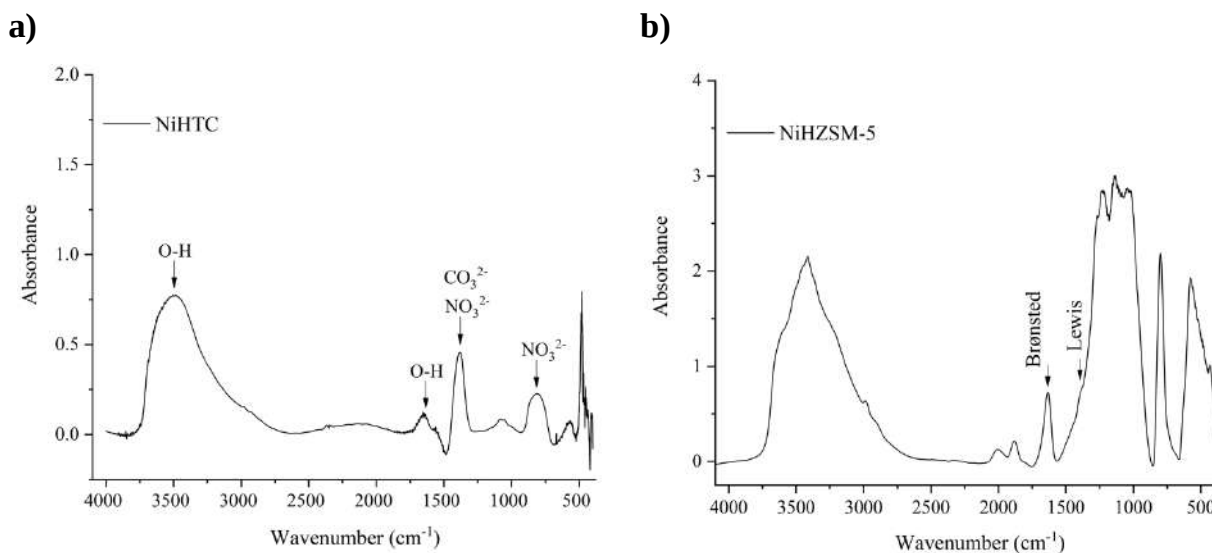


Fig. 4.8. Fourier transform infrared spectra of (a) NiHTC and (b) NiHZSM-5.

The zeolite spectra present bands in the 1650 and 1400 cm^{-1} regions, which are associated with Brønsted and Lewis sites, respectively. Brønsted acid sites predominated for this sample and can be related to $\text{Si}(\text{OH})\text{Al}$ (Parsafard et al., 2017). On the other hand, Lewis acid sites can be associated with the presence of aluminum species. The spectra had a stronger band at 1650 cm^{-1} (Brønsted acid sites), indicating a more significant amount of Brønsted sites (Parsafard et al., 2014). The band at 1250 cm^{-1} can also be identified as resulting from the overlap of bands associated with the two types of sites (Veiga et al., 2017). As the XRD, the FTIR analysis on both catalysts revealed characteristic peaks associated with HTC and HZSM-5, respectively. These feature confirmations are vital to validate the successful synthesis of HTC and the quality of the supplied HZSM-5. Consequently, these two catalysts are expected to play a role in optimizing bio-oil in line with the literature's expectations.

Table 4.4 presents the X-ray fluorescence (XRF) results, showing the catalysts' compounds' contents. NiHTC presented 63.29 % of MgO and 25.77% of Al₂O₃, which agrees with the XRD patterns that the Al³⁺ cations were dispersed in the structure of MgO that is in accordance with the chosen 3:1 Mg/Al ratio of the catalyst.

Table 4.4. XRF results of NiHTC (a) and NiHZSM-5.

Catalyst	Compound	Content (%)
NiHTC	MgO	63.29
	Al ₂ O ₃	25.77
	NiO	10.69
NiHZSM-5	SiO ₂	85.72
	Al ₂ O ₃	1.66
	NiO	9.87

NiHZSM-5 showed 85.72% of SiO₂ and 1.66% of Al₂O₃, corroborating FTIR results that showed predominated Brønsted acid sites related to Si(OH)Al and the supplier specification of ab 80:1 SiO₂/Al₂O₃ ratio. The 10 wt.% was successfully applied in both catalysts for the nickel impregnation process since they presented 10.69 and 9.87% of NiO for NiHTC and NiHZSM-5, respectively.

NiHTC and NiHZSM-5 microscopy images are shown in Figures 4.9 and 4.10. The morphology shown is typical of the layered double hydroxides (LDHs) (Wiyantoko et al., 2015). The formation of flat, thin, and well-developed crystals, characteristic of its layered structure, is observed. The commercial zeolite consists of agglomerated crystals with a certain degree of roughness, analogous to the material studied by Li et al. (2017). The materials appear to possess bi-modal particle size distribution with abundant large spherical particles, believed to be the HZSM-5 phase and small hexagonal/cubic and HMS phase, correspondingly (Parsafard et al., 2014). Scherer et al. (2009) stated that clusters are more prominent for higher Si/Al ratios.

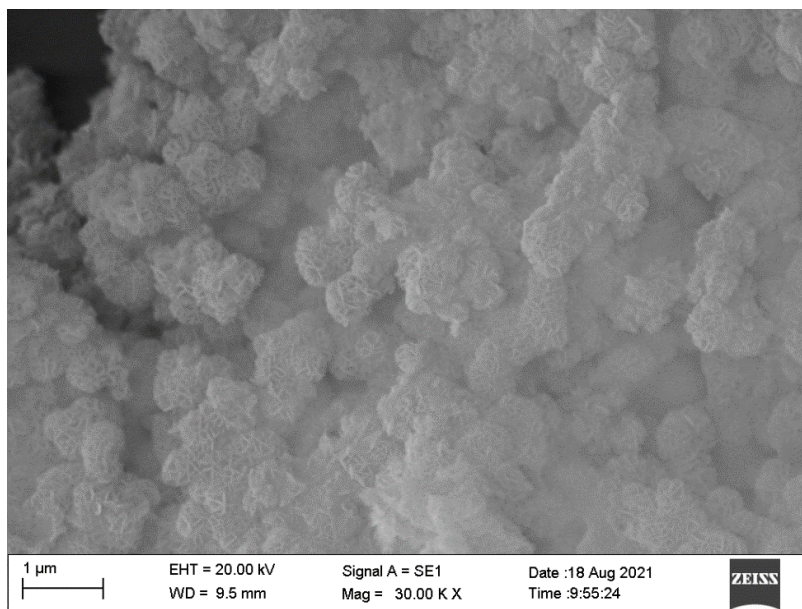


Fig. 4.9. Microscopic image of the NiHTC catalyst (30 Kx of magnification, scanning electron microscope EVO MA 10 Zeiss, Laboratory of Scanning Electron Microscopy at FEQUI/UFU).

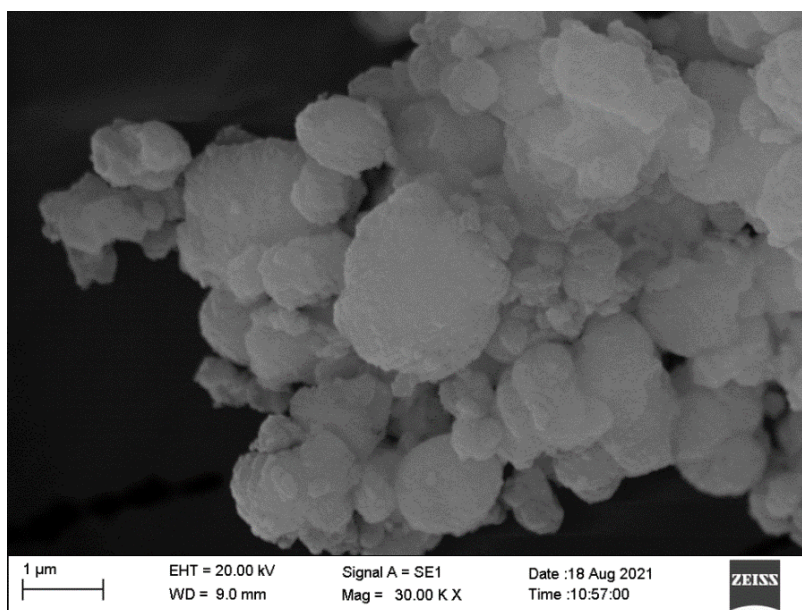


Fig. 4.10. Microscopic image of the NiZSM-5 catalyst (30 Kx of magnification, scanning electron microscope EVO MA 10 Zeiss, Laboratory of Scanning Electron Microscopy at FEQUI/UFU).

4.3. Conclusions

Schizochytrium limacinum presented desirable characteristics to be employed in pyrolysis processes. Since bio-oil is the product of interest, *Schizochytrium limacinum* high volatile content of 88.7% is satisfactory for reaching more liquid generation. Considering the high lipid and carbohydrate content and low nitrogen percentage, the percentage of proteins found for *Schizochytrium limacinum* microalgae was 14.5%. On the other hand, the lipid and carbohydrate compounds represented 52.4 and 21.8% of the microalgae chemical composition, respectively. These data can be correlated to the relatively high C content (56.3%) and low N (2.7%) and O (21.5%) percentages, which led to a H/C_{eff} of 1.08, a value slightly higher than 1. The degradation of biomasses with higher H/C_{eff} resulted in more aromatic and olefin products. The chemical composition indicates that the *Schizochytrium limacinum* can be an excellent material for bio-oil production, and it is the main reason this material was chosen to be pyrolyzed in this study.

A catalyst design can affect the selectivity of the product formation, and a proper catalyst application might change the chain of reactions resulting in the bio-oil upgrade. Hydrotalcite (HTC) was chosen to achieve good deacidification, while zeolite (HZSM-5) could assist in the deoxygenation/aromatization reactions and consequently provide high-energy outputs through hydrocarbon generation. Incorporating a transition metal such as nickel (Ni) moderates the acid sites, and might lead to less coke formation, besides creating additional transport channels that assist hydrocarbon formation by cracking heavy fractions. The increase in metal load can raise catalytic cracking and hinder coke formation due to the moderation of the catalysts' acid sites. However, metallic impregnation can be responsible for forming large metallic particles in the catalyst support. These large particles become unattractive since they can decrease the catalysts' specific surface area. Thus, the amount of 10 wt.% of nickel was chosen. The catalysts' characterization showed well-known HTC and zeolite characteristics, which agrees with other research studies. As indicated by the XRD and XRF results, the nickel impregnation was successfully applied for both catalysts. NiHTC and NiHZSM-5 presented approximately 10 wt.% de NiO that was highly dispersed as designed by the author of this study.

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CHAPTER 5

5. ANALYTICAL PYROLYSIS OF SCHIZOCHYTRIUM LIMACINUM MICROALGAE PYROLYSIS IN A TANDEM CATALYTIC BED

This chapter presents and discusses the results of analytical pyrolysis in the tandem catalytic bed composed of hydrotalcite and zeolite. Effects of the temperature, catalysts' ratios, catalysts synthesis, and pre-treatment are evaluated.

5.1. Results and discussion

5.1.1. Effects of the reaction temperature, tandem catalytic bed (NiHTC and NiHZSM-5), and total catalysts to biomass ratio on analytical pyrolysis

The composition of products resulting from the analytical pyrolysis (Py-GC/MS) experimental runs were analyzed. A semi-quantitative approach that relies on the chromatograph peak area percentages of the 60 major components detected was employed to assess their relative yields. This semi-quantitative method has been widely embraced by several researchers in the field, as documented in references (Lee et al., 2022; Moogi et al., 2022; Prabhakara et al., 2022). These values can estimate how much of a measured substance is present (Domínguez et al., 2003). The identified compounds were categorized and grouped based on their organic functional groups, which included oxygenated species (such as ketones, alcohols, and carboxylic acids), nitrogenated species (like amines and nitriles), hydrocarbons and other compounds, as shown in Figure 5.1. The total relative peak percentage ranged from 96.5% to 98.9% across the 3 different temperature conditions, as the unidentified compounds were not included in the overall composition summation. The significant influence of temperature on biomass pyrolysis behavior is a widely acknowledged fact. Therefore, in this research, the impact of temperature on the distribution of pyrolytic products from *S. limacinum* was examined.

Regarding the non-catalytic tests, the highest hydrocarbon formation is observed at 650°C as shown in Fig. 5.1. There is an increase in the product of interest (hydrocarbons) from approximately 35 to 60% with increasing temperature. This phenomenon can be primarily

attributed to the endothermic nature of the pyrolysis process. Specifically, higher temperatures supply greater energy, facilitating the efficient cleavage of stronger bonds (Du et al., 2013). In this case, it led to an increase in the overall hydrocarbon content, likely resulting from the rupture of =O and -OH bonds. Aniza et al. (2021) explain that the C-H-O chemical bonds within microalgal biomass primarily arise from carbohydrates and lipids, with negligible protein contribution. Conversely, oxygenated compounds, such as alcohols, ketones, and carboxylic acids, remain more prominent at lower temperature ranges.

The nitrogenated compounds exhibit relatively minor variations, suggesting that -CN bonds may require catalytic assistance to reduce their energy activation barrier for breaking, thereby facilitating nitrogen removal. Supporting this assertion, the research conducted by Du et al. (2013) demonstrated that indole compounds generated through non-catalytic pyrolysis remained stable despite the increase in temperature. This observation implies a high degree of stability in indole derivatives. However, the nitrogen-containing compounds were generally detected in lower quantities than the oxygen-containing compounds, primarily because *Schizochytrium limacinum* exhibited a protein content of only 14.5% in its composition.

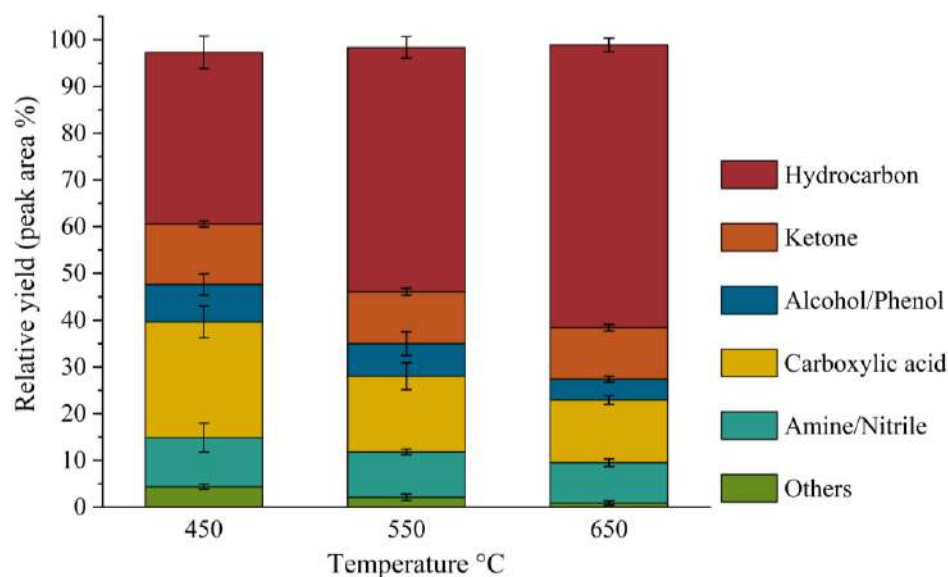


Fig. 5.1. Effects of temperature on bio-oil composition (non-catalytic tests).

Figure 5.1 shows a general trend where alcohols, ketones, amines, and nitriles exhibit a slight decrease with increasing temperature. In contrast, carboxylic acids undergo a significant

reduction, nearly halving at the highest reaction temperature of 650°C. This decline in carboxylic acids is primarily attributed to decarboxylation reactions, with acetic and octadecanoic acids as the major constituents, diminishing as temperature rises. The elevated temperature promotes the cracking of carbonyl and carboxyl groups, as elucidated by Wang et al. (2013a).

Microalgae composition is primarily from proteins, carbohydrates, and lipids (Lee et al., 2020). The pyrolysis process suggests that the thermos-degradation extent follows the order of carbohydrates > protein > lipid (Li et al., 2019a). Lipid and carbohydrate pyrolysis can produce oxygenated compounds such as carboxylic acids, esters and ketones but can also form long chains of hydrocarbons derived from the transformation of fatty acids present in triacylglycerols (Chen et al., 2017). Among the nitrogenous compounds, we can mention the amines, amides, and nitriles most likely formed from the degradation of proteins in microalgae. Contrary to hydrocarbons, acidic and nitrogenated compounds are considered unwanted products for bio-oil, as they confer instability and may cause a decrease in their HHV (Zhang et al., 2021). The calorific values of the three constituents show that protein, which presents an HHV of around 5 MJ/kg, is not a suitable biofuel feedstock. In contrast, lipids and carbohydrates with HHVs of 34 and 15 MJ/kg, respectively, can be considered potential feedstocks for liquid biofuel production. (Awad et al., 2018; Lin et al., 2021).

Anticipating an improvement in hydrocarbon generation, this investigation's primary focus, catalytic experiments were conducted to assess the efficacy of NiHTC and NiHZSM-5 catalysts within a tandem catalytic bed system. The results from catalytic experimental runs are presented in Fig. 5.2. The catalytic experiments revealed that irrespective of the catalyst employed, the highest temperature led to a more substantial hydrocarbon generation, aligning with the findings from the non-catalytic experimental runs.

Upon closer examination of the data concerning the catalysts usage, when using NiHZSM-5 alone there was an increase in nitrogen-containing compounds, particularly at the lowest temperature of 450°C comparing to the non-catalytic control. On average, there was an approximately 7.5% increase in nitrogenated substances, with nitriles being the predominant components. One possible explanation is that the zeolite (NiHZSM-5) may have facilitated the incorporation of nitrogen in larger hydrocarbon chains, generating nitrile molecules, given that the most abundant compound with 17 carbon atoms was heptadecanenitrile. Conversely, the presence of oxygenated compounds decreased by approximately 15% at 650°C compared to the non-

catalytic control conducted at the same temperature. Consequently, this reduction resulted in an 8% increase in hydrocarbons in the catalytic test employing solely NiHZSM-5 (Azreena et al., 2021).

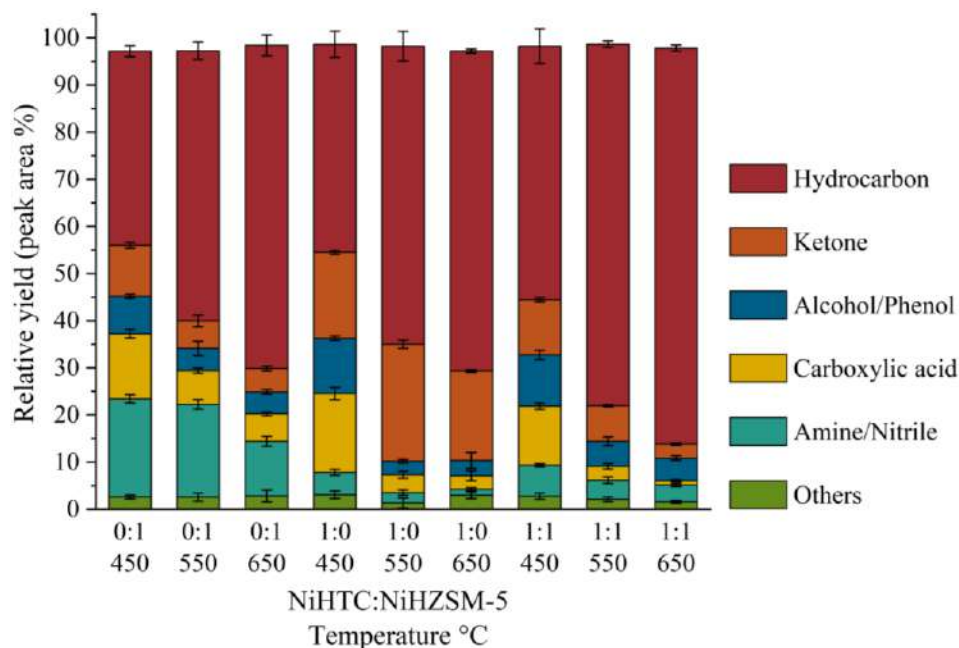


Fig. 5.2. Effects of temperature and the dual-catalyst ratio (NiHTC:NiHZSM-5) on bio-oil composition.

When scrutinizing the experiments involving only hydrotalcite (NiHTC), notable differences emerge when compared to experiments involving only NiHZSM-5 or non-catalytic controls. Specifically, carboxylic acid levels were reduced to 3%, whereas the production of ketones increased, reaching more than 20% at 550 and 650°C. At the lowest temperature, the usage of NiHTC had less influence and the carboxylic acid suffered a reduction by around 10% compared to the non-catalytic test at the same temperature. The ketone compounds consisted of chains ranging from 3 to 8 carbon atoms, with acetone and 2-pentadecanone being the predominant substances. Furthermore, hydrocarbon generation was around 67% in test conditions of 1:0/650°C, probably due to deacidification and denitrification promoted by the NiHTC. The deacidification can be attributed to the basicity of the hydrotalcite catalysts since it has a bifunctional character (acid/basic). Lamellar mixed hydroxides like hydrotalcite possess positively charged layers, which make them proficient in capturing inorganic anions, primarily -OH. Additionally, nickel catalysts

can also assist in the elimination of -OH, helping to promote the acylation of carboxylic acids (Goh et al., 2008; Amani et al., 2017). Ding et al. (2018) used CaO to deacidify pyrolysis products from hemicellulose and plastic, reaching similar results of acid decrease and ketone increment.

Regarding the nitrogen-containing compounds, due to organonitrogen compounds' comparatively lower reactivity when compared to oxygen compounds, cleaving the C-N bond is a bigger challenge than breaking a C-C bond. This complexity is amplified in microalgae oils due to their nitrogen concentrations and the robustness of the C-N bond. To address this issue, functionalized mesoporous catalysts and metal-organic frameworks can offer a solution by providing the necessary acidity to adsorb basic amine components in bio-oil. Adsorptive denitrogenation entails the selective adsorption of nitrogen compounds onto active sites, effectively segregating them from the remaining oil (Ahmed et al., 2013). The NiHTC catalyst appears to play a role in nitrogen removal. According to Andrade et al. (2018), hydrotalcite's acidic and basic properties work in tandem to eliminate nitrogen, possibly through the Hofmann mechanism. In this process, the acid site protonates the -NH group of a heterocyclic nitrogenous molecule, forming a primary amino -NH₂ group, while the basic site attracts the β -H. This interaction leads to the cleavage of the C-N bond, allowing for the removal of the nitrogen molecule (Prado et al., 2017). In this study, the most significant decrease is seen in the nitrile molecules.

The outcomes from the tandem catalytic bed experiments demonstrated the most favorable result for hydrocarbon production, reaching 84% at 650°C. The factor contributing to the success of hydrocarbon formation was the deacidification effect facilitated by NiHTC, which reduced carboxylic acid content and increased the formation of intermediate compounds, notably ketones (Andrade et al., 2018; Ding et al., 2018). These ketones were subsequently transformed into aromatic hydrocarbons through deoxygenation reactions catalyzed by NiHZSM-5. Zainan et al. (2018) conducted catalytic pyrolysis on microalgae *Chlorella vulgaris*. In a manner akin to this study, their findings revealed that employing Ni-supported zeolites in catalytic pyrolysis led to increased hydrocarbon content while reducing the presence of oxygenated compounds compared to non-catalytic pyrolysis. The nitrogenous compounds were also diminished when using the tandem catalytic bed. However, the reduction achieved was less significant than when using only NiHTC.

Examining the generation of aromatic compounds in the non-catalytic tests (depicted in Figs. 5.3), it becomes evident that despite the increase in the hydrocarbon formation within the temperature escalation, aromatic content consistently remained at approximately 20%. These aromatic hydrocarbons predominantly consist of benzene-like compounds. In contrast, most aliphatic hydrocarbons are primarily composed of alkenes (ranging from 48 to 55%), which exhibit an increase with the temperature increment, reaching twice as much as the formation of alkanes. Among the alkenes, acyclic chains such as propene and butene constitute the majority. One possible explanation could be that the carbohydrates within the microalgae underwent decomposition into monosaccharides. At elevated temperatures, these monosaccharides may undergo ring-opening reactions, resulting in the formation of linear carbon chains (Barbosa et al., 2021; Wang et al., 2013b; Patwardhan et al., 2010).

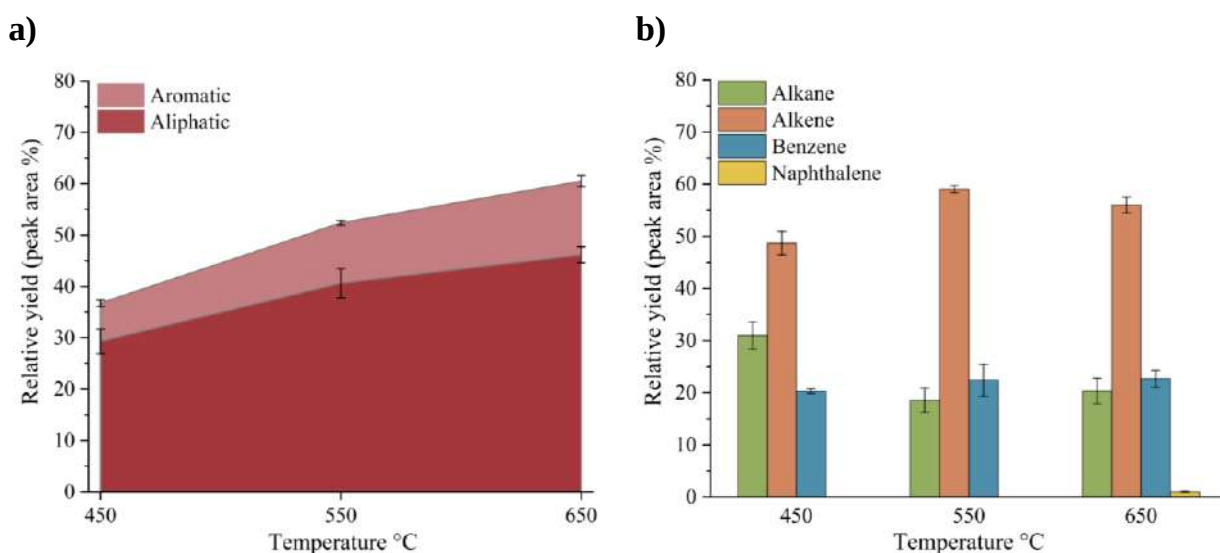


Fig. 5.3. Effects of the temperature on (a) bio-oil aromatization and (b) hydrocarbon compound in the non-catalytic tests.

Regarding the catalytic influence on the aromatization of the hydrocarbon compounds, as shown in Fig. 5.4, it is possible to affirm that NiHTC did not significantly impact the conversion of hydrocarbons into aromatic compounds during the analytical pyrolysis. When comparing the results of experiments with a NiHTC:HZSM-5 catalyst ratio of 1:0 to those without any catalyst (control), it is evident that in both cases, the aromatization levels remained approximately constant

at around 20%, despite an increase in the production of hydrocarbons. On the other hand, alkenes reached approximately 55% with only hydrotalcite catalyst.

In contrast, the use of NiHZSM-5 resulted in more aromatic formation, reaching approximately 53 and 61% for tests with only zeolite and tests conducted under the tandem catalytic bed (NiHTC followed by NiHZSM-5), respectively. The presence of aromatic compounds is particularly advantageous since they can be blended with gasoline, serving as valuable fuel additives, as highlighted by Muley et al. (2016). Experiments involving NiHZSM-5 in the catalyst ratio demonstrated an enhanced level of aromatization. These findings are in line with existing literature, which has consistently highlighted the exceptional performance of the acidic sites of zeolites in aromatization reactions (Lashchinskaya et al., 2023).

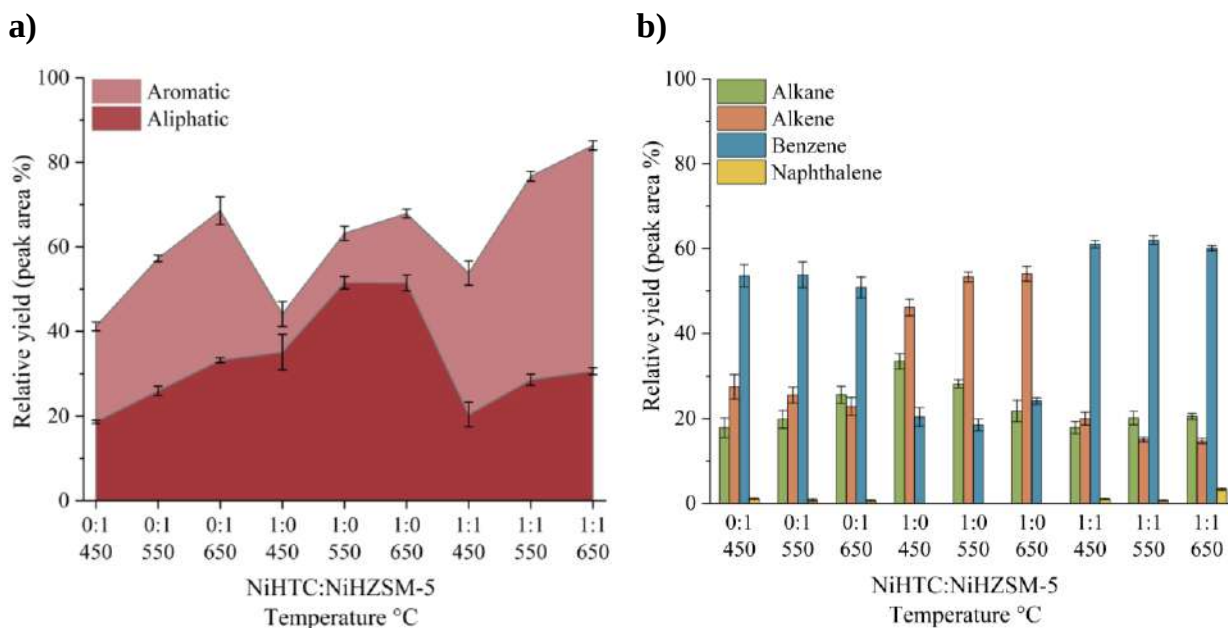


Fig. 5.4. Effects of the temperature and the catalysts' ratio (NiHTC:HZSM-5) on (a) bio-oil aromatization and (b) hydrocarbon compounds.

According to Wang et al. (2013b), the aromatic amino acids found in microalgae proteins, such as tyrosine and phenylalanine, can undergo pyrolysis to yield aromatic hydrocarbons like toluene and various other benzene-like compounds. We suggested that not only the amino acids but also the cyclic monosaccharides, and triglycerides within the *S. Limacinum* microalgae suffered this transformation, which notably might be intensified under the influence of a catalyst.

Li et al. (2018) proposed a pathway in which triglycerides undergo a base-catalyzed process, removing ester functionalities, which led to linear (saturated and unsaturated) hydrocarbon chain formation. These aliphatic hydrocarbons are subsequently transformed into aromatic compounds through zeolite catalysts, with the Diels-Alder reaction being a potential route (Zhao et al., 2013).

In addition, the alkanes and alkenes might undergo cyclization reactions of C—C bonds, forming hexatomic rings, with benzene, toluene, and ethylbenzene as the most significant products. Kanazirev et al. (1995) investigated the conversion of short-chain alkanes, such as propane, into aromatic hydrocarbons using metal-modified zeolites, revealing a notable selectivity for benzene formation. In the current study, similar conclusions can be drawn, as the predominant alkene compound observed was propene, and following catalytic pyrolysis, the major products were benzene-like compounds. This phenomenon may be attributed to the dehydrogenation reaction (i), as discussed by Horiguchi et al. (2020). Under the test conditions with a 1:1 ratio at elevated temperatures of 550 and 650°C, the alkenes were substantially reduced to 15%. To elucidate this observation, the following pathway is suggested:



In examining hydrocarbon chain lengths (Fig. 5.5), the influence of temperature is noted, wherein elevated temperatures facilitate the breakdown of longer carbon chains. Additionally, it is noteworthy that both catalysts enhance the cracking of molecules, leading to shorter carbon chains containing between 3 to 9 carbon atoms in their structure.

Nonetheless, experimental runs employing NiHZSM-5 generated a higher proportion of shorter carbon chains, surpassing 80% under test conditions with NiHTC:HZSM-5 ratios of 0:1 and 1:1 at 650°C, compared to 70% observed in the non-catalytic control at the same temperature. This observation demonstrates the significant impact of catalytic cracking, in this case, especially alkenes that mainly were converted into benzene-like compounds containing under 9 carbon atoms, such as benzene, toluene, and indane. The catalytic cracking of alkenes and alkanes might be associated with the presence of metal-loaded zeolites (Chen et al., 2018).

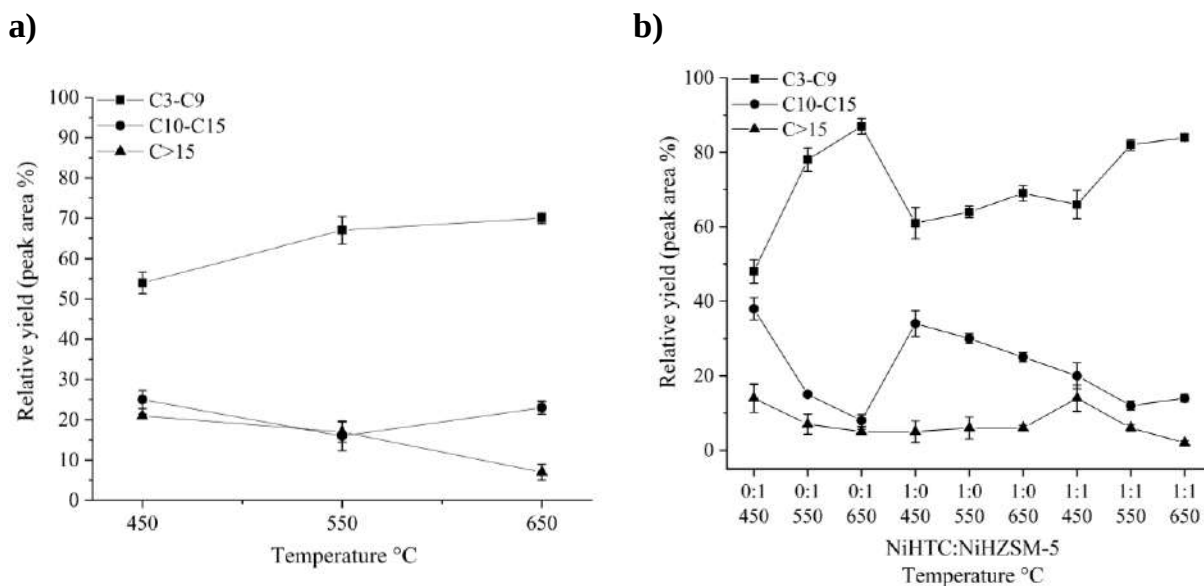
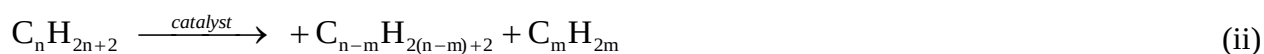


Fig. 5.5. Effects of the temperature on hydrocarbon lengths (a) non-catalytic tests (b) catalytic tests at different catalysts' ratio (NiHTC:HZSM-5).

A pathway is proposed for the division of alkanes and alkenes into smaller alkane, alkene molecules (ii) (Morris, 2011). Introducing nickel (Ni) can further enhance the catalytic cleavage of molecules (da Rocha Filho et al., 1993). Maia et al. (2010) observed that the catalytic cracking of alkenes and alkanes increased as the percentage of Ni incorporated into HZSM-5 zeolite increased. Additionally, the findings of Peng et al. (2012) demonstrated a selectivity of approximately 43% for alkane cracking when a metal loading of 10 wt.% Ni in HZSM-5 zeolite was employed. Employing only NiHTC also contributed to catalytic cracking. However, the production of more intermediate carbon chains within the C10-C15 range is notable. This phenomenon might be explained by the reduced extent of catalytic cracking in certain alkenes. Consequently, compounds like 1-decene, 1-tridecene, and 1-pentadecene persisted in the resulting products.



5.1.2. Effects of the total catalyst to biomass ratio (CB_A) using a tandem catalytic bed in the analytical pyrolysis

To investigate the catalyst performance on the product composition, the total catalyst to biomass ratio (CB_A) was studied at three different levels: 0.5:1; 1:1; and 5:1. The tests were performed at 650°C and the NiHTC:NiHZSM-5 catalysts ratio was fixed at 1:1 to generate more significant hydrocarbon content. Fig. 5.6 shows the impact of varying the total catalyst-to-biomass ratio (CB_A) on product composition and aromatization. It can be confidently stated that increasing the total catalyst ratio not only promotes the generation of hydrocarbons but also enhances aromatization reactions. It is conceivable that the increase in the general hydrocarbon content might facilitate these reactions.

Fig. 5.6 (a) shows that an increase in the tandem-catalytic bed load resulted in more substantial hydrocarbon production. The upward trend in hydrocarbon formation, which rose from approximately 65 to 89% as the total catalyst ratio increased from 0.5 to 5, underscores the role of longer residence times in promoting desirable reactions. The escalation in catalyst concentration led to the formation of a more extensive catalyst bed, promoting enhanced contact time between steam and the catalyst, as well as improving their interaction (Dai et al., 2020). This improved interaction likely favored reactions leading to increased hydrocarbon formation. Appendix A shows a chromatogram for the pyrolysis of *S. Limacinum* in a tandem catalytic bed. Gopakumara et al. (2012) and Rossi et al. (2021) similarly observed increased hydrocarbon content in bio-oil with increasing catalyst load. Conversely, the oxygenated compounds (carboxylic acids and ketones together) plummeted from 17 to 2% once the total catalyst-to-biomass ratio was raised from 0.5 to 5. Nitrogen-containing compounds such as nitriles and amines reached the lowest concentration of close to 2%. In this scenario, the greater catalyst quantity may favor decarboxylation, decarbonylation, and denitrification reactions, thus minimizing oxygen and nitrogen in the products that can be mostly released as CO, CO₂, and NH₃ (Resende, 2016).

Comparing the results when using the extreme ratios 0.5 and 5, it was observed that the process of aromatization exhibited a significant increase, rising from around 22 to 60%, meaning that, in this condition, approximately 70% of the hydrocarbons formed were aromatic in nature. This notable increase in aromatic compounds demonstrated an inverse relationship with the aliphatic ones.

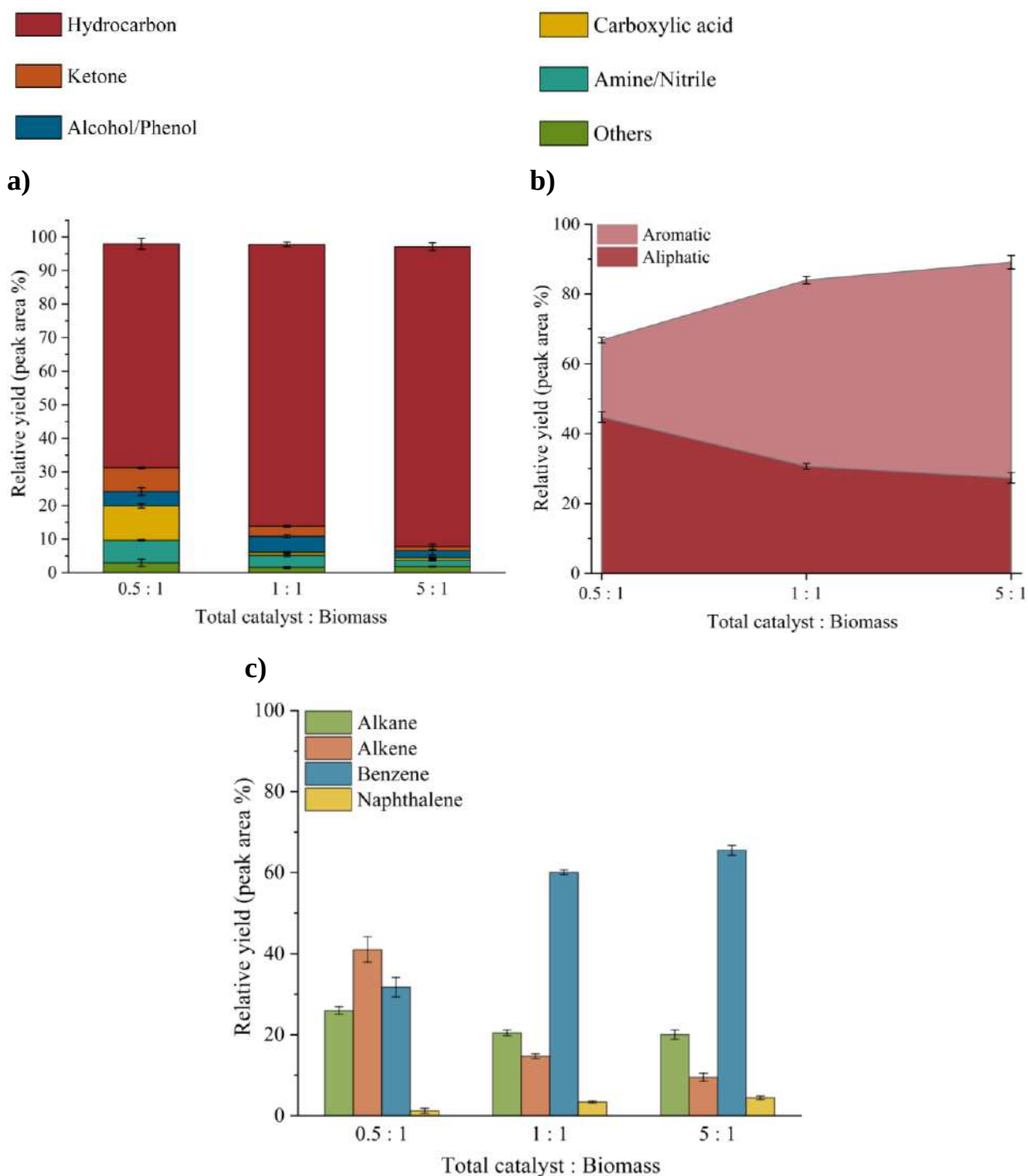


Fig. 5.6. Effects of the total catalyst to biomass ratio at 650°C and catalysts' ratio (NiHTC:HZSM-5) of 1:1 on the (a) bio-oil composition, (b) bio-oil aromatization, and (c) hydrocarbon compounds.

Notably, a variety of aliphatic hydrocarbons (specifically, C3-C9) were identified, primarily comprising alkanes and alkenes. As the catalyst-to-biomass ratio soared, the linear chains, especially alkenes, reduced by 30%, were probably transformed into aromatics, more precisely benzene-like compounds. The generation of naphthalene-like substances and other polyaromatics was not expressive. An additional factor that may have contributed to the heightened generation of aromatic compounds is the *ex-situ* configuration that assists the generation of diverse aromatic hydrocarbons. In contrast, the *in-situ* setup might favor the production of olefins (Wang et al. 2014). Furthermore, aromatic hydrocarbons can be generated from triglycerides and amino acids by eliminating hydroxyl bonds from phenolic compounds. This can occur either through direct elimination or via thermal dehydration of saturated cyclic alcohols, ultimately leading to hexatomic rings formation (Wang et al., 2013a; Yang et al., 2019). These conversions hold significant value, as aromatic hydrocarbons can be blended with gasoline to enhance octane rating, improving overall fuel properties.

5.1.3. Effects of the NiHTC catalyst synthesis method on the tandem catalytic bed in analytical pyrolysis

To explore the influence of the NiHTC catalyst synthesis method, the tandem catalytic bed, besides NiHZSM-5, was also composed of HTC-type catalytic precursor with varying Ni mass contents, synthesized through the precipitation (ppt.) of magnesium, aluminum, and nickel nitrate-based solutions (Ferreira, 2016). In this phase, nickel nitrate was employed as part of the synthesis solution (precipitated/ppt.) rather than used in the impregnation process as before. The tests were performed at 650°C, the NiHTC:NiHZSM-5 catalysts ratio was set at 1:1, and the total catalyst to biomass ratio (CB_A) was varied at two different levels: 0.5:1 and 5:1. Fig. 5.7 shows the effect related to the NiHTC synthesized by precipitation on product composition and aromatization.

Upon analyzing Fig. 5.7 (a), it becomes evident that the variation in the weight percentage (wt. %) of nickel in the precipitation method for the HTC catalyst did not seem to influence the composition of the resulting product significantly. Nevertheless, similar to the experiments conducted using NiHTC synthesized via impregnation (as described in sections 5.1.1.1 and 5.1.1.2), it is also observed an increase in hydrocarbon formation, rising from 72% to approximately 80% as the catalytic bed load increases, regardless of the synthesis technique employed. However, when comparing these findings to those presented in Fig. 5.6 (a), one

noteworthy aspect is the carboxylic acid content. These tests (Fig. 5.7 a) revealed a higher content of this organic functional group. Specifically, the levels were close to 1% when using the impregnation technique and remained at 11 and 8% when employing the Ni precipitation at total catalyst-to-biomass ratios of 1:1 and 5:1, respectively. This observation suggests that when nickel is incorporated into the hydrotalcite structure via precipitation, it likely hinders deacidification reactions. One plausible explanation is that nickel within the structure is more challenging to react and may require more retention time. Additionally, it reduces the molar ratio of Mg/Al in the HTC catalyst, resulting in decreased deacidification, likely achieved at the basic sites of the hydrotalcite. In the precipitation technique, the Mg/Al molar ratios ranged from 1 to 2, rendering the catalyst more acidic than the catalyst in which nickel was impregnated (Mg/Al=3).

Prinetto et al. (2000) explain that an increase in the catalyst's acidity is associated with higher aluminum content. Díez et al. (2003) were able to substantiate this observation through temperature-programmed desorption (TPD) analyses of CO₂ (quantification of basic sites) and NH₃ (measurement of acidic sites). The acid properties, expressed in site density ($\mu\text{mol}/\text{m}^2$), increased as the molar ratio of Mg/Al decreased.

Regarding the aromatization process, even though the NiHZSM-5 catalyst remained unmodified, there was a noticeable inhibition in the formation of aromatic compounds. The aromatic compounds constituted 40 and 52% of the hydrocarbons at total catalyst-to-biomass ratios of 1:1 and 5:1, respectively. This phenomenon can be attributed to the overall reduction in hydrocarbon generation. Consequently, fewer hydrocarbons were available to reach the zeolite sites, which play a pivotal role in facilitating aromatization reactions (Lashchinskaya et al., 2023). This, in turn, resulted in fewer collisions among aliphatic hydrocarbons (Bai et al., 2012; Zu et al., 2017), potentially impeding the pathway described in section 5.1.1.1 (denoted as pathway (i)). Consequently, a significant proportion of alkenes persisted in the final product composition. It is worth noting that despite these changes, the fundamental nature of the hydrocarbon composition remained consistent. The predominant alkenes were primarily propene and butene, while most aromatics consisted of benzene-like compounds, including benzene, toluene, and xylene (often referred to as BTX). This is expected to since the microalgae and the catalysts are the same.

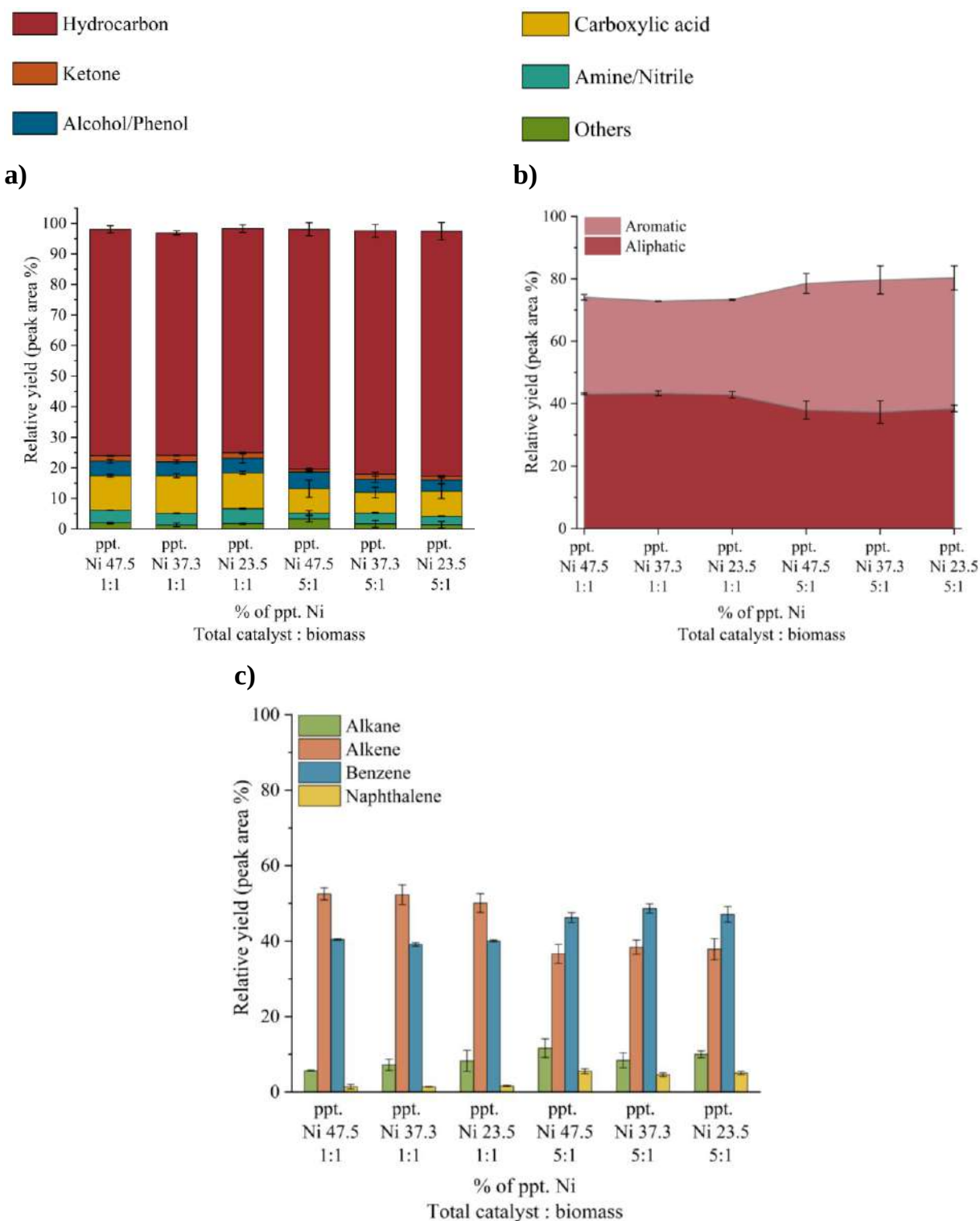


Fig. 5.7. Effects of the NiHTC catalyst synthesis method at 650°C and catalysts' ratio (NiHTC:HZSM-5) of 1:1 on the (a) bio-oil composition, (b) bio-oil aromatization, and (c) hydrocarbon compounds.

5.1.4. Effects of the pre-treatment (reduction and passivation) of NiHTC and NiHZSM-5 catalysts in the tandem catalytic bed in analytical pyrolysis

To assess the influence of catalysts pre-treatment, NiHTC and NiHZSM-5 were reduced and passivated before pyrolysis reaction. In this phase, the tests were performed at 650°C, the NiHTC:NiHZSM-5 catalysts ratio (C_A) was set at 1:1, and the total catalyst-to-biomass ratio (CB_A) was varied at two different levels: 0.5:1 and 5:1. Fig. 5.8 shows the effect of catalysts pre-treatment on product composition and aromatization compared to tests performed in section 5.1.1.1. in which the catalysts were only calcinated.

During the reduction process, hydrogen undergoes dissociation in a two-step process. Initially, it dissociates on the surface of NiO and, subsequently, on the surface of Ni clusters as they become available. The presence of hydrogen atoms initiates the rupture of Ni-O bonds, leading to the formation of Ni⁰ atoms. Over time, nickel atoms come together to form metallic clusters, and finally, these clusters grow into larger crystallites (Richardson et al., 1994; Richardson et al., 2004). After reduction, the catalyst was passivated (under O₂ flow) to preserve the metallic phase (Moura, 2022). The pre-treatment process exhibited some variations when compared to the standard calcination method, as shown in Fig. 5.8. In terms of product composition, the catalysts that underwent reduction and passivation demonstrated a marginal increase in hydrocarbon production, specifically 6% and 3% for tests conducted at CB_A ratios of 1:1 and 5:1, respectively.

The most notable distinctions were observed in the composition of oxygenated compounds, particularly ketones and alcohols. The reduction process may have enhanced the catalysts' oxophilicity. The probable reaction pathway might involve the transformation of ketones, alcohols and carboxylic acids into hydrocarbons through hydroxyl elimination and carbonyl reduction. This, in turn, results in the formation of alkenes while reducing the content of oxygenated products (Li et al., 2019b; Moura, 2022). Interestingly, the denitrification process appeared to be unaffected by the pre-treatment. The increase in hydrocarbons was relatively modest.

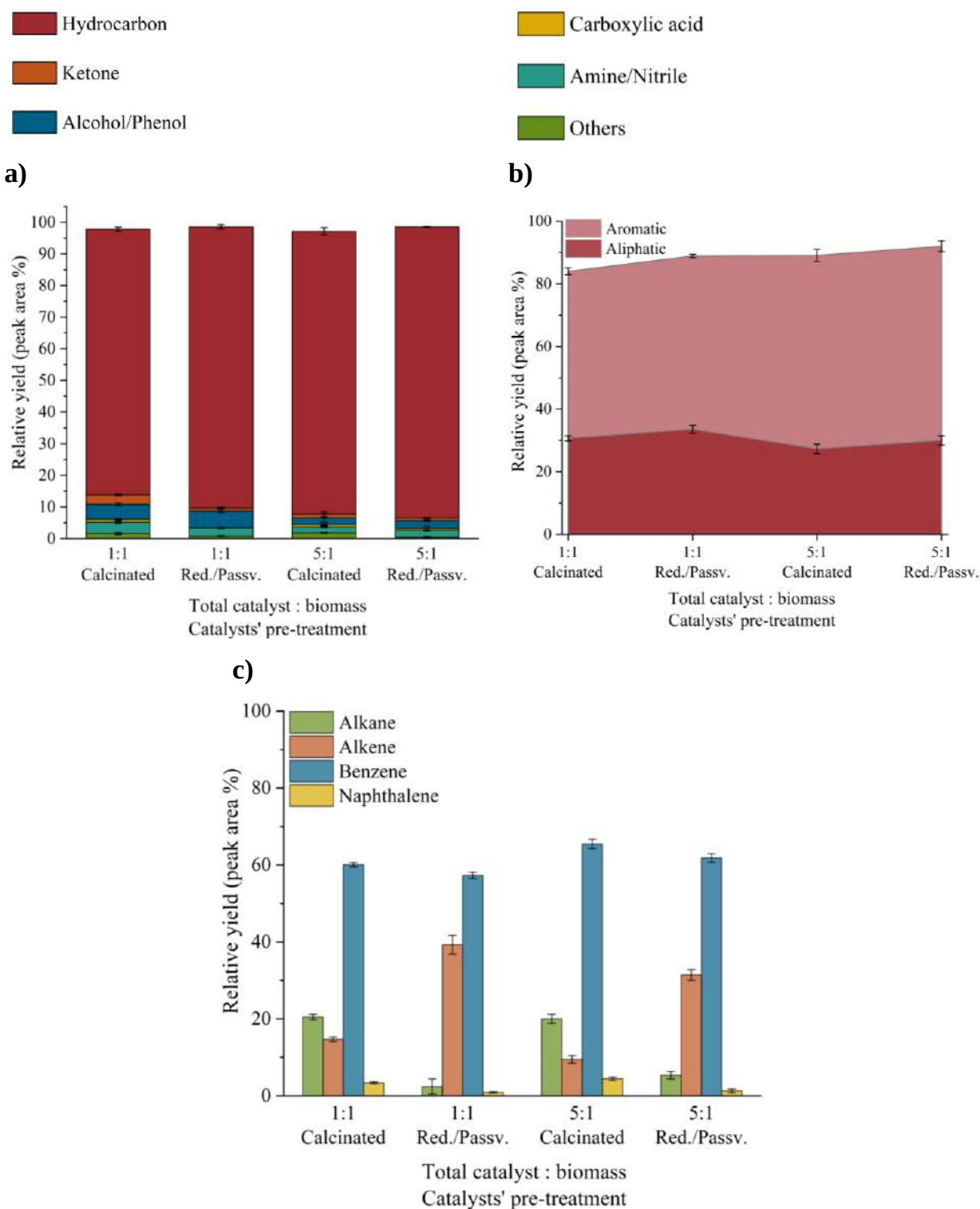


Fig. 5.8. Effects of the pre-treatment (reduction and passivation) of NiHTC and NiHZSM-5 catalysts at 650°C and catalysts' ratio (NiHTC:HZSM-5) of 1:1 on the (a) bio-oil composition, (b) bio-oil aromatization, and (c) hydrocarbon compounds.

One plausible explanation for this observation is that the selected microalgae already presented a relatively low O/C ratio of 0.38. Consequently, the hydrogen spared during the reduction pre-treatment, which would typically ease the removal of oxygen during the pyrolysis reaction, had a limited impact. It is hypothesized that the pre-treatment may have a more significant effect on biomasses with higher O/C ratios.

Regarding the formation of aromatic rings, an interesting pattern is observed. Notably, unlike the calcinated catalysts, the reduced and passivated catalytic bed converted alkanes instead of alkenes into benzene-like compounds (proposed pathway (iii)) (Schwab et al., 1988). In comparison to the conventional calcination process, there was a slight decrease in the formation of aromatics, which might have occurred due to the cleavage of the aromatic rings of the aromatic amino acids found in microalgae proteins (Wang et al., 2013b), resulting in more alkenes, which increased by approximately 20%. Although the benzene content remained relatively constant, the naphthalene compounds suffered a reduction by one-third. One possible explanation for this phenomenon is that the reduction and passivation process facilitated the incorporation of hydrogen (H₂) into polyaromatic molecules, forming monoaromatic (like benzene) and alkene compounds (Shen et al., 2019; Kaiser et al., 2022). A proposed pathway is depicted in (vi).



5.2. Conclusions

In this research, we investigated the catalytic pyrolysis of *Schizochytrium limacinum* microalgae using an *ex-situ* configuration. Our study delved into the unexplored territory by examining the interplay between the double catalytic bed and various reaction temperatures. During analytical pyrolysis tests, it is noted that the utilization of the double catalytic bed and the modulation of reaction temperature significantly affected pyrolysis products. Furthermore, a marked increase in hydrocarbon formation became evident, remaining at 80%, when the reactions occurred at the highest temperature tested (650°C) with a catalysts' ratio NiHTC:NiHZSM-5 of 1:1. This outcome is notably promising compared to previous research on other biomasses,

underscoring the potential of microalgae as a valuable biomass source for bio-oil production. Turning our attention to the hydrocarbons, notably, when the total catalyst-to-biomass ratio was set at 5:1, the hydrocarbon generation soared to 89%, simultaneously prompting an aromatization level of approximately 70%. The performance of the catalytic bed was affected by either the synthesis technique of the hydrotalcite either by the catalysts' pre-treatment (reduction and passivation). The precipitation method generated less favorable compounds, as it appeared to hinder deacidification reactions. Conversely, reduction and passivation likely promoted the formation of hydrocarbons. However, a minor reduction in aromatics production was noted, leading to a higher proportion of alkenes, which exhibited an increase of approximately 20%.

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CHAPTER 6

6. SOLAR PYROLYSIS OF *SCHIZOCHYTRIUM LIMACINUM* MICROALGAE IN A TANDEM CATALYTIC BED

This chapter presents and discusses the results of solar pyrolysis in the double catalytic bed composed of hydrotalcite and zeolite. Initially, the yields of the solid, liquid, and gas products were quantified, as well as the influence of the variables on the distribution of the products. Subsequently, the bio-oil chemical composition and HHV were investigated.

6.1. Results and discussion

6.1.1. Product distribution

Figures 6.1 shows the product distribution obtained in each test, which the conditions are presented in Tables 6.1 and 6.2, corresponding to the non-catalytic and catalytic configurations, respectively. The variables T_s and C_s are the reaction temperature (x_{1s}) and NiHTC/(NiHTC+NiHZSM-5) ratio (x_{2s}). The total catalysts/biomass ratio (CB_s) was fixed for these tests at 1:1. There is a pattern in which liquid product yield is highest for tests when the temperature reaction was 750°C. The increase in liquid production was directly affected by the reaction temperature, most likely because higher temperatures favored the decomposition of the organic material, which reduces the percentage of solid remaining in the reactor and increases the production of liquid and gas. Although the most significant weight losses for the *Schizochytrium limacinum* occurred at approximately 400 and 500°C, as shown by TGA analysis, the liquid generation was benefited at 750°C. The author suggests that owing to the relatively small focal zone cross-section to collect solar energy, the heat transfer during the pyrolysis occurs from the focal point located at the base of the reactor and propagates from bottom to top, causing biomass degradation in layers. Thus, the higher temperature of 750°C most likely provided faster heat transfer to the biomass, resulting in a more homogenous and efficient biomass decomposition.

Table 6.1. Non-catalytic solar pyrolysis tests' conditions.

Test	T_s [°C]	x_{1s}
1S	550	-1
2S	750	+1

Table 6.2. Experimental design matrix for catalytic solar pyrolysis.

Tests	T_s [°C]	x_{1s}	C_s		x_{2s}
			NiHTC:NiHZSM-5	NiHTC/(NiHTC+NiHZSM-5)	
3S	550	-1	0:1	0	-1
4S	750	+1	0:1	0	-1
5S	550	-1	1:2	0.33	0
6S	750	+1	1:2	0.33	0
7S	550	-1	1:1	0.50	0.5
8S	750	+1	1:1	0.50	0.5
9S	550	-1	2:1	0.67	+1
10S	750	+1	2:1	0.67	+1
11S	550	-1	1:0	1.00	+2
12S	750	+1	1:0	1.00	+2

Andrade et al. (2016) studied dynamic heating in solar dish concentrators. They explained that the time to heat the materials tends to decrease with higher equilibrium temperatures, which are a function of the solar collector's diameter, the specimen's mass in the reactor, and the solar radiation. The use of concentrated solar energy to heat and degrade biomass might also favor the production of liquid. The high heating rates promoted by using concentrated solar energy allow high temperatures to reach the focal point quickly. In this way, the gas produced crosses a high-temperature zone towards a lower-temperature area very quickly. This sharp difference in the temperature can minimize secondary reactions and favor the formation and condensation of the liquid (Zeng et al., 2017).

Regarding the SY_s , the amounts of solid obtained in this study were lower than those obtained by Barbosa et al. (2021) under similar reaction times. The average solid yield obtained by Barbosa et al. (2021) (that used the same solar unit and reactor employed in this present study) for *ex-situ* catalytic solar pyrolysis of the microalgae *Chlamydomonas reinhardtii* was 40.5%, while in the present study, an average value of 29% was found. This fact can be explained by the greater biomass quantity (3.75 g) used by Barbosa et al. (2021). The material decomposition during solar pyrolysis occurs in layers due to the unit design and features. Thus, moderate amounts of biomass,

such as the 1.5 g used in the present work, could provide better heat distribution and a more homogeneous degradation of the organic material.

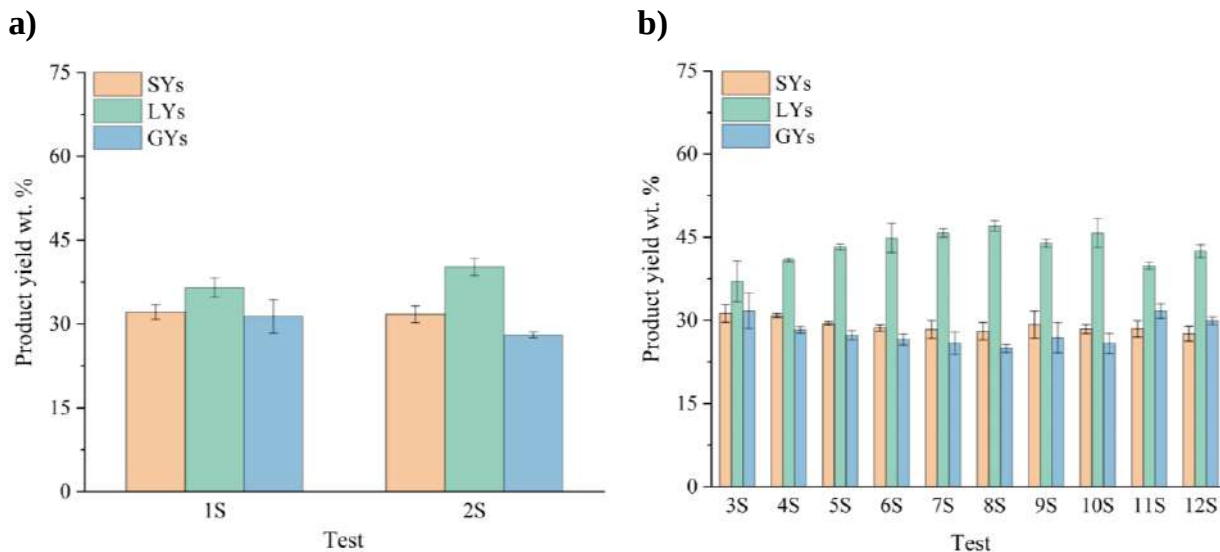


Fig. 6.1. Product distribution for *Schizochytrium limacinum* (a) non-catalytic and (b) catalytic solar pyrolysis.

6.1.1.1. Effect of independent variables on the products distribution

After studying the distribution of the products, statistical analysis was used to obtain the regression equations to quantify the effects of the variables reaction temperature (x_{1S}) and catalysts ratio (x_{2S}) on the yields of solid (SYs), liquid (LYs), and gas (GYs). Products' yield data showed normal distribution and statistical analysis indicated small residuals and independently distributed. The regression equations for the products' yield are presented by Equations 6.1 to 6.3 with significant effects $p < 0.05$ and $R^2 > 0.9$. Response surfaces for solid, liquid, and gas yields were plotted as functions of the two independent variables to further analyze their effects on products' generation. Figures 6.2 to 6.4 show the influence of the variables on the products' distribution for the solar tests.

$$SY_s = 29.16 - 0.28x_{1S} - 1.36x_{2S} - 0.07x_{1S}x_{2S} + 0.43x_{2S}^2 \quad (6.1)$$

$$R^2 = 0.93$$

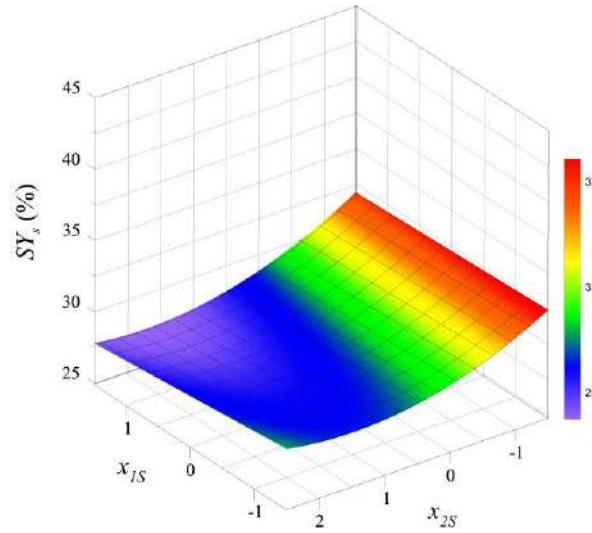


Fig. 6.2. Response surface for pyrolysis solid yield as a function of temperature reaction (x_{1s}/T_s) and catalysts' ratio (x_{2s}/C_s).

It is observed that there was no wide fluctuation in the yields of solids in the experiments. The solid formation remained between 27.5 and 32%. The use of small amounts of microalgae and the absence of a catalyst inside the pyrolysis reactor (*ex-situ* configuration) favored biomass degradation assisting in reducing the amount of remaining solid inside the pyrolytic reactor. Smaller masses help in heat and mass transfer, which occurs from the focal point at the bottom of the reactor to the top. Due to the perpendicular alignment of the surface of the paraboloid with the sun's rays, a slight inclination occurs in the reactor that may have concentrated the biomass in a small region. This fact may have hindered biomass degradation during pyrolysis, leading to an overall higher solid yield. However, this effect was reduced at higher temperatures due to the faster degradation intrinsic of the dynamic heating in the solar dish concentrator, a function of the specimen's mass in the reactor, and the solar radiation (Andrade et al., 2016). The time to heat the materials tends to decrease with higher equilibrium temperatures, implying more homogeneous degradation. Thus, as expected, the response surface revealed that the higher temperature of 750°C (T_s) might lead to lower solid yields that reached the smaller amount of 27.5% on test 12 due to more significant biomass degradation. The opposite is also true. The lower reaction temperature of 550°C (T_s) can lead to a higher solid fraction. Despite the pyrolysis *ex-situ* configuration, the catalysts' ratio (x_{2s}/C_s) influenced the solid product. Lowest catalysts' ratios (x_{2s}/C_s) led to the highest values of yields of solids. The response surface indicates that at C_s ratios between 0.5 to

1.0 the solid production might suffer a downgrade. The author suggests that the formation of condensable gases due to the catalytic cracking of molecules facilitated the entrainment of the vapors, which consequently may have helped in the mass transfer, turning biomass degradation more homogeneous.

$$LY_s = 44.56 + 1.20x_{1s} + 3.20x_{2s} - 0.16x_{1s}x_{2s} - 2.46x_{2s}^2 \quad (6.2)$$

$$R^2 = 0.97$$

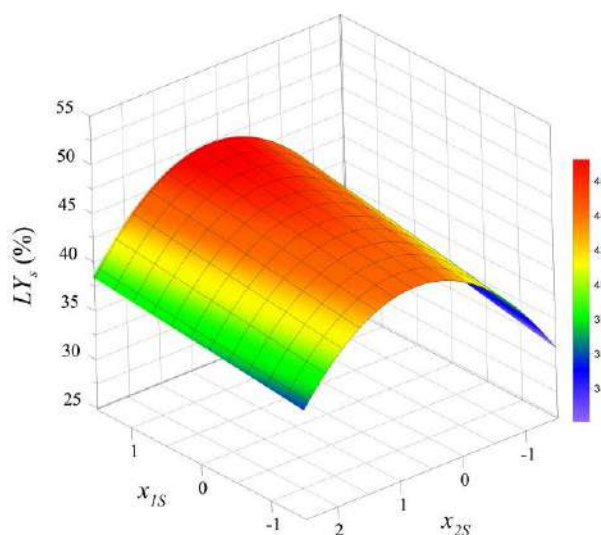


Fig. 6.3. Response surface for pyrolysis liquid yield as a function of temperature reaction (x_{1s}/T_s) and catalysts' ratio (x_{2s}/C_s).

Figure 6.3 shows the response surface in which it is possible to visualize the effects of the independent variables temperature reaction (x_{1s}) and catalysts' ratio (x_{2s}) on liquid yield. It is observed that the highest level (750°C) of the reaction temperature variable (x_{1s}/T_s) associated with intermediate values (0.50 and 0.67) of catalysts' ratio (C_s) showed a higher product yield liquid, reaching approximately 47% in test 8. This fact can be explained by the adequate choice of the degradation temperature, which favored the decomposition of the organic matter since the increase in temperature is capable of, initially, releasing large amounts of volatiles (Xie et al., 2015). This availability of pyrolytic vapors, combined with the reactions promoted by the catalytic double bed, resulted in recombination reactions between gaseous molecules, favoring condensable product formation (Gao et al., 2017). The catalysts' ratio [NiHTC/(NiHTC+NiHZSM-5)] of 0.50 favored

the increase in liquid production, while the ratios of 0 and 1 were the ones that most disfavored the generation of liquid. This indicates that the use of two catalysts instead of just one was more suitable for the solar pyrolysis system of the microalgae *Schizochytrium limacinum* since to reach the highest liquid production (47%). The presence of catalysts can significantly reduce the energy demand to break chemical bonds (Lee et al., 2020a). Thus, catalytic cracking/reforming provides an effective strategy in the thermal conversion of biomasses and has been seen as a promising method to convert organic materials into fuel products (Lee et al., 2020b).

$$GY_s = 40.90 + 0.79x_{1s} + 6.53x_{2s} + 0.35x_{1s}x_{2s} - 3.23x_{2s}^2 \quad (6.3)$$

$$R^2 = 0.94$$

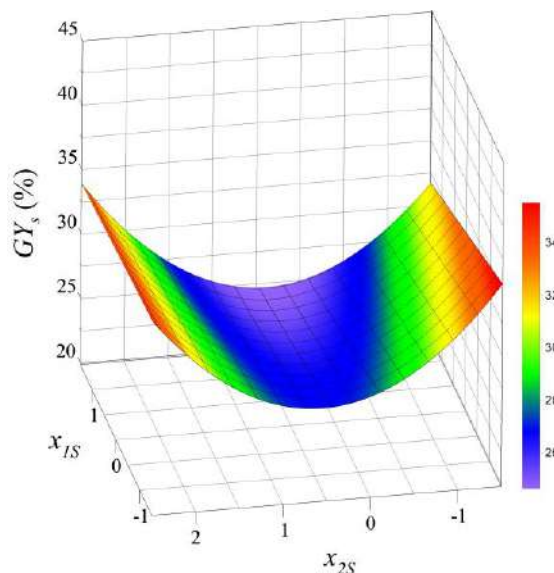


Fig. 6.4. Response surface for pyrolysis gas yield as a function of temperature reaction (x_{1s}/T_s) and catalysts' ratio (x_{2s}/C_s).

As can be seen in Figure 6.4 (response surface for gas yield), the intermediate ratio of catalysts, as well as lower reaction temperatures, disfavor the production of gas. This means that gas minimization and liquid maximization happen in the same region, demonstrating that when condensation reactions are favored, thermal cracking is hindered, and vice versa (Guedes et al., 2018; Pattiya et al., 2012). The yields of the gaseous fraction remained between 25 and 32% and consistently lower than those of the liquid fraction. The extreme levels of catalysts' ratios 0 and 1

might assist gas generation and reduce the liquid yield, once again indicating that the use of the double catalytic bed of NiHTC and NiHZSM-5 was adequate for liquid generation. Rossi et al. (2020) studied the solar hydrolysis of *Chlamydomonas reinhardtii* microalgae and found similar results, where the region that maximizes liquid generation is the same, where the gas is minimized.

6.1.2. Bio-oil composition

The bio-oil product of each experimental run was analyzed by GC/MS and classified according to their organic functional group, including oxygenated (ketones, alcohols, carboxylic acids), nitrogenated (amines and nitriles), hydrocarbons, and other compounds as shown in Fig. 6.5. The total relative peak percentage ranged from 98 to 99.5% since the unidentified compounds are not part of the composition sum. The relative abundance of each functional group is correlated to the temperature reaction and the catalysts' ratio [NiHTC/(NiHTC+HZSM-5)].

These products compounds are derived from the degradation of proteins, carbohydrates, and lipids present in the composition of microalgae (Lee et al., 2020). Lipid pyrolysis can produce oxygenated compounds such as carboxylic acids and esters but can also form long chains of hydrocarbons derived from the transformation of fatty acids present in triacylglycerols (Chen et al., 2017). Contrary to hydrocarbons, acidic compounds are considered unwanted products for bio-oil, as they confer instability and may cause a decrease in their HHV (Zhang et al., 2021). The nitrogenous compounds were generally found in smaller amounts than the oxygenated ones since the *Schizochytrium limacinum* presented only 14.5% of protein in its composition. Among the nitrogenous compounds, we can mention the amines, amides, and nitriles formed from the degradation of proteins in microalgae. These nitrogenous compounds' catalytic cracking can generate aromatic hydrocarbons, as previously reported by Wang et al. (2013) and Yang et al. (2019). Figure 6.5 (a) shows that, overall, alcohols, carboxylic acids, amines, and nitriles remained the same for both studied reaction temperatures. On the other hand, ketones halved while hydrocarbons increased by around 10% under the higher reaction temperature of 750°C. At higher temperatures, the cracking of ketones can most likely be favored, leading to the formation of alkanes and cyclic hydrocarbons (Ding et al., 2018).

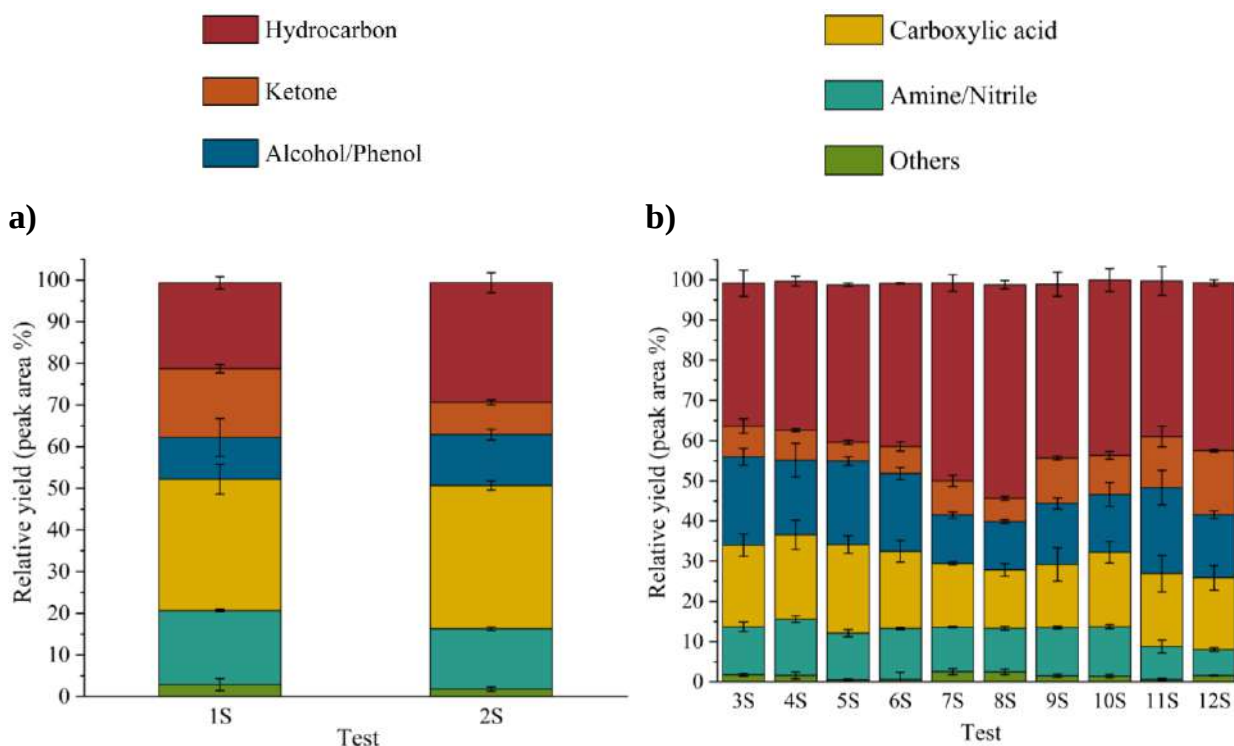


Fig. 6.5. Effects of (a) temperature and the (b) dual-catalyst ratio [NiHTC/(NiHTC+HZSM-5)] on bio-oil composition.

Figure 6.5 (b) presents the bio-oil composition for both temperatures under 5 different levels of catalysts' ratio [NiHTC/(NiHTC+HZSM-5)]. Test with catalysts' ratios of 0 and 1 produced the minor hydrocarbon content. Tests 3S and 4S, which used only NiHZSM-5, did not reach satisfactory deacidification and denitrification, presenting, on average, 22 and 13% of carboxylic acids and nitrogenated compounds, respectively. One possible explanation is that incorporating a transition metal such as nickel (Ni) moderated the zeolite acid sites in the present study, which can raise catalytic cracking and create additional transport channels that assisted hydrocarbon formation by cracking heavy fractions and led to higher percentages of hydrocarbon of 35.5 and 37% in tests 3S and 4S, respectively (Jafarian et al., 2018). On the other hand, tests 11S and 12S performed under NiHTC only, resulted in less nitrogenated compounds of 6.5%. However, the ketones and alcohols were not sufficiently converted into aromatic hydrocarbons. These two tests reached around 30% of ketones and alcohols in their compounds' totality, suggesting that the NiHTC catalyst might be more selective to C-N than the C-OH dissociation. Amphoteric oxides, such as MgO within NiHTC, can promote ketonization reactions, resulting in

the production of extended-chain ketones during the pyrolysis of the *S. limacinum* microalgae (Lee et al., 2020b). In the present study, for instance, the ketonization reaction of hexadecanoic acid might have led to the formation of long-chain ketones, notably 3-octadecanone and 2-nonadecanone. Tests with minor NiHTC amounts resulted in less nitrogen removal. Nevertheless, the relatively low content of nitrogen-containing compounds observed in this alga, regardless of the reaction temperature and catalysts' ratio, can be attributed to its low nitrogen content.

Hydrocarbons are the products of interest in the present study, and it is observed that their generation was most benefited under the higher temperature of 750°C and using the catalysts' ratio (C_S) of 0.5. Test 8S reached the highest hydrocarbon generation (53%), possibly due to the conversion of other chemical group compounds, mainly carboxylic acids, alcohols, ketones, and nitriles. The author suggests that NiHTC favored the deacidification and denitrification reactions. While the deacidification resulted in the formation of ketones and alcohols (Amani et al., 2017; Mansir et al., 2022), the denitrification is most likely achieved through Hofmann elimination (Prado et al., 2017) due to the catalyst's acid-base characteristics. The C–N bond scission can produce nitrogenous gases (e.g., NH_3), which are eliminated from the liquid phase (Zhang et al., 2019). Subsequently, the pyrolytic vapors pass through the zeolite bed, where the ketones and alcohols could be converted into aromatic hydrocarbons through the deoxygenation reactions promoted by the NiHZSM-5 (Du et al., 2013). Compared with the non-catalytic controls, all catalytic tests achieved better results regarding carboxylic acid cracking and hydrocarbon formation. The author proposes that both catalysts can promote an increase in the cracking reactions of macromolecules, resulting in a higher proportion of desirable products. These catalytic reactions become the primary driver of hydrocarbon formation when the NiHZSM-5 catalyst is placed downstream of the NiHTC catalyst in the fixed bed. Interestingly, using both catalysts resulted in remarkable hydrocarbon production compared to the non-catalytic controls, suggesting that a dual-catalytic bed is a more suitable pyrolysis setup for the *Schizochytrium limacinum*.

Aromatic and aliphatic hydrocarbons were found in the bio-oil obtained in the solar pyrolysis tests. The formation of these compounds is highly desirable, as they can be mixed with gasoline and used as fuel additives (Muley et al., 2016). Figure 6.6 displays the impact of catalyst ratio [NiHTC/(NiHTC+HZSM-5)] on the aromatization of bio-oil at reaction temperatures of 550 and 750°C. Figures 6.6 (a) and (b) exhibit similar behavior regardless of the temperature, although greater aromatization was observed in the tests conducted at 750°C. In addition, tests with more or

equal NiHZSM-5 proportion in the catalysts' ratio variable led to enhanced aromatization. These findings align with previous literature, which has demonstrated the excellent performance of zeolites in aromatization reactions (Lashchinskaya et al., 2023). In the test involving an equal proportion of both catalysts at 750°C (test 8S), the resulting bio-oil contained 35% aromatics, in contrast to 7.5% in the non-catalyst test (2S). These data suggest that most alkanes and alkenes were converted into aromatic compounds. The catalytic cracking of alkenes/alkanes can be attributed not only to the utilization of zeolite but also to the Ni impregnation. Maia et al. (2010) and Peng et al. (2012) observed an increase in alkane cracking when the Ni metal load in the HZSM-5 zeolite catalyst was increased to 10 wt.%.

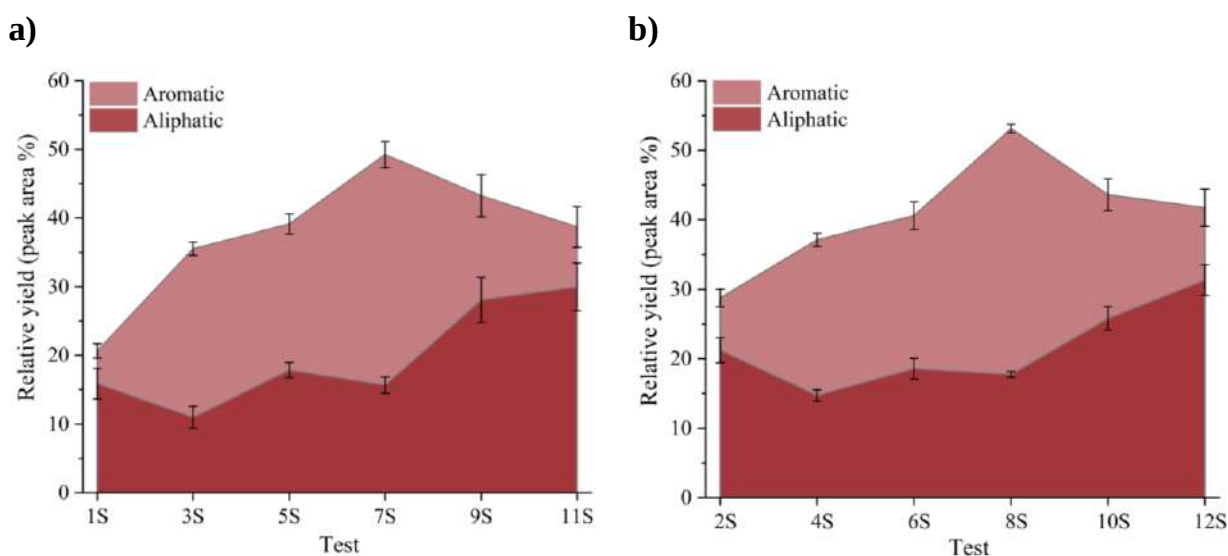


Fig. 6.6. Effects of catalysts' ratio [NiHTC/(NiHTC+HZSM-5)] on bio-oil aromatization at the two reaction temperatures of (a) 550°C and (b) 750°C.

6.1.2.1. Effect of independent variables on the bio-oil composition and energy generation

After analyzing the bio-oil composition, statistical analysis was employed to derive regression equations that assess the relationship between the reaction temperature (x_{1S}) and catalysts' ratio (x_{2S}) with the formation of oxygenated, nitrogenated, and hydrocarbon compounds as well as energy generation. The effect of each variable and their interactions on each response have been quantified using the experimental design coupled with response surface methodology (RSM). The RSM technique couples the experimental designs with statistical methods, aiming to

develop an empirical equation that establishes a relationship between the responses and control variables (Myers et al., 1989; Kamal et al., 2019). The independent variables were transformed into dimensionless (coded) forms using Equations 3.14 and 3.15. Table 6.2 shows the levels (actual and coded) of the independent variables for the complete experimental design. Regression equations were obtained by fitting the experimental data of each studied response and quantifying the effects of the independent variables in these responses. The equations fitted to the bio-oil composition and energy generation data exhibited a normal distribution, and statistical analysis indicated minimal residuals with independent distribution. The regression equations (Equations 6.4 to 6.7) were obtained with significant effects ($p < 0.05$) and high R^2 values (>0.85). Response surfaces regarding these regression equations were plotted to further evaluate the independent variables' impact on bio-oil characteristics. Figures 6.7 to 6.9 depict these variables' influence on the bio-oil composition and energy generation in the solar tests.

The hydrocarbon formation and the bio-oil energy generated per test are benefited by intermediate levels of the catalysts' ratio variable and the highest reaction temperature of 750°C. The response surfaces in Fig. 6.7 showed that the maximization of these components follows a similar behavior since the energy content is a function of the bio-oil HHV and the liquid formation. The increment in hydrocarbon generation is the main reason for reaching bio-oil with more desirable characteristics, including substantial energy density. When the rise in liquid production can be associated with hydrocarbon enhancement, an advantageous scenario in biomass pyrolysis is presented, as the one that is shown in this study. The same levels that benefited the liquid formation are the ones that favored hydrocarbon generation and, consequently, the rising in bio-oil HHV. The higher temperature of 750°C facilitated faster heat transfer to the biomass, leading to a more uniform and efficient decomposition process in the solar unit.

$$\text{Hydrocarbon}_S = 43.99 + 0.93x_{1S} + 4.96x_{2S} + 0.18x_{1S}x_{2S} - 3.43x_{2S}^2 \quad (6.4)$$

$$R^2 = 0.92$$

$$\text{Energy}_S = 19.71 + 0.60x_{1S} + 1.94x_{2S} - 0.03x_{1S}x_{2S} - 1.34x_{2S}^2 \quad (6.5)$$

$$R^2 = 0.96$$

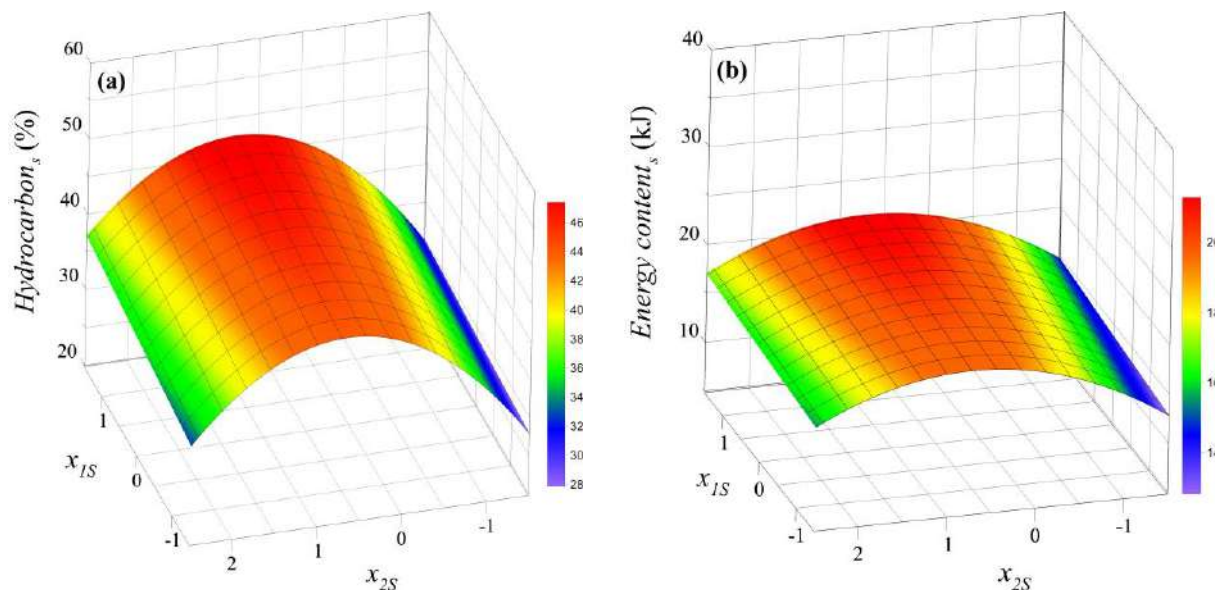


Fig. 6.7. Response surface for pyrolysis (a) hydrocarbon generation and (b) bio-oil energy content as a function of temperature reaction (x_{1s}/T_s) and catalysts' ratio (x_{2s}/C_s).

Furthermore, the combination of the two catalysts (NiHTC and NiHZSM-5) promoted the necessary residence time for deacidification and deoxygenation. The short-chain molecules' recombination reactions in the pyrolytic vapors generate more liquid and might occur through alkylation, aromatization, and isomerization, which favor the formation of condensable compounds (Hao et al., 2021). Ding et al. (2018) studied the analytical pyrolysis of xylan in the dual-catalyst bed of CaO and HZSM-5 and found similar results to those presented in this work. They observed a bio-oil quality improvement when using both catalysts instead of one. Fig. 6.8 reveals more clearly the correlation between liquid generation and hydrocarbon formation that can lead to a more significant energy density in the bio-oil. The HHV in the bio-oil varied from 26.5 in the non-catalytic control to 30.5 MJ/kg in test 8S. It is observed that the bio-oil HHV in each experimental run is closely dependent on the hydrocarbon generation trend. The HHV of nitrogenated, oxygenated, and hydrocarbon compounds such as nitrile, ethanol, and octane are 22, 30, and 48 MJ/kg, respectively (Demirbas et al., 2018). Thus, reducing these undesirable components and incrementing the hydrocarbon can guarantee satisfactory bio-oil features. Crude oil with an HHV of 30.5 MJ/kg exhibits between 75 and 80% in gasoline equivalence (Pacheco et al., 2019). Bordoloi et al. (2016) studied the pyrolysis of *Scenedesmus dimorphus* microalgae and their results

showed an HHV bio-oil of 28.5 MJ/kg, indicating that microalgae pyrolysis is a promising technique to generate biofuels that can be viable competitors against fossil fuels.

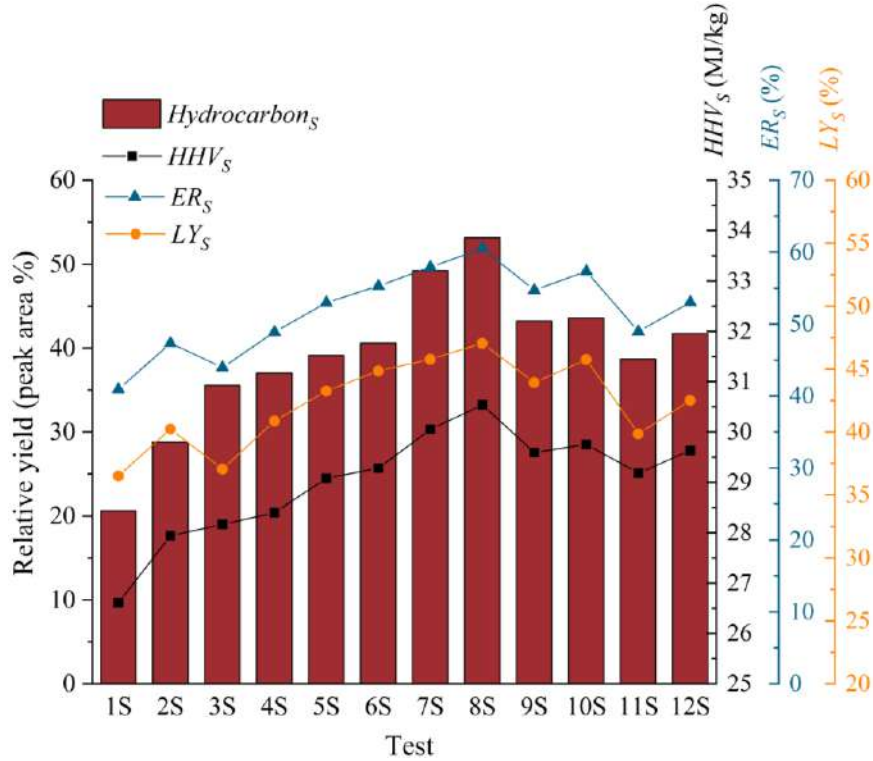


Fig. 6.8. Bio-oil HHV and energy content for solar pyrolysis.

The energy recovery for solar pyrolysis (ER_S) is calculated by Eq. 3.19 as the reason of the bio-oil weight multiplied by its HHV by the biomass weight multiplied by its HHV. The results indicated that the values of energy recovered (ER_S) from the bio-oil produced through catalytic solar pyrolysis of the microalgae *Schizochytrium limacinum* were satisfactory. Miao et al. (2004) produced bio-oil from the autotrophic microalgae *Chlorella protothecoides* and found a value of 22.2% of recovered energy, much lower than that of the present study. This happened due to the lower bio-oil yield produced by Miao et al. (2004), which led to low energy efficiency. Babich et al. (2011) performed conventional catalytic pyrolysis using the algae *Chlorella* and the Na_2CO_3 catalyst reached a higher bio-oil content. Still, the recovered energy was reduced (42%) due to the lower HHV value. This relationship between liquid yield, hydrocarbon production, and HHV of the bio-oil can be observed in tests 8S and 10S. The data indicate that these two tests resulted in similar values (around 60%) for ER_S . Overall, the loss of the liquid yield can be compensated by

the improvement in bio-oil quality and vice-versa. Generally, the satisfactory results of energy recovery achieved in the present study using solar energy have the potential to reduce the environmental impact while indicating a reduction in the cost of production since it uses a clean heating source.

The same levels of the independent variables that increase hydrocarbon content ($C_s=0.5$ and $T_s=750^\circ\text{C}$) also reduce oxygenated compounds as shown in Fig. 6.9 (a). The decrease of these compounds may be related to deoxygenation and thermal cracking reactions in long reaction times, which removed oxygen in the form of CO and CO₂ and favored the formation of gases (Aniza et al., 2021). Another fact related to the decrease in oxygen is the use of higher temperatures, indicating that mainly oxygenated compounds derived from the degradation of lipids, which are more thermostable, suffered thermal and catalytic cracking (Andrade et al., 2020). In contrast, the levels with NiHTC alone ($C_s=1$) are responsible for the decline in nitrogen content [Fig. 6.9 (b)]. Prado et al. (2017) stated that the Hofmann mechanism is a possible route for nitrogen removal due to the acidic and basic sites of the hydrotalcite catalyst. The zeolite catalysts do not present such a dual characteristic. Therefore, the zeolite alone showed lower nitrogen removal, and a more significant reduction in nitrogen content is still necessary. The author suggests that a greater catalyst-to-biomass ratio than 1:1 could contribute to a rise in the residence time of the vapors in each catalyst inside the bed and improve bio-oil quality. Section 6.1.3 will discuss the use of larger catalyst-to-biomass ratios.

$$\text{Oxygenated}_s = 40.99 - 1.22x_{1s} - 4.11x_{2s} + 0.15x_{1s}x_{2s} + 4.43x_{2s}^2 \quad (6.6)$$

$$R^2 = 0.87$$

$$\text{Nitrogenated}_s = 12.53 + 0.45x_{1s} - 0.97x_{2s} - 0.61x_{1s}x_{2s} - 0.72x_{2s}^2 \quad (6.7)$$

$$R^2 = 0.86$$

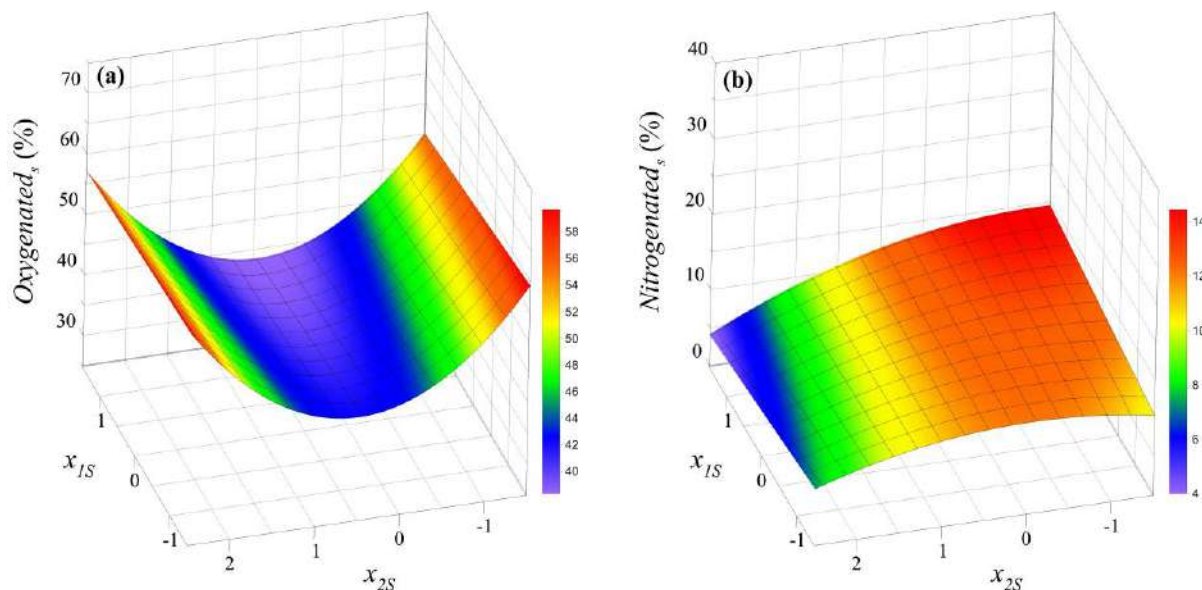


Fig. 6.9. Response surface for pyrolysis (a) oxygenated and (b) nitrogenated compounds generation as a function of temperature reaction (x_{1s}/T_s) and catalysts' ratio (x_{2s}/C_s).

6.1.2.2. Bio-oil multi-response optimization: yield and HHV

The desirability function (Derringer et al., 1980) was used in the present work as a multiple-response optimization technique, considering simultaneously liquid yield and bio-oil HHV as responses, whose results are presented in Figure 6.10 (Price et al., 1997; Derringer et al., 1980). This optimization approach aligns with the widely adopted framework of Response Surface Methodology (RSM). The primary concept behind this approach is the conversion of multiple responses into a unified metric by amalgamating individual responses within a composite function referred to as the Global Desirability function. The aim is to achieve the most favorable overall responses. The desirability values remain between 0 and 1, where 0 corresponds to an undesirable response, and 1 represents an entirely desirable value (Costa et al., 2011).

The best experimental range was obtained by the convenience function of this technique. The optimum variables' levels were found to be $x_{1s}=1$ ($T_s=750^\circ\text{C}$) and $x_{2s}=0.5$, which means a catalysts' ratio $[\text{NiHTC}/(\text{NiHTC}+\text{NiHZSM-5})]$ of 0.5. The predicted value of the responses in this optimized operating condition is a liquid yield of approximately 47%, with an HHV of 31 MJ/kg, which is approximately the same as ethanol's HHV. The predicted values of this optimized conditions were close to the results found in test 8S, which was performed in this condition, and

which presented the best results regarding the liquid yield and bio-oil quality, demonstrating good agreement between the predicted values by optimization study and experimental data. This indicates that the regression equations developed for both responses adequately describe the *Schizochytrium limacinum* solar pyrolysis process. These results will be used in study larger catalyst-to-biomass ratios in Section 6.1.3.

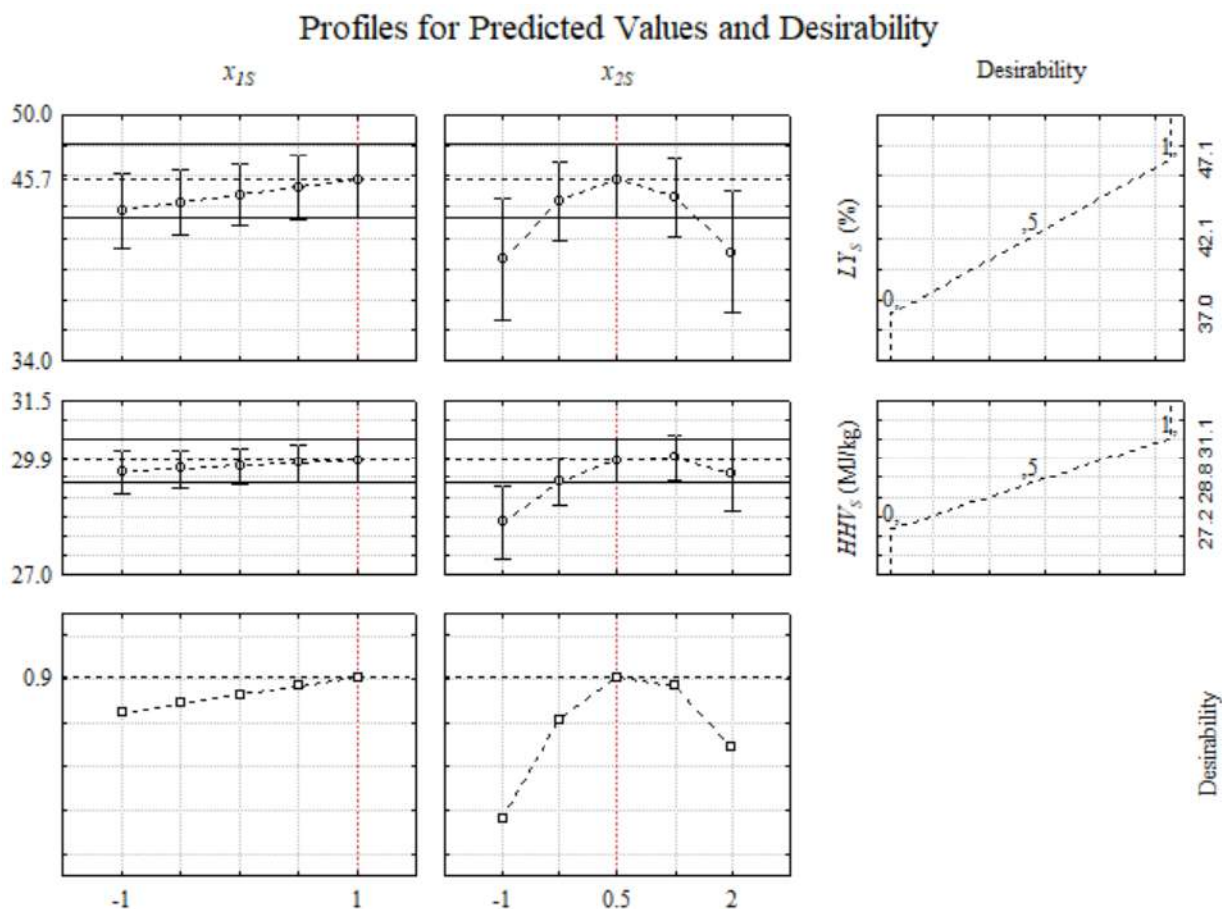


Fig. 6.10. Multiple-response optimization for o liquid yield (LY_s) and bio-oil HHV (HHV_s) of the solar pyrolysis process, as a function of reaction temperature (x_{1s}/T_s) and catalysts' ratio (x_{2s}/C_s).

6.1.3. Effects of the total catalyst/biomass ratio (CB_S) in the catalytic solar pyrolysis

To investigate the catalyst performance on the product distribution and composition, the total catalyst to biomass ratio (CB_S) was studied at three additional levels: 0.5:1; 2:1; and 4:1. The tests were performed at 750°C to obtain higher liquid fraction and NiHTC/(NiHTC+HZSM-5) catalysts' ratio was fixed at 0.5 to generate more significant hydrocarbon content, i.e., at optimized condition. Figure 6.11 shows the product distribution and bio-oil composition for the additional tests, which the conditions are presented in Table 6.3. Test 8S is also shown in Fig. 6.11 since it presented best results (optimum conditions) of the previous analyzes, which was performed at total catalyst-to-biomass ratio (CB_S) of 1:1. It can be seen from Fig. 6.11 (a) that the yield distribution presented a slight fluctuation. The solid, liquid, and gas products remained around 29, 45, and 25%, respectively.

The liquid yield showed an upward trend (about 5%) if the tests in Table 5.3 were compared with the non-catalytic control (test 2S). Even the smallest amount of catalyst (CB_S of 0.5:1) can generate more liquid since short-chain molecules' recombination reactions might be favored from the dual-catalyst bed. Consequently, reactions such as alkylation, aromatization, and isomerization that tend to benefit the formation of condensable compounds are increased, leading simultaneously to a higher liquid generation and lower gas yield (Ghenai et al., 2020). A liquid formation of 45% is significant since bio-oil is the product of interest, especially when pyrolyzing microalgae, which is considered noble biomass (Chia et al., 2018). Bordoloi et al. (2016) performed conventional pyrolysis of *Autotrophic C. protothecoides* microalgae, finding 17% of bio-oil yield, while Rossi et al. (2021) and Barbosa et al. (2021) carried out solar pyrolysis of *Chlamydomonas reinhardtii* that led to approximately 48% of liquid.

The raw material, experimental unit features, and the process operating parameters can strongly affect the product distribution due to the various chemical reactions favored in each condition (Guedes et al., 2018). Fig. 6.11 (b) displays the bio-oil composition. Test 13S resulted in a minor hydrocarbon formation of 33%, which can be explained by the lower total catalyst-to-biomass ratio of 0.5:1. The test 13S results generally presented similar values to the non-catalytic test 2S for all the studied compounds. One explanation for this fact could be that the residence time in the shorter catalytic bed was not sufficient to arouse the catalytic cracking (Li et al., 2019).

Table 6.3. Experimental conditions to evaluate the total catalyst/biomass ratio effects in solar pyrolysis.

Tests	T_s [°C]	C_s	CB_s
8S	750	0.5 or 1:1	1:1
13S	750	0.5 or 1:1	0.5:1
14S	750	0.5 or 1:1	2:1
15S	750	0.5 or 1:1	4:1

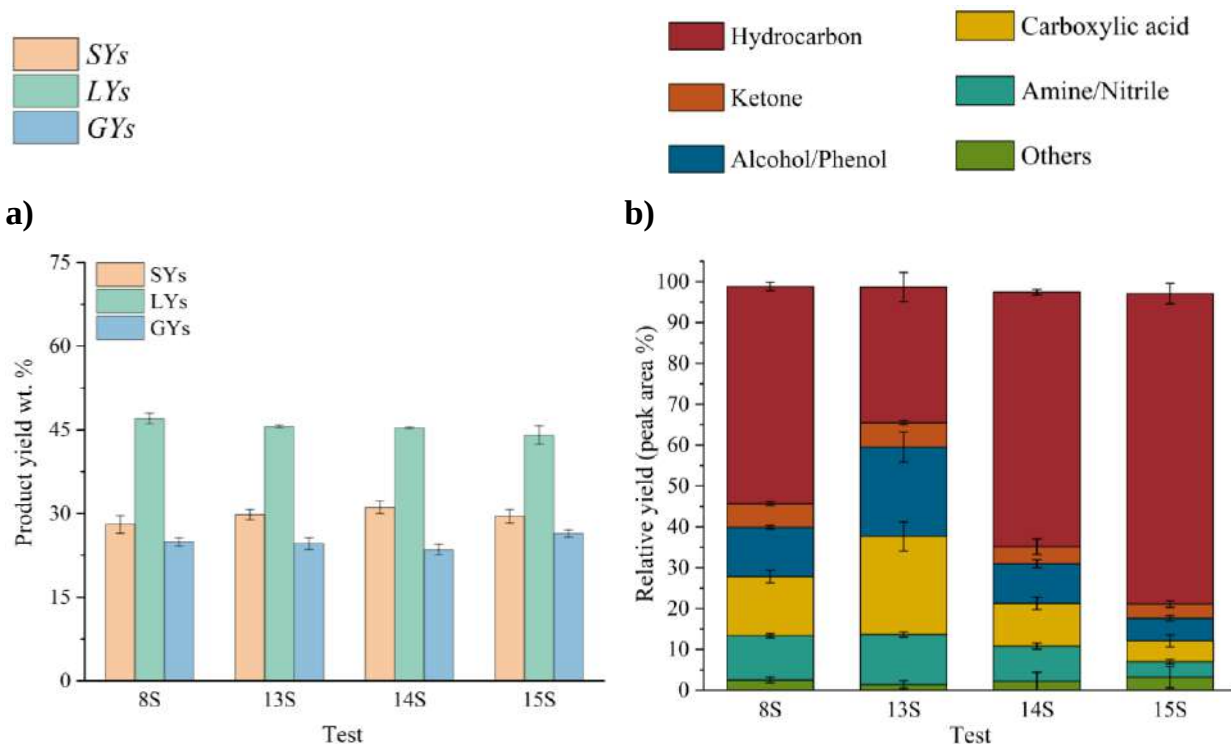
**Fig. 6.11.** Effects of the total catalyst to biomass ratio on the (a) product distribution and (b) bio-oil composition.

Fig. 6.11 (b) also indicates that the increment in the dual-catalytic led to more significant hydrocarbon generation. The upward trend for hydrocarbon increased from around 30 to 75% when the total catalyst ratio increased from 0.5 to 4, reinforcing that longer residence times assisted the desirable reactions. In this case, the larger amount of catalyst may favor decarboxylation over decarbonylation, minimizing the CO/CO₂ ratio in the gas, promoting a minor loss of carbon to the gas and, therefore, maximizing the carbon in the liquid fraction (Resende, 2016). When comparing tests 8S and 15S, the percentage of ketones and alcohols/phenols was almost halved, and the

content of carboxylic acids and amine/nitriles was reduced by approximately 10%. These compounds were converted into hydrocarbons in both tests, most likely through: (I) the Hofmann elimination that uses the hydrotalcite dual character (acid-base catalyst) to eliminate -NH_3 and (II) deacidification followed by aromatization, in which the two catalysts play different roles (Prado et al., 2017; Ding et al., 2018). The basicity of the NiHTC most likely promotes deacidification as NiHZSM-5 performs the aromatization (Lee et al., 2020c). However, the catalyst bed length led to higher resident time and favored the product of interest generation that reached 75% (test 15S) (Dai et al., 2020). Increasing the catalyst percentage led to the formation of a longer catalyst bed, which favors the contact time between the steam and the catalyst, as well as improves the interaction between them. This better interaction possibly favored reactions that led to the formation of hydrocarbons. Appendix B shows a table containing the main compounds for test 15S of solar pyrolysis. Gopakumara et al. (2012) also observed an increase in hydrocarbons in the bio-oil with increasing the catalyst load.

The water content of sample 15S (the optimized condition) was determined using the Karl Fischer method. The liquid portion exhibited a moisture content of approximately $4.5 \pm 0.40\%$, considerably lower than the typical bio-oil moisture content of that ranges from 10 to 25%, as reported by Bridgwater (2018). The presence of water in bio-oil can have several adverse effects, including changes in viscosity and stability, potential phase separation, reduction in calorific value, density, and stability, as well as an increase in pH. These factors can pose challenges related to the miscibility of bio-oil in fuels and its storage.

Fig. 6.12 shows the effects of the total catalyst-to-biomass ratio (CB_5) on bio-oil aromatization. It is possible to affirm that the raise in the total catalyst ratio besides assisting the hydrocarbon generation also benefited aromatization reactions. It is possible that the increment in the total hydrocarbon content facilitated these reactions. When comparing tests 13S and 15S, the aromatization increased from 35 to 80%, which led to close to 60% of aromatic compounds in test 15S. The upward trend of aromatic compounds is inversely proportional to the aliphatic ones. Many long-chain aliphatic hydrocarbons (C15, C16, C17, C18) have been found, that mainly include alkanes and alkenes. Another explanation that might have favored the aromatic generation is the *ex-situ* configuration. Wang et al. (2014), compared bio-oil produced by *in-situ* and *ex-situ* pyrolysis of pine wood. The author observed that the *ex-situ* configuration favored the production of different aromatic hydrocarbons, while the *in-situ* configuration favored the production of

olefins. Wang et al. (2013) and Yang et al. (2019) proposed that aromatic hydrocarbons can be formed from triglycerides and amino acids by removing the hydroxyl bonds from phenolic substances either through its direct elimination or by thermal dehydration of saturated cyclic alcohols that form aromatic rings by adding H_2 . These conversions are extremely valuable since aromatic hydrocarbons are potent products that can be mixed with gasoline to raise the octane number and, consequently, the calorific value of the bio-oil, improving its general fuel properties.

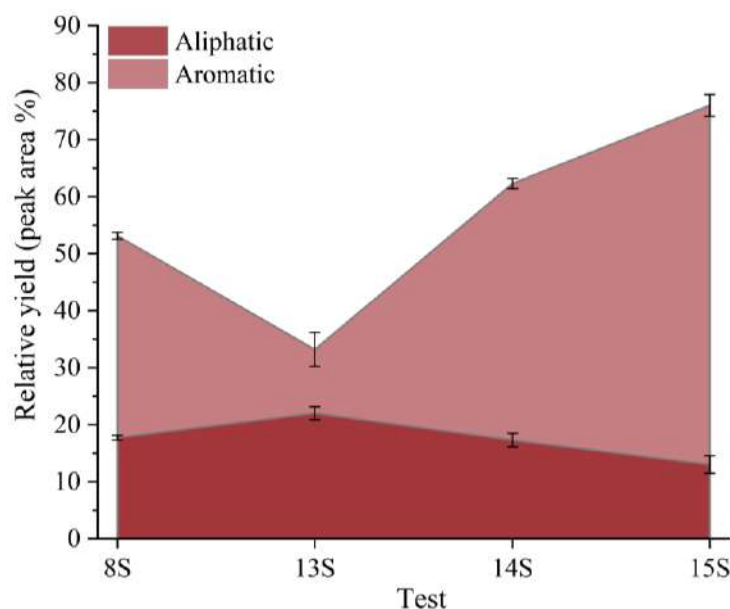


Fig. 6.12. Effects of the total catalyst-to-biomass ratio (CB_5) on bio-oil aromatization.

6.1.4. Energy conversion and efficiency of solar catalytic pyrolysis

This study focused on developing efficient thermochemical processes and identifying biomass species capable of providing high-energy outputs. The energy content of bio-oil was assessed as part of this endeavor. Figure 6.13 shows the energy content of bio-oil resulting from catalytic solar pyrolysis in the four tested scenarios. Since bio-oil derived from pyrolyzed biomass holds the potential for heat and power generation, it is crucial to evaluate energy efficiency. The Energy Recovery (ER_5) parameter for the bio-oil obtained through the optimization process in solar pyrolysis was determined using Equation 3.19 as the reason of the bio-oil weight multiplied by its HHV by the biomass weight multiplied by its HHV. The data indicates that the bio-oil with more aromatic hydrocarbon content presented more energy density, and consequently, the energy

recovery efficiency also reached a higher value. Test 15S's efficiency (around 65%) increased by more than 10% compared with test 13S since the latter presented a lower hydrocarbon formation of approximately 30%. Compared with the non-catalytic control (test 2S), the energy recovery increment reached almost 20%.

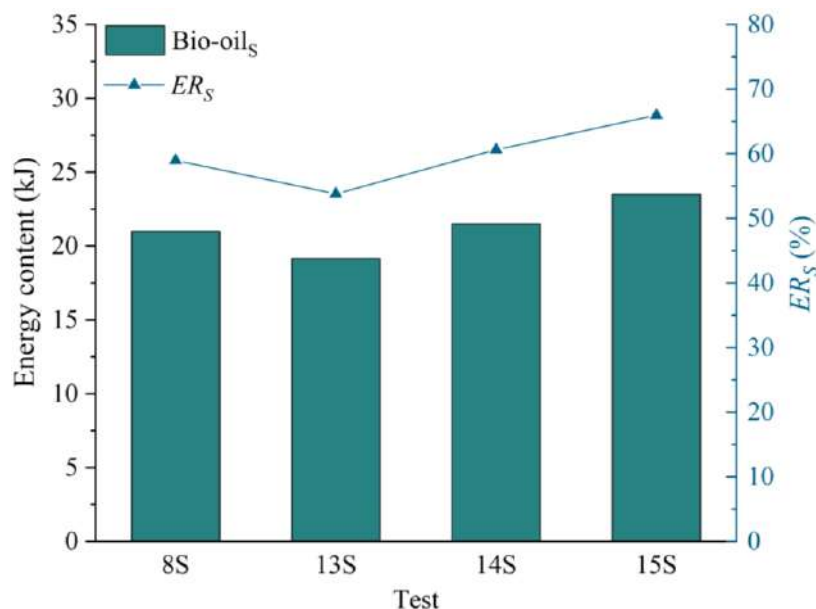


Fig. 6.13. Bio-oil energy content and energy recovery efficiency (ER_s) for different total catalyst-to-biomass ratios in the catalytic solar pyrolysis.

Rossi et al. (2021) and Barbosa et al. (2021) studied the solar pyrolysis of *Chlamydomonas reinhardtii* microalgae. Their findings showed energy recovery values up to approximately 60%. On the other hand, Miao et al. (2004) and Borges et al. (2014) performed conventional and microwave pyrolysis of microalgae biomass and reached 22 and 87% of energy recovery efficiency. These data prove that the heating processes and pyrolysis parameters features can highly influence the efficiency. Thus, solar pyrolysis has great potential since it uses free energy, which can decrease production costs. Considering the satisfactory energy recovery results achieved by the studies using solar energy have the potential to reduce environmental impact. The lab-scale solar pyrolysis has satisfactorily stored energy as a liquid fuel. These results might help further scale up solar pyrolysis technologies. According to the United States Environmental Protection Agency (EPA, 2018) and Eq. 3.20, the emissions of CO₂ equivalent for fossil crude oil and the renewable bio-oil generated in this study (on average) are 70331 and 3357 g CO₂ eq/GJ,

respectively. These data represent approximately 95% less CO₂ eq emissions as regards fossil crude oil usage, since microalgae are considered renewable biomass, and the heating power also comes from a renewable energy source. In the environmental aspect, this fact can be a great form of mitigating the emissions of CO₂ and earning carbon credit potential (Fodah et al., 2022).

6.2. Conclusions

In this work, the catalytic pyrolysis of the microalgae *Schizochytrium limacinum* was studied in the *ex-situ* configuration to explore different configurations between the double catalytic bed, a condition still little explored today, and reaction temperatures. In the solar tests, it was observed that the double catalytic bed and the reaction temperature had little influence on the distribution of the pyrolysis products. However, the increment in the liquid yield can be observed for reactions under the highest temperature (750°C) and NiHTC/(NiHTC+NiHZSM-5) of 0.50. This condition reached about 47% of liquid, which can be considered a yield satisfactory compared to other works, affirming that microalgae are an excellent biomass for bio-oil generation.

Regarding the composition of the bio-oil phase, which is the product of interest in this study, the bio-oil produced in the solar tests presented compounds highly desirable as long-chain hydrocarbons (aliphatic and aromatic). The formation of these hydrocarbons was more favored at the highest reaction temperature of 750°C, at NiHTC/(NiHTC+NiHZSM-5) of 0.50, demonstrating the positive performance of the double catalytic bed in the constitution of these compounds. When the ratio of total catalyst to biomass was 4:1, the generation of hydrocarbons reached 75%, a condition that also led to an aromatization of approximately 80%. Just as hydrocarbon production benefited under these conditions, the energy density of the bio-oil and the energy recovery efficiency (*ERs*) also achieved their peak, reaching approximately 25 KJ and 65% in the 15S test. These data represent about 95% less CO₂ eq emissions as regards fossil crude oil usage since microalgae are considered renewable biomass, and the heating power also comes from a renewable energy source. In the environmental aspect, this fact can be a great form of mitigating the emissions of CO₂ and earning carbon credit potential.

6.3. References

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CHAPTER 7

7. BIO-FUEL PRODUCTION FROM CATALYTIC MICROWAVE-ASSISTED PYROLYSIS OF THE MICROALGAE *SCHIZOCHYTRIUM LIMACINUM* IN A TANDEM CATALYTIC BED

This chapter presents and discusses the results of microwave-assisted pyrolysis in the tandem catalytic bed composed of NiHTC/SiC and NiHZSM-5/SiC.

7.1. Results and discussion

7.1.1. Effect of Temperature

Temperature plays a crucial role in the biomass pyrolysis behavior. To determine the optimal temperature for obtaining more significant amounts of condensable organic compounds, the temperature was varied from 400 to 750°C during non-catalytic tests of *Schizochytrium limacinum*. In Fig. 7.1 (a), it can be observed that the condensable fraction peaked at 500°C, which represents an intermediate temperature. This temperature range supplied sufficient energy to break the bonds between molecules, leading to higher yields of condensable products. Nevertheless, with increasing pyrolytic temperature, the presence of condensable organic compounds decreases significantly, reaching approximately 40 wt.% at 750°C. This reduction is attributed primarily to secondary cracking processes, indicating intensified decarbonylation and decarboxylation reactions at higher temperatures. As a result, non-condensable gases, including H₂, C1-C5 hydrocarbons, CO, and CO₂, are released (Wang et al., 2020). Fig. 7.1 (b) indicates the product distribution under 3 different processing temperatures without catalyst usage. The products were classified into solid, liquid, and gas. It is noteworthy that out of the liquid fraction, approximately 20% accounts for water generation. In accordance with Bridgwater (2018), pyrolysis liquid typically contains a water content ranging from 10 to 25 wt.%. Azizi et al. (2020) studied the pyrolysis of three different microalgae species, finding an average water content of 25% across all three species.

The reaction temperature of 400°C was insufficient to achieve a significant degree of thermal degradation, resulting in a higher solid yield (34 wt. %) being obtained. The highest liquid yield, 57 wt.%, was obtained at 500°C. As the processing temperature increased from 500 to 600°C, the non-condensable gas yield increased by approximately 10 wt.% while the solid yield remained around 20 wt.%. One possible explanation for achieving a more significant liquid formation could be the residence time in the microwave reactor. An adequate residence time allied with a suitable temperature implies more liquid production. Attaining an appropriate thermal degradation degree enables molecular bond breaking, maximizing biomass conversion while simultaneously preventing secondary cracking. The residence time of the pyrolysis volatiles in the microwave reactor was estimated to be 50 seconds at 500°C. This value represents the average time difference between the initiation of biomass feed and the first detection of gas exiting the reactor. On the other hand, the 50 seconds of residence time under higher temperatures is suitable for non-condensable gas production.

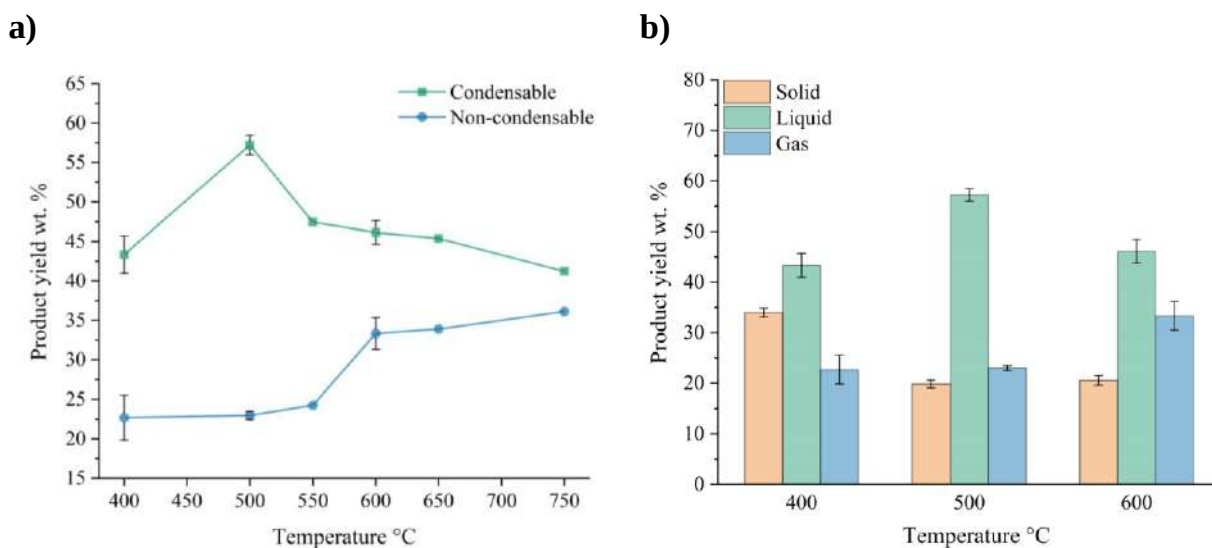


Fig. 7.1. Effects of temperature on (a) condensable and non-condensable products and on (b) product yields.

From the perspective of liquid generation, intermediate residence time could be a notable way of demanding lower temperatures for cracking reactions, reducing the process's energy consumption. The liquid fraction obtained from biomass tends to reach its maximum (40 to 60 wt.%) on pyrolysis performed at temperatures up to 550°C and residence times between 30 to

1500 seconds (Lee et al., 2020a). Ojha et al. (2017) conducted lignin pyrolysis at 500°C and reported a drastic drop of approximately 85 wt.% in pyrolysis conversion when the residence time was reduced from 20 to 2 seconds. Miao et al. (2004) reported a minor liquid production of 17 and 24 wt.% while performing pyrolysis of *Chlorella protothecoides* and *Microcystis aeruginosa* microalgae, respectively, using a fluid bed reactor which had a residence time of 3 s.

Fig. 7.2 shows the detailed chemical composition of bio-oil products regarding the 60 major components detected in the GC-MS analysis. The compounds were classified and divided according to their organic functional groups: oxygenated (ketones, alcohols, carboxylic acids), nitrogenated (amines and nitriles), hydrocarbons, and other compounds. The total relative peak percentage ranges from 89 to 98.5% for the 3 different temperature conditions since the unidentified compounds are not part of the composition sum. The relative abundance of each functional group is correlated to temperature reaction.

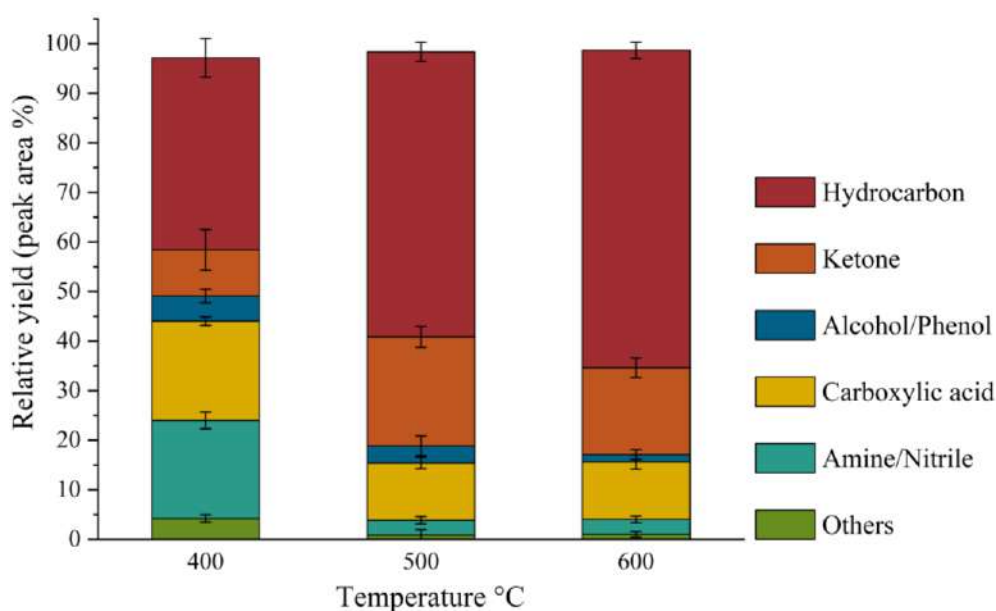


Fig. 7.2. Effects of temperature on condensable product composition.

Overall, alcohols, carboxylic acids, amines, and nitriles decreased while ketones and hydrocarbons increased with the temperature rise. The relative fraction of nitrogenated compounds reduced by approximately 16% with the increase in temperature. The protein in the microalgae was first decomposed to produce amines and nitriles, which existed in the bio-oil fraction at low pyrolysis temperatures (Chagas et al., 2016). These substances were then decomposed with further

increasing temperature into nitrogenous gases (e.g., NH_3), reducing the bio-oil nitrogen content (Li et al., 2019). Nevertheless, the overall low content of NCO, irrespective of the reaction temperature, can be attributed to the low nitrogen content present in this particular type of algae.

On the other hand, hydrocarbon content increased from 38 to 67% when the reaction temperature was raised from 400 to 600°C. At higher temperatures, cracking of the long-chain carboxylic acids and alcohols' hydrocarbon portions was favored, leading to the formation of alkenes and cyclic hydrocarbons. It is evident that reaction temperature allied with heating rate played an essential role in the quality of microalgae pyrolysis products.

Another important point is that the absorbent material (SiC) was kept heated inside the oven cavity in the experimental apparatus. Thus, the biomass was put in contact with the hot absorbers and could be instantaneously heated to the desired temperature as it was fed into the system (D'Ambrosio et al., 2021). This absorbent material can improve the process heating rate, as it maintains a steady temperature, preventing over-temperature reactions. Li et al. (2013) performed pyrolysis of *Schizochytrium limacinum* microalgae. Their results showed a bio-oil with approximately 45% hydrocarbon content under non-catalytic tests at 600°C. This aligns with the findings of the present work that higher temperatures favor hydrocarbon formation.

7.1.2. Effect of the tandem catalytic bed of NiHTC/SiC and NiHZSM-5/SiC

The catalytic experiments were carried out at 500°C to assess the impact of the tandem catalytic bed on the distribution and composition of the products. This temperature was chosen to achieve a maximum yield of the liquid fraction. The NiHTC/SiC:HZSM-5/SiC catalysts' ratio studied were 1:0, 0:1, and 1:1, with a total catalyst (NiHTC/SiC + HZSM-5/SiC) to biomass ratio of 0.5:1 (tests conditions are presented in Table 7.1).

Table 7.1. Catalytic microwave-assisted pyrolysis tests' conditions.

T_M [°C]	C_M	CB_M
500	0:0	0:0
500	0:1	0.5:1
500	1:0	0.5:1
500	1:1	0.5:1

Fig. 7.3 shows the experimental data obtained from catalytic and non-catalytic pyrolysis at the same temperature condition. In Figure 7.3 (a), it can be observed that the product distribution remained relatively stable with minimal variations. The formation of liquid products exhibits a variance of approximately 2%, indicating that the catalysts' ratio has little effect on the liquid formation. The water content persisted at around 30%, most likely due to dehydration and aromatization reactions (Babich et al., 2011; Yuan et al., 2021). Babich et al. (2011) investigated catalytic pyrolysis using *Chlorella* microalgae. Their findings indicated a higher water content of 35% in the catalytic experimental runs.

Nevertheless, despite minor fluctuations in the product distribution, the NiHZSM-5/SiC zeolite catalyst experiments demonstrated a slight uptrend in liquid yield. The tests with catalysts' ratios of 0:1 and 1:1 resulted in yields of approximately 58%. In comparison, the test using only NiHTC/SiC catalyst yielded 54%. One possible explanation is that the NiHTC/SiC catalyst can cause a greater extent of secondary cracking reactions of macromolecules and lead to higher vapors content (Navarro et al., 2018). However, these secondary reactions, which generate volatiles, are the leading cause of aromatic hydrocarbon formation when the NiHZSM-5/SiC is put in the sequence of the NiHTC/SiC in the catalyst fixed bed. The tandem catalytic bed resulted in a product distribution that closely resembled the non-catalytic control. This observation suggests a minimal negative impact of the dual-catalyst ratio of 1:1 on product distribution.

Figure 7.3 (b) displays the composition of the bio-oil products. The results obtained using the NiHTC/SiC catalyst (NiHTC/SiC:HZSM-5/SiC = 1:0) exhibited minimal contents of carboxylic acids, nitrogenated compounds (amines and nitriles), and alcohols in comparison to the non-catalytic control. These substances were reduced from 10, 3, and 2.5% in the non-catalytic test to approximately 0. These results indicate a satisfactory deacidification performance of the NiHTC/SiC catalyst. Goh et al. (2008) reported that lamellar mixed hydroxides, such as hydrotalcite, contain positively charged layers and exhibit an excellent ability to capture inorganic anions. After calcination, most carbonate anions are eliminated, opening spaces for significant incorporation of guest anions such as -OH that can be adsorbed, most likely through ion exchange on the surface of hydrotalcite or at the edge of its interlayer. In addition, Amani et al. (2017) proposed that carboxylic acids could be converted into ketones by using nickel catalysts that will promote acylation of the carboxylic acids by eliminating the -OH.

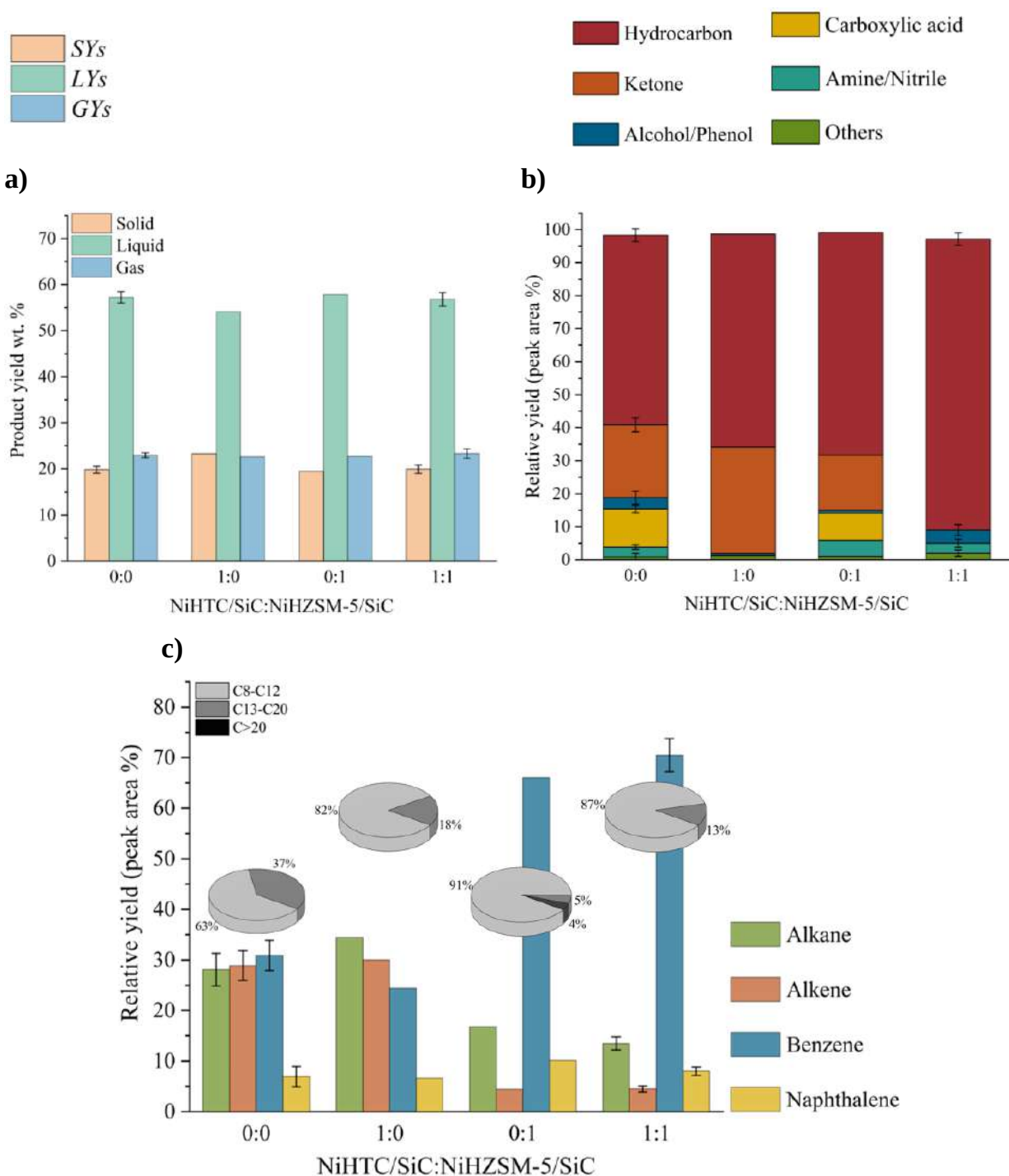
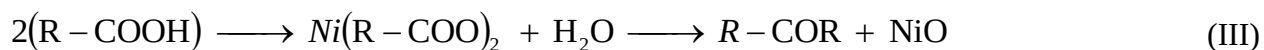
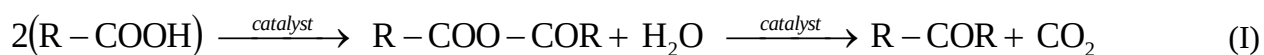


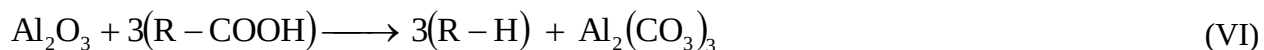
Fig. 7.3. Effects of the dual-catalyst ratio (NiHTC/SiC:HZSM-5/SiC) on the (a) product distribution, (b) bio-oil composition and (c) hydrocarbon compounds and carbon chain distribution.

Along with the de-acidification, the NiHTC/SiC can be responsible for nitrogen removal. Andrade et al. (2018) explained that the hydrotalcite acidic and basicity functions work together to remove nitrogen, probably via Hofmann elimination, in which the $-NH$ of a heterocyclic nitrogenous molecule is protonated by the acid site forming a radical amino $-NH_2$, while the basicity site attracts the $\beta-H$. This way, the C-N bond is broken, and the nitrogen molecule can be removed. In summary, the cracking reactions aroused using NiHTC/SiC probably favored the denitrification and deacidification of the bio-oil fraction, which resulted in a sharp increment of the ketones generation (test NiHTC/SiC:HZSM-5/SiC = 1:0). To explain this fact, the following pathways are suggested:



The bio-oil undergoes deacidification through reactions (I), (II), and (III), resulting in the formation of ketones and esters and therefore decreasing the content of acid compounds (Amani et al., 2017; Nicholson et al., 2004). However, the hydrocarbon formation in the catalytic test with NiHTC/SiC was not strongly affected, remaining at 64.5% close to the non-catalytic test (61%). This fact suggests that the NiHTC catalyst might be more selective to C-OH dissociation. The reaction (IV) scission of the C-N bond is the most probable mechanism responsible for the nitrogenated compounds' downward. The catalyst's bifunctional acid-base character favors nitrogen removal, most likely through Hofmann elimination (Prado et al., 2017). Under the condition of NiHTC/SiC:HZSM-5/SiC = 0:1, the formation of ketones was reduced by approximately 50%, resulting in a content of 17%. This suggests that the NiHZSM-5/SiC catalyst might be comparatively less effective in terms of bio-oil neutralization [specifically in reactions

(I), (II), and (III)] and denitrification [reaction (IV)]. At this same condition (NiHTC/SiC:HZSM-5/SiC = 0:1), the acid and the amine/nitrile increased from negligible content to 8 and 5%, respectively, revealing a weaker catalytic performance of NiHZSM-5/SiC as regards these compounds. On the other hand, the hydrocarbon content was around 67%, which indicates that the NiHZSM-5/SiC can be in charge of deoxygenation due to its acid sites. Li et al. (2017) studied the deoxygenation of methyl laurate using Ni/HZSM-5 catalyst, finding low yields of oxygenate products, which remained at less than 8%. Along with the ketone formation, the acids can also be converted directly into hydrocarbons, as suggested by the pathways indicated in reactions (V) and (VI) (Mansir et al., 2022; Zhu et al., 2020).



The test using the same proportion of both catalysts (NiHTC/SiC:HZSM-5/SiC =1:1) achieved the best result, which showed a dramatic increase in hydrocarbon generation, from around 65% when using only one catalyst to approximately 90% under the tandem catalytic bed. The deacidification provided by the NiHTC/SiC is the primary effect responsible for decreasing the carboxylic acids content, increasing the content of intermediate compounds such as ketones, which were subsequently converted into aromatic hydrocarbons through the deoxygenation reactions promoted by the NiHZSM-5/SiC. Appendix C shows a table containing the main compounds for the test with NiHTC/SiC:HZSM-5/SiC =1:1 of microwave-assisted pyrolysis.

Oxygen is commonly removed by the generation of carbon monoxide (CO), carbon dioxide (CO₂), and water vapor (H₂O), while nitrogen can be eliminated through nitrogen-containing gases such as NH₃ and HCN (Zadeh et al., 2020; Zhan et al., 2019; Lee et al., 2020b; Zhang et al., 2015), as shown by the composition trends in the gas generation (Fig. 7.4). One can discern an upward trend in CO and CO₂ release during the catalytic tests. Additionally, it was observed that the hydrotalcite (NiHTC/SiC) catalyst-containing tests exhibited a more pronounced inclination toward nitrogen release (NH₃ trend). As expected, this aligns with the findings observed in the bio-oil data.

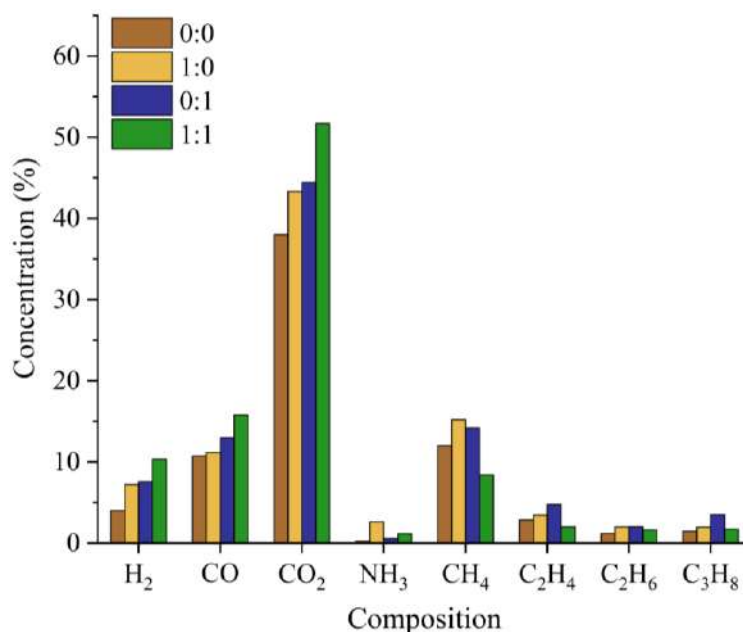


Fig. 7.4. Gas compositions at different catalysts' ratios (NiHTC/SiC:HZSM-5/SiC).

Thus, for the *Schizochytrium limacinum* microalgae, using both catalysts in the tandem bed achieved better results, regarding the product of interest (hydrocarbons). Ding et al. (2018) investigated the pyrolysis of hemicellulose in a dual-catalyst bed of CaO and HZSM-5 and found similar results, in which using two catalysts reached more significant hydrocarbon content.

Fig. 7.3 (c) presents the hydrocarbons' classification, showing a sharp rise in the benzene percentage in the tests when NiHZSM-5/SiC was used. These obtained results align with existing literature, which have extensively reported the excellent performance of zeolites in aromatization reactions, and consistently acknowledged the remarkable capabilities of zeolites in this regard (Lashchinskaya et al., 2023). The test containing both catalysts resulted in a bio-oil with approximately 70.5% of benzene in contrast with 30% in the non-catalytic test. These data suggest that the alkanes and alkenes were converted, in their majority, into aromatic compounds. On the other hand, the naphthalene fraction remained stable, which indicates that its formation might be related to the pyrolysis temperature reaction. The content related to the carbon chain demonstrates that regardless of the catalyst, the chains with less carbon number, overall, showed an upward trend by more than 20% in comparison to the non-catalytic control. The rise in the shorter carbon chains (C8-C12) and, consequently, the reduction in carbon chains longer than C13 resulted from catalytic cracking, which was also responsible for generating desirable compounds such as aromatic

hydrocarbons. These results indicate that the incorporation of metal into the catalysts might assist the rise in cracking of heavier fractions, and strongly promote the formation of lighter fractions, most likely because of changes in total acidity, which improves catalyst stability against coking (Peng et al., 2012). Maia et al. (2010) found that catalytic cracking of alkenes/alkanes increased as the percentage of Ni in HZSM-5 zeolite was also enlarged. Peng et al. (2012) findings revealed a selectivity of approximately 43% for alkane cracking using a metal load (Ni) of 10 wt.% in the HZSM-5 zeolite.

7.1.3. Effect of the catalyst placement

A distinct *ex-situ* configuration of the dual-catalytic bed was investigated, comparing a setup with bare powder to a configuration comprising NiHTC/SiC followed by NiHZSM-5/SiC. Both setups were evaluated under identical reaction conditions, including a temperature of 500°C, a NiHTC:HZSM-5 catalyst ratio of 1:1, and a catalyst-to-biomass ratio of 0.5:1. Fig. 7.5 shows the product yields and bio-oil characteristics of the MACFP under these conditions. The bare powder in the catalytic bed led to a lower liquid generation (47%) and a higher gas yield (29%) compared with 57% and 23%, respectively, in the control experiment with the catalysts/SiC foam. The configuration that used the catalyst/SiC foam generated a liquid fraction as high as the non-catalytic test (around 57%), which showed a minimal negative effect of the catalytic bed on the product distribution. At a gas volumetric flow of 2.5 mL/s, the bare powder bed pressure drop was about three times higher than the test using the catalyst/SiC foam. The higher-pressure drop contributed to secondary undesirable reactions and coking deposition, which can lead to faster catalyst deactivation (Gamliel et al., 2015). The coking yield (determined by the weight difference of the catalysts after the experimental runs) was found to be 3.1 and 2.3%, comparing the bare powder to the structured catalysts in the SiC foam, respectively. Among the various factors that contribute to the selection of the SiC foam, one of the most significant is its ability to maintain low-pressure drop. This is primarily attributed to the uniform dispersion of catalysts, which enhances mass transport within the system.

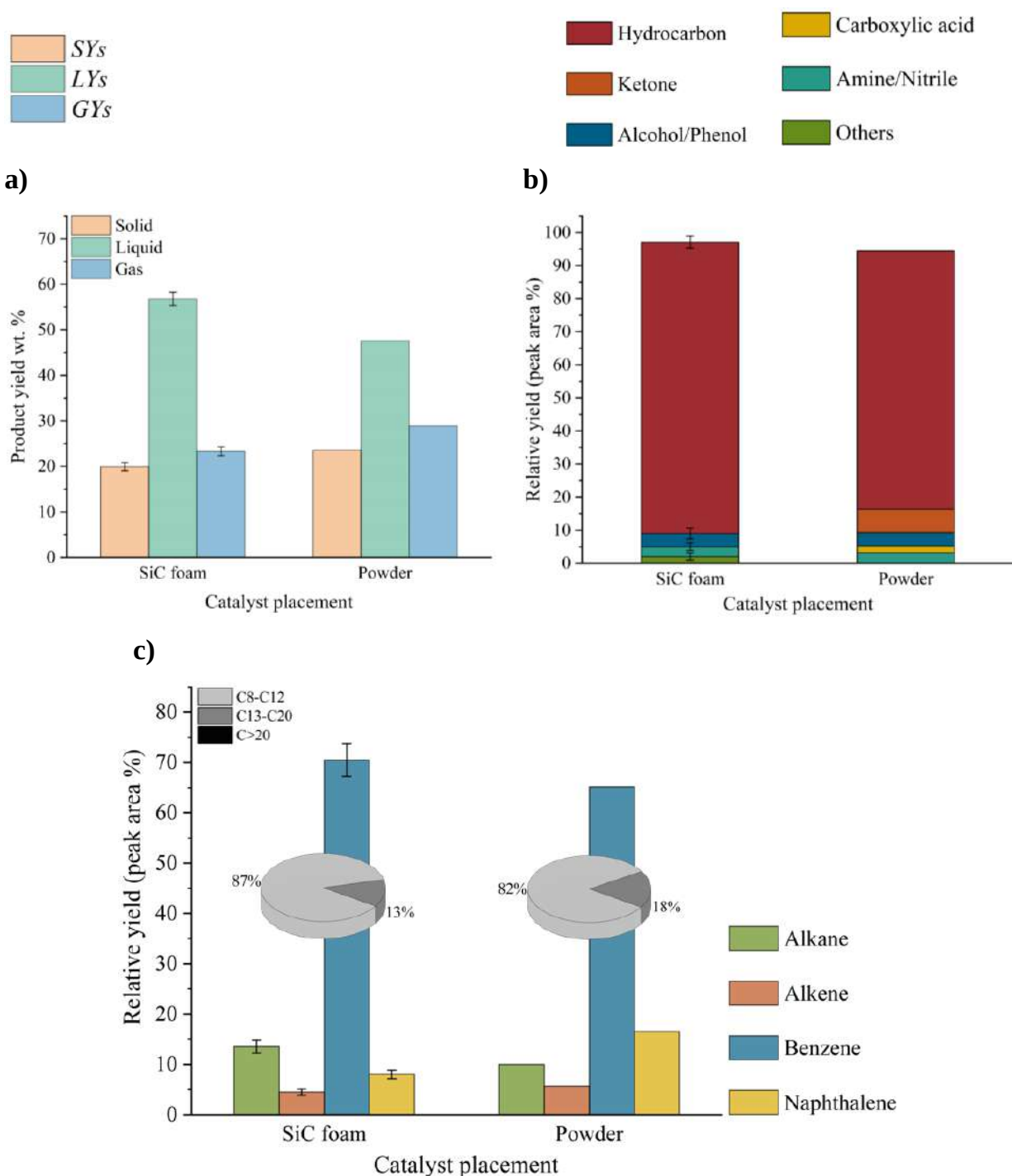


Fig. 7.5. Effects of the catalyst placement on the (a) product distribution, (b) bio-oil composition and (c) hydrocarbon compounds and carbon chain distribution.

In addition, the SiC material is chemically inert and has good thermal conductivity, which enables more precise temperature control and stability. This reduces the possibility of localized

high temperatures inside the catalytic bed, contributing to better catalyst performance. The catalytic bed loaded with bare powder prolonged the residence time of pyrolytic vapors, resulting in more undesirable compounds (Pattiya et al., 2012), as shown in Fig. 7.5 (b). The hydrocarbon formation was 78% using the bare powder, compared to 91% with the catalysts/SiC setup. Although the hydrocarbon production was smaller in the bare powder configuration, Fig. 7.5 (c) shows a satisfactory aromatization of the alkanes and alkenes as well as shorter carbon chain hydrocarbon generation. On the other hand, the naphthalene formation reached the highest value of 16.5% using the bare powder, which might be assigned to possible hot localized spots inside the powder catalytic bed.

7.1.4. Effect of the total catalyst to biomass ratio

To investigate the catalyst performance on the product distribution and composition, the total catalyst to biomass ratio (CB_M) was studied at three different levels: 0.25:1; 0.5:1; and 1:1 (Table 7.2). The tests were performed at 500°C to obtain higher liquid fraction and NiHTC/SiC:HZSM-5/SiC catalysts ratio was fixed at 1:1 to generate more significant hydrocarbon content.

Table 7.2. Catalytic microwave-assisted pyrolysis tests' conditions.

T_M [°C]	C_M	CB_M
500	1:1	0.5:1
500	1:1	0.25:1
500	1:1	1:1

It can be seen from Fig. 7.6 (a) that the yield distribution presented a slight fluctuation, where the solid and gas products remained around 20 and 23%, respectively while it is possible to observe a downward trend in the liquid fraction as the CB_M ratio increased from 0.5 to 1. Possibly, the catalyst performance in deoxygenation was enhanced, possibly due to decarbonylation, decarboxylation, and dehydration reactions, which facilitated the removal of CO, CO₂, and H₂O, resulting in reduced bio-oil production (McCann et al., 2008).

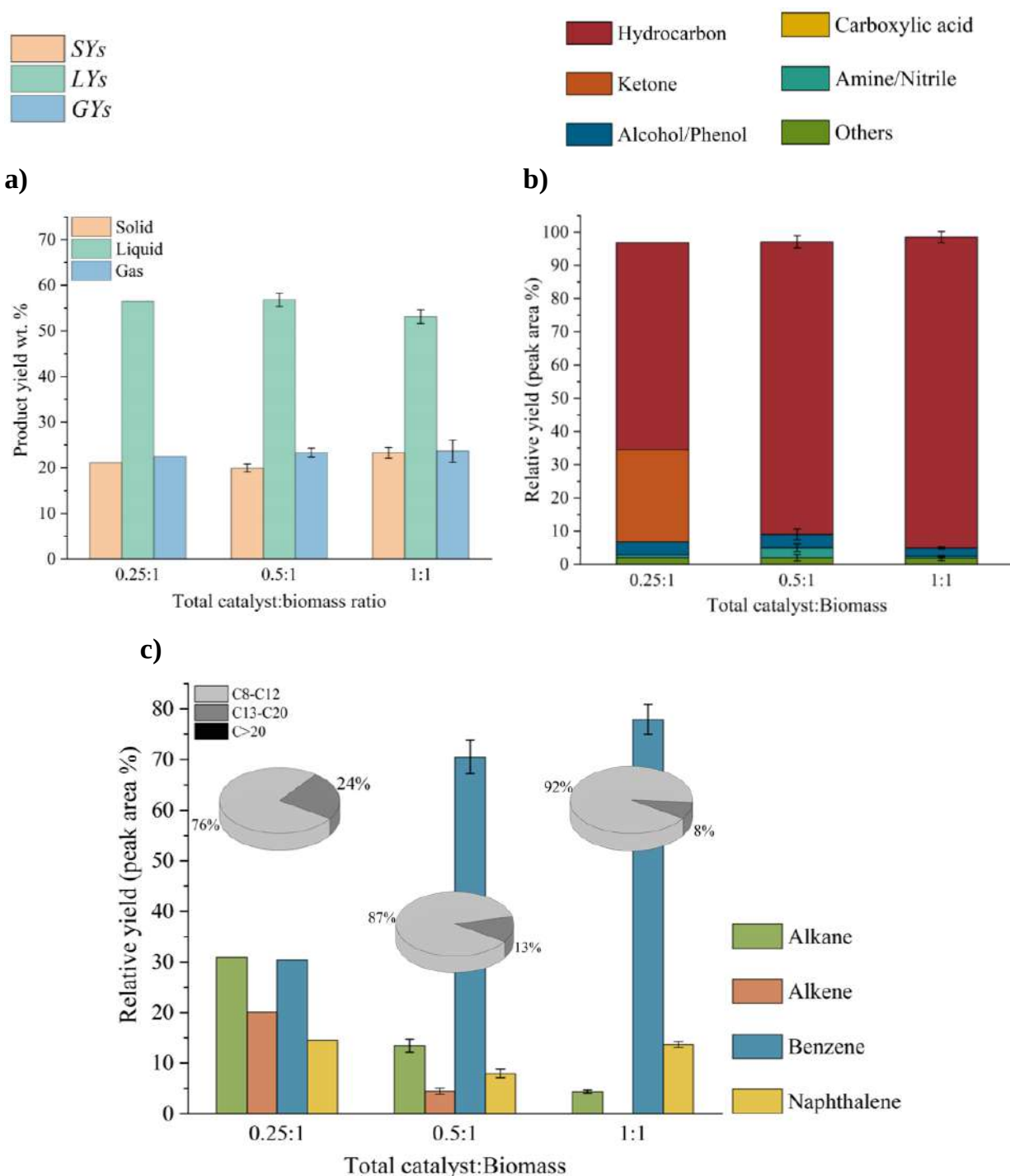


Fig. 7.6. Effects of the total catalyst to biomass ratio on the (a) product distribution, (b) bio-oil composition and (c) hydrocarbon compounds and carbon chain distribution.

The primary pyrolytic vapors pass through the NiHCT/SiC that promotes deacidification, converting acids into ketones, alcohols, and esters. Subsequently, the vapors enter the pore

structure of NiHZSM-5/SiC which removes the oxygen content. This is also supported by the bio-oil composition results presented in Fig. 7.6 (b). While the CB_M ratio increased, the oxygen-containing compounds such as ketones, alcohols, and acids lessened.

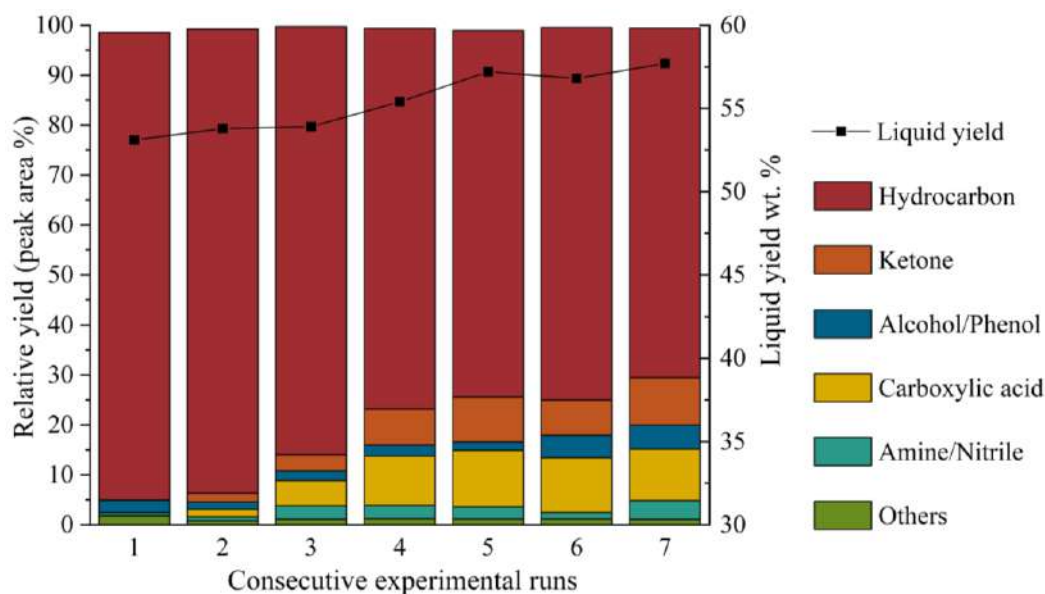
The total oxygenated compounds started at 29% under a CB_M ratio of 0.25 and were sharply reduced to 5 and 2.5% under CB_M ratios of 0.5 and 1, respectively. The opposite happened with the hydrocarbon percentage, which soared as the CB_M ratio was increased, reaching the highest value of close to 93% in the test with the total catalyst to biomass ratio as 1:1. The content of aliphatic and aromatic compounds in Fig. 7.6 (c) also corroborates that the deoxygenation cracking allied with the aromatization reactions benefited from the increment in the CB_M ratio. Along with the carbon chain shortening, where the C8-C12 range reached 92%, the alkanes and alkenes together were reduced from 51 to 4.5% as the CB_M ratio increased from 0.25 to 1, while the benzene content raised from 30 to 78%. Zhang et al. (2015) found similar results, when the rise in SiO_2 also resulted in more aromatic compounds. The naphthalene percentage remained stable at approximately 14%, which indicates that its generation has a weak relation to the catalyst quantity. It might be more strongly related to the reaction temperature.

7.1.5. Catalyst reuse and regeneration

The deactivation of the catalysts was studied through a series of seven consecutive experimental runs, in which the same catalytic bed was used in all seven tests. The test conditions were chosen for more liquid yield and significant hydrocarbon generation. Therefore, the temperature was set at 500°C, and the NiHTC/SiC:HZSM-5/SiC and the CB_M ratios were fixed at 1:1. The liquid yield, bio-oil composition, and hydrocarbon compounds are shown in Fig. 7.7. The liquid fraction increased in each run, from 53% in run 1 to approximately 60% in the last consecutive experimental run. This fact might be explained by the gradual loss in catalyst activity and/or catalyst pore closure, which most likely occurred due to coke accumulation. This could lead to less oxygen and nitrogen removal in the gaseous form, consequently resulting in more liquid. Although the liquid phase increased, the coke that accumulated and blocked the catalyst's active sites most likely led to poorer bio-oil quality (Dai et al., 2020). Zhou et al. (2018) studied the reuse of ZSM-5 catalyst in biomass pyrolysis, and found a similar behavior of more liquid generation, but with less desirable compounds as the catalyst was used several consecutive times. The

formation of coke might have led to a decrease in deacidification and deoxygenation reactions, as evidenced in Fig. 7.7 (a).

a)



b)

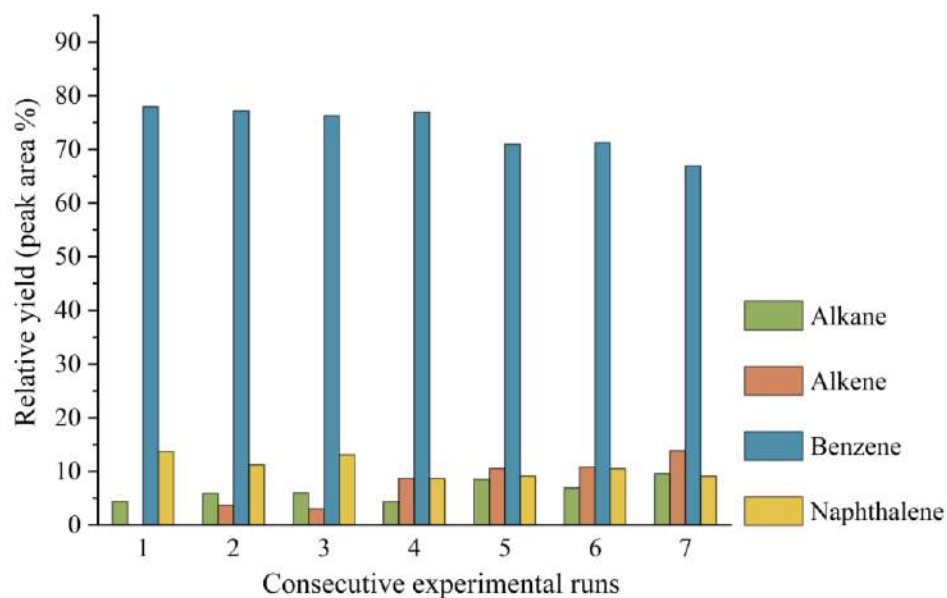


Fig. 7.7. (a) Liquid yield and bio-oil composition and (b) hydrocarbon compounds in consecutive experimental runs.

This trend is characterized by a notable increase, particularly in carboxylic acids and alcohols, with their combined content rising from negligible to 15.5%. This means that the NiHTC/SiC probably showed a more significant loss in activity than the NiHZSM-5/SiC since the ketone content raised less sharply, indicating that the deacidification was more affected than the deoxygenation reactions. From run 3 onwards, the removal of amines and nitriles was also affected, reaffirming the more significant deactivation of the NiHTC/SiC.

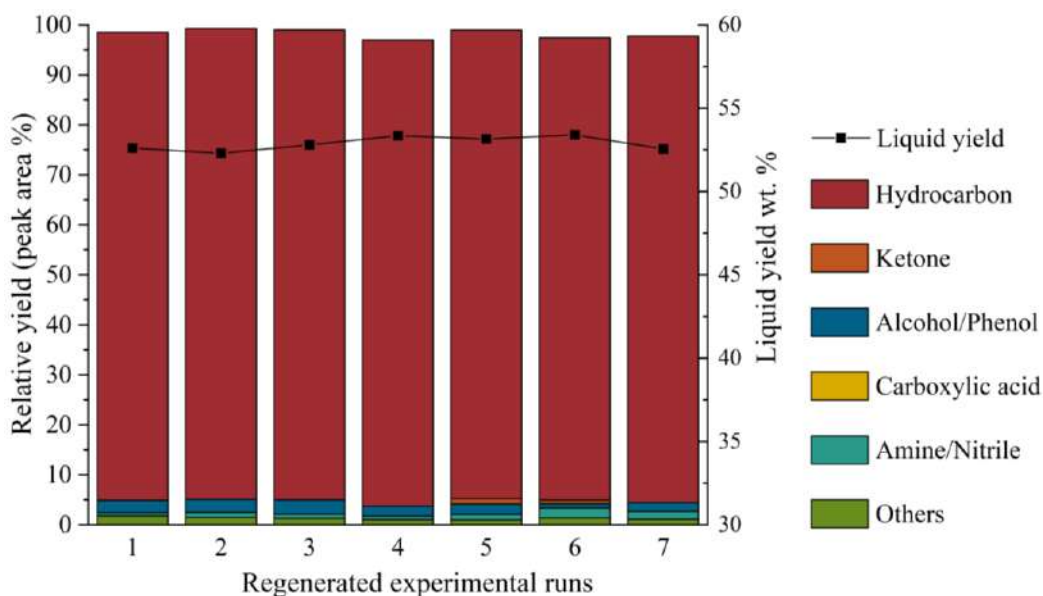
The small loss in the NiHZSM-5/SiC activity can be further reassured by Fig. 7.7 (b) which reveals a minor downward tendency in aromatic compounds, especially benzene, as the consecutive experiments were performed. The benzene content suffered a steady reduction that went from 78 to around 70% from the 5th test onwards, while the aliphatic hydrocarbons (alkanes and alkenes) increased by 19% after the 7th test. This means the selectivity to aromatics production was lessened. However, the NiHZSM-5/SiC was far from being completely deactivated, which reveals its great stability, which might have been enhanced by the load of Ni. Dai et al. (2019) studied different loads of Ni in the HZSM-5 and found that the addition of Ni can reduce the activation energy and improve the selectivity of mono-aromatics while reducing the coke formation.

To study the regeneration and reuse of the catalytic bed, a series of seven tests were performed under the same conditions (Fig. 7.8). However, this time, the catalysts were regenerated after every single experimental run. After each test, the catalysts were calcinated at 550°C in air atmosphere, overnight, which means recycling the catalysts and reducing operational costs. It can be seen in Fig. 7.8 (a) that overall, the liquid yield slightly fluctuated around 53%, and the hydrocarbon generation remained around 93%, indicating the stability of the catalytic bed after each regeneration cycle. Regarding the formation of nitrogenated components, a modest increment can be seen in the last two tests. The explanation suggested is that after some regeneration cycles, some of the carbon deposits were not totally removed from the catalysts during calcination, which might have caused the sintering of the nickel particles and affected the behavior in the catalytic routes, which slightly hindered nitrogen removal (Galetti et al., 2012).

Fig. 7.8 (b) shows the presence of alkenes after the 4th test, which might indicate a slight loss in the catalytic activity. Nevertheless, the benzene content remained around 75%, which shows that the aromatization reactions did not suffer wide impacts. This, once more, confirmed that *ex-situ* pyrolysis can be successfully performed with regenerated catalysts. The thorough coke elimination

during the catalysts' calcination, over seven regeneration cycles, can explain their continued stability.

a)



b)

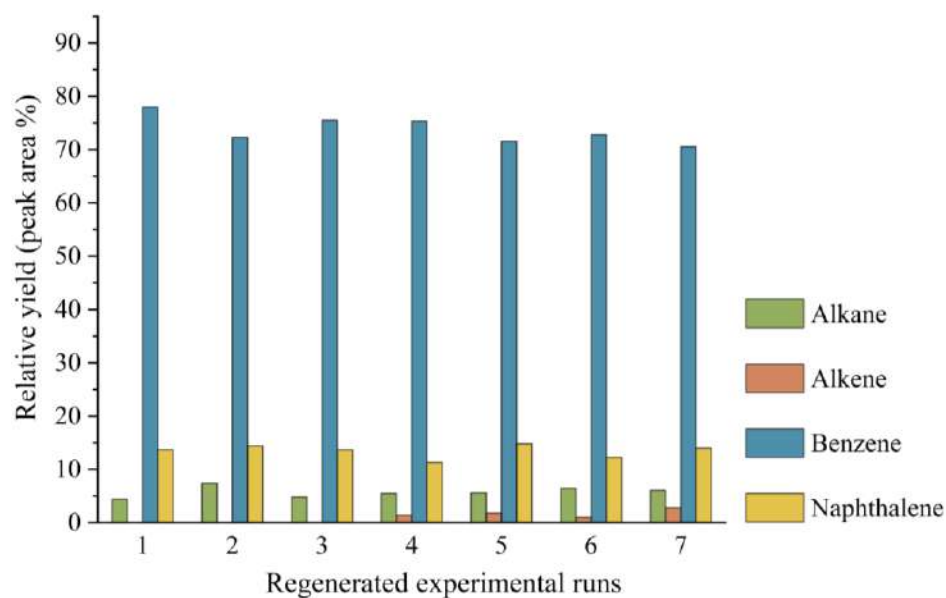


Fig. 7.8. (a) Liquid yield and composition and (b) hydrocarbon compounds in regenerated experimental runs.

The acid site density (n_a) of catalysts, the BET-specific area (S_{BET}), and the texture properties (pore volume - V_p and pore diameter - D_p) of the catalysts before and after regeneration tests are presented in Table 7.3.

Table 7.3. Catalysts' textural and acidity properties.

Catalyst	S_{BET} [m ² /g]	V_p [cm ³ /g]	D_p [nm]	Acid site density (n_a) [μmol/m ²]
NiHTC after calcination	186	0.70	8.23	0.81
NiHTC after regeneration	174	0.48	8.40	0.67
NiHZSM-5 after calcination	390	0.24	2.88	1.76
NiHZSM-5 after regeneration	358	0.21	2.62	1.63

The S_{BET} parameters of the regenerated catalysts were marginally lower than the value of the fresh catalysts. This suggests the catalyst's porosity was well-maintained, and coke products were mostly removed from the porous structures during regeneration. Furthermore, while the pore volume (V_p) for NiHTC after regeneration exhibited an inferior value, no significant changes were observed in pore diameter and pore volume. The acid site density exhibited a slight downward trend for both catalysts following the regeneration process. This observation suggests the possible presence of minimal residual coke on the catalyst surfaces. This aligns with the findings from Fig. 8, where there was a modest increase in the formation of nitrogenated components and a reappearance of alkenes in the latter tests. The residual coke might have accumulated on the catalyst surfaces due to the rapid formation of aromatics. This could have resulted in pore blockage, hindering access to catalytic sites and causing a reduction in the catalysts' acidity (Vogt et al., 2023; Guisnet et al., 2001). Notably, NiHTC appeared to be more adversely affected than NiHZSM-5, likely due to its position as the first catalyst in the tandem bed. The accumulation of catalyst coke arises from having the earliest contact with the incoming reactant (Liu et al., 2016). However, despite the possibility of some residual coke remaining on the catalysts even after the regeneration process, it did not significantly impact hydrocarbon generation. The marginal decrease in catalyst acidity suggests that burning off the coke deposits was sufficient to regenerate the catalysts, and additional rejuvenation procedures were likely unnecessary for a batch of 7 tests. There is little indication that other structural modifications, such as dealumination processes, occurred during this period (Vogt et al., 2023; Devaraj et al., 2016).

7.1.6. Energy conversion and efficiency

Focused on identifying biomass species that can provide high-energy outputs, the energy efficiencies for the MACFP experiments at different catalysts' ratios (distinct NiHTC/SiC:HZSM-5/SiC and CB_M ratios) were evaluated (Fig. 7.9). The energy content and efficiencies were calculated according to equations 4 to 7. These data can express the potential of the process regarding biomass conversion. The liquid yield and hydrocarbon percentage were placed to facilitate data visualization.

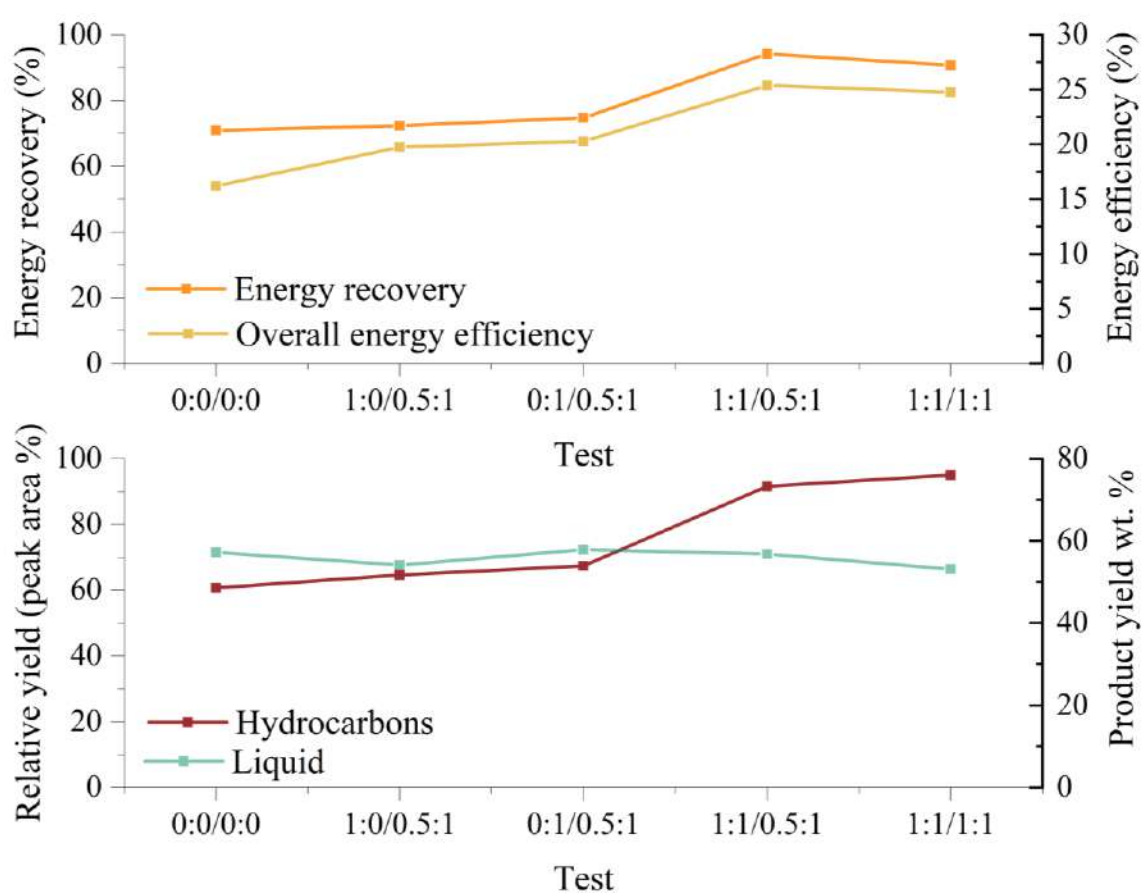


Fig. 7.9. MACFP energy efficiencies for different catalysts' ratios (distinct NiHTC/SiC:HZSM-5/SiC and CB_M ratios).

The non-catalytic control (test 0:0/0:0), despite its liquid production of 57%, presented the lowest energy content due to its minor hydrocarbon content of 60%. On the other hand, the catalytic tests indicated that their bio-oil energy density increased as the hydrocarbon fraction rose. Tests

conducted with catalyst ratios of 1:0/0.5:1 and 0:1/0.5:1 exhibited average hydrocarbon generation and liquid production rates of 66% and 56%, respectively, resulting in an overall increase in the energy content of the products. However, these same tests also presented an increase in the energy density of the biogas portion compared to the other experiments. Most likely, this was due to higher C-C bond breaking, which produced more gaseous hydrocarbons that account for most of the syngas heating value. Since the biogas yield did not have a significant range fluctuation, remaining around 23%, the difference in the total energy content mainly occurred due to the variance in the HHV of the gas. This suggests an undesirable energy transfer occurred from the liquid to the gas phase, probably due to secondary cracking reactions (Zhang et al., 2019). This behavior can be observed in Fig. 5, where the tests conducted with catalyst ratios of 1:0/0.5:1 and 0:1/0.5:1 showed some increments in hydrocarbons (C_xH_y) release. However, further fundamental investigations are needed to understand the biogas behavior based on their decomposition pattern.

Upon analyzing the last two experimental runs (1:1/0.5:1 and 1:1/1:1) in Fig. 10, it was observed that the bio-oil contained even higher energy levels. This can be attributed to the sustained hydrocarbon content, which remained above 90% in both tests and led to an HHV of approximately 39 MJ/kg. It was observed that with the increase in hydrocarbon content, both efficiencies steadily raised and reached their highest values (94 and 25.5%, respectively) in the 1:1/0.5:1 experimental run. Despite resulting in the second-highest hydrocarbon percentage of 92, the more significant liquid production of 57% established compensation and resulted in more energy density, which determined the energy efficiency of the process. Test 1:1/1:1 led to the hydrocarbon generation and the liquid yield of 93 and 53%, respectively. This resulted in the second-best values regarding the recovery energy and the overall energy efficiency parameters.

Regarding the bio-oil energy content, it is possible to affirm that the energy varies according to the hydrocarbon content (directly affecting the HHV) and the liquid formation. Overall, improved bio-oil quality at high CB_M ratios can compensate for the loss of the liquid yield. Borges et al. (2014) performed *Chlorella sp.* algae pyrolysis and reached an energy recovery of 87%. Their results and the present study's accomplishments indicate the satisfactory efficiency of a microwave process. In contrast, Cai et al. (2016) only achieved 27.1% of energy recovery and 3.8% of overall energy efficiency through the conventional pyrolysis of rice husks. Suntivarakorn et al. (2018) also studied conventional pyrolysis using Napier grass as biomass. Their findings on ER_M and $\eta M_{overall}$ were 24.88 and 16.12%, respectively.

In addition, along with the energy distribution, the upgrading factor (U_M) follows the tendency of the bio-oil energy density. In other words, the U_M factor went from 1.17 to 1.36 as the bio-oil energy content increased in the above-considered tests, as the liquid is the most significant energy carrier compared to char and gas fractions. This study intentionally pursued the rise in liquid yield and its hydrocarbon contents to make the most of the used fine biomass. The U_M values greater than 1 for MACFP indicate that the biomass energy and the electricity used in the process were successfully stored as a liquid fuel. Unquestionably, the U_M factor depends on the biomass and the pyrolytic operational conditions since different materials and processes entail enthalpy and kinetics changes, which affect heat transfer and mass transport, resulting in different product and energy distributions. Nevertheless, the capability to store distinct types of energy as a liquid energy carrier presents a commercial interest since liquid biofuels can be more easily stored and transported. Envision that the electricity supplied to the microwave may come from a renewable source such as wind or solar energy. This can have an even greater environmental appeal in the search for alternatives to fossil fuels (Liu et al., 2023).

7.2. Conclusions

In this study, composite catalysts of HTC and ZSM-5 coatings on SiC foam supports were developed for *ex-situ* catalytic upgrading of the pyrolytic vapors, and microwave-assisted pyrolysis of *Schizochytrium limacinum* microalgae was conducted in a novel catalytic bed of NiHTC/SiC followed by NiHZSM-5/SiC for biofuel production. In summary, the tandem catalytic bed showed an excellent performance in improving hydrocarbon generation, reaching around 93% at the optimized condition. In this process, deacidification and denitrification reactions led to a more significant generation of intermediate compounds such as ketones and alcohols. These compounds were then transformed into hydrocarbons, and the benzene content soared from 30% in the non-catalytic control to the utmost 78% in the test that used 1:1 and 1:1 ratios. The catalytic bed exhibited a decline in activity after the second consecutive run. Nevertheless, the regeneration process was successfully carried out, and after seven reaction-regeneration cycles, the catalyst composites displayed nearly identical hydrocarbon formation. This finding suggests that the reuse of the catalyst could contribute to reducing operational costs in the pyrolysis process. The system's energy consumption findings showed a maximum energy recovery and overall energy efficiency

of 25.5% and 94%, respectively. The upgrading value remained between 17 to 36% over that of the feedstock depending on the bio-oil yield and composition, which indicates that the energy derived from biomass was effectively stored as a liquid fuel, highlighting the success of the process.

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CHAPTER 8

8. CONCLUSIONS

This thesis focused on strategies to optimize hydrocarbon generation and the energy density in the liquid phase of the pyrolytic products of the *Schizochytrium limacinum* microalgae. Thus, three types of pyrolysis were performed under different temperatures and distinct catalysts' ratios in a dual-catalytic bed of NiHTC followed by NiHZSM-5. Below, the key conclusions are summarized.

Firstly, the *Schizochytrium limacinum* presented satisfactory characteristics for liquid and possible hydrocarbon formation, such as a high content of volatiles, carbohydrates, and lipids, approximately 90, 50, and 20%, respectively. These data are correlated to the high C content (56.3%) and low N (2.7%), and O (21.5%), which can lead to more aromatic and olefin production. The *Schizochytrium limacinum* chemical composition was the main reason this material was chosen to be pyrolyzed in this study. The catalysts' features showed well-known HTC and zeolite characteristics, which agrees with other research studies. As indicated by the XRD and XRF results, the nickel impregnation was successfully applied for both catalysts. NiHTC and NiHZSM-5 presented approximately 10 wt.% de NiO that was highly dispersed as designed by the author of this study.

Secondly, the pyrolysis experiments were conducted and revealed that: (1) in analytical pyrolysis the double catalytic bed and reaction temperature substantially impacted pyrolysis products. Notably, a significant rise in hydrocarbon, ranging from 80 to 89%, was observed when reactions were conducted at the highest tested temperature (650°C) with a catalyst ratio of NiHTC:NiHZSM-5 at 1:1. Remarkably, setting the overall catalyst-to-biomass ratio at 5:1 resulted in an impressive 89% hydrocarbon generation, accompanied by an aromatization level of around 70%. The precipitation method of the hydrotalcite catalyst generated fewer desirable compounds, seemingly impeding deacidification reactions. The reduction and passivation employed as a pre-treatment showed a slight reduction in aromatics production, leading to a higher proportion of alkenes, which increased by approximately 20%. (2) in the solar pyrolysis, the higher temperature of 750°C and the NiHTC/(NiHTC+NiHZSM-5) of 0.50 resulted in more liquid and hydrocarbon

generation, which reached 47 and 53%, respectively. When the ratio of total catalyst to biomass was 4:1, the generation of hydrocarbons went to 75%, a condition that also led to an aromatization of approximately 80%. This experimental condition resulted in higher energy recovery efficiency (ER_S) of 65%. These data represent about 95% less CO_2 eq emissions as regards fossil crude oil usage since microalgae are considered renewable biomass, and the heating power also comes from a renewable energy source. (3) in microwave-assisted pyrolysis, the liquid and hydrocarbon formation, especially benzene, reached 57 and 90%, respectively, under $500^\circ C$ and $NiHTC/(NiHTC+NiHZSM-5)$ of 0.50. The energy recovery for the microwave ranged from about 70 to 95% and indicated a satisfactory efficiency of the microwave process. For both processes, the dual-catalytic bed improved hydrocarbon content, reaching the best results when compared with non-catalytic control and experimental conditions that used only one catalyst. The NiHTC most likely benefited the deacidification and denitrification reactions, leading to a more significant generation of intermediate compounds such as ketones and alcohols. These compounds were then transformed into hydrocarbons by the NiHZSM-5. The nickel impregnation can moderate the acid sites and lead to less coke formation, besides creating additional transport channels that assist hydrocarbon formation by cracking heavy fractions. Overall, the feedstock conversion indicated that the biomass energy was successfully stored as a liquid fuel.

From my point of view, there remains a journey ahead in the process of scaling up pyrolysis with solar/microwave heating as the energy source. Nonetheless, there has been progress in understanding the pyrolysis reaction and the resultant product formation, which holds the potential for optimizing bio-oil production. This knowledge development should be seen with optimism and eager eyes as a sustainable future continues to be pursued.

CHAPTER 9

9. RECOMMENDATIONS FOR FUTURE WORK

This chapter presents suggestions for future work.

9.1. Suggestions for future work

To improve the thermochemical processes studied in this paper, some suggestions for future work are presented:

- Optimization of the solar unit reactor's insulation to improve the unit's performance in the formation of hydrocarbons.
- Use of molten salts to heat the pyrolysis reactor, thus enabling the optimization in heat transfer.
- Continuous pyrolysis process on larger scales.
- Detailed study of the influence of microwaves and sunlight on the composition of bio-oil.
- Adapt the microwave unit to receive electricity from a renewable source such as solar or wind to improve CO₂ mitigation.
- Use the SiC foams to structure the catalysts and optimize the liquid phase in solar pyrolysis.
- Estimate bio-oil production costs on larger scales (even if theoretical, making a conceptual scale-up, modeling)
- Life cycle assessment study of bio-oil in a possible partnership with Embrapa-Meio Ambiente.

APPENDIX A - ANALYTICAL PYROLYSIS CHROMATOGRAM

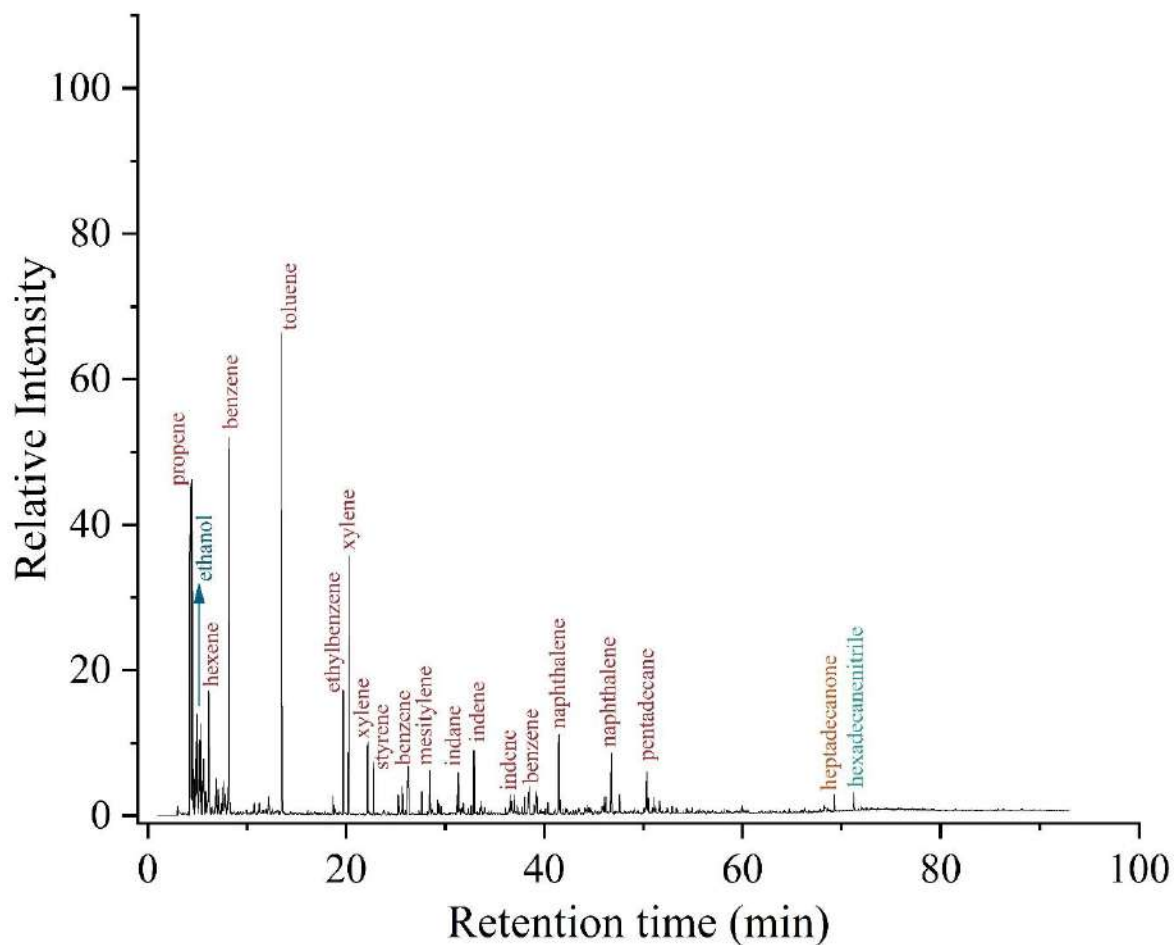


Fig. A. Chromatogram for the analytical pyrolysis of *S. Limacinum* in a tandem catalytic bed. Test performed at 650°C, NiHTC:NiHZSM-5 catalysts ratio of 1:1, and catalyst-to-biomass ratio of 5:1.

APPENDIX B - MAIN COMPOUNDS IDENTIFIED IN SOLAR PYROLYSIS

Table B. Part I - Main compounds identified in solar pyrolysis of *S. Limacinum* in a tandem catalytic bed at 750 °C (NiHTC:NiHZSM-5 catalysts ratio of 1:1, and catalyst-to-biomass ratio of 4:1).

Retention time (min)	Compound	Chemical structure
4.406	Propene	C ₃ H ₆
4.586	Bicyclobutane	C ₄ H ₆
4.886	1-Pentene	C ₅ H ₁₀
4.973	2-Methyl-1-butene	C ₅ H ₁₀
5.075	1,3-Pentadiene	C ₅ H ₈
5.447	1,3-Cyclopentadiene	C ₅ H ₆
5.655	Acetone	C ₃ H ₆ O
5.734	1-Pentene, 2-methyl	C ₆ H ₁₂
6.228	Acetonitrile	C ₂ H ₃ N
6.586	2,4-Hexadiene	C ₆ H ₁₀
7.045	1,3,5-Hexatriene	C ₆ H ₈
7.600	2-Butanone	C ₄ H ₈ O
7.788	Cyclopentane, 1,2-dimethyl	C ₇ H ₁₄
8.276	Benzene	C ₆ H ₆
12.322	Heptane, 2,4-dimethyl	C ₉ H ₂₀
12.434	1-Octene	C ₈ H ₁₆
13.610	Toluene	C ₇ H ₈
18.780	E,Z-3-Ethylidenecyclohexene	C ₈ H ₁₂
18.961	1-Nonene	C ₉ H ₁₈
19.800	Ethylbenzene	C ₈ H ₁₀
22.267	p-Xylene	C ₈ H ₁₀
22.866	Styrene	C ₈ H ₈
25.462	1-Decene	C ₁₀ H ₂₀
25.750	Benzene, propyl	C ₉ H ₁₂
27.697	Benzene, 1-ethyl-2-methyl	C ₉ H ₁₂
31.242	Undecane	C ₁₁ H ₂₄
31.384	Cyclopropane, nonyl	C ₁₂ H ₂₄
32.957	Indene	C ₉ H ₈
36.602	Dodecane	C ₁₂ H ₂₆
36.748	1-Dodecanol	C ₁₂ H ₂₆ O
38.005	Phenol	C ₆ H ₆ O
39.306	Naphthalene	C ₁₀ H ₈

Table B. Part II - Main compounds identified in solar pyrolysis of *S. Limacinum* in a tandem catalytic bed at 750 °C (NiHTC:NiHZSM-5 catalysts ratio of 1:1, and catalyst-to-biomass ratio of 4:1).

Retention time (min)	Compound	Chemical structure
41.519	Tridecane	C ₁₃ H ₂₈
42.155	p-Cresol	C ₇ H ₈ O
46.102	Tetradecane	C ₁₄ H ₃₀
46.266	1-Tetradecene	C ₁₄ H ₂₈
50.393	Heptadecane	C ₁₇ H ₃₆
50.559	1-Heptadecene	C ₁₇ H ₃₄
54.608	2-Pentadecanone	C ₁₅ H ₃₀ O
60.250	Tetradecanoic acid	C ₁₄ H ₂₈ O ₂
62.071	Palmitic Acid	C ₁₆ H ₃₂ O ₂
63.472	Pentadecanoic acid	C ₁₅ H ₃₀ O ₂
69.328	Heptadecanenitrile	C ₁₇ H ₃₃ N
73.716	Octadecanoic acid	C ₁₈ H ₃₆ O ₂
85.831	Hexadecanamide	C ₁₆ H ₃₃ NO

APPENDIX C - MAIN COMPOUNDS IDENTIFIED IN MICROWAVE PYROLYSIS

Table C. Main compounds identified in microwave pyrolysis of *S. Limacinum* in a tandem catalytic bed at 500 °C (NiHTC:NiHZSM-5 catalysts ratio of 1:1, and catalyst-to-biomass ratio of 0.5:1).

Retention time (min)	Compound	Chemical structure
5.244	Ethylbenzene	C ₈ H ₁₀
5.426	Benzene, 1,3-dimethyl	C ₈ H ₁₀
5.943	Cyclopentene, 1-ethenyl-3-methylene	C ₈ H ₁₂
6.077	Nonane	C ₉ H ₂₀
7.487	Benzene, propyl	C ₉ H ₁₂
8.204	Benzene, 1-ethyl-2-methyl	C ₉ H ₁₂
8.460	Phenol	C ₆ H ₆ O
8.597	Benzene, 1,2,3-trimethyl	C ₉ H ₁₂
9.356	1H-Pyrrole, 2,3,5-trimethyl	C ₇ H ₁₁ N
9.519	Benzene, 1-ethenyl-3-methyl	C ₉ H ₁₂
9.778	Indane	C ₉ H ₁₀
10.040	Indene	C ₉ H ₈
10.239	Benzene, 1-methyl-3-propyl	C ₁₀ H ₁₄
10.370	Benzenepropanol	C ₉ H ₁₂ O
10.531	Phenol, 2-methyl	C ₇ H ₈ O
11.242	Benzene, 2-butenyl	C ₁₀ H ₁₄
11.649	Undecane	C ₁₁ H ₂₄
12.402	Benzene, 2-methyl-1-propenyl	C ₁₀ H ₁₂
13.303	Tetrahydrocyclopropaindene	C ₁₀ H ₁₀
13.529	Naphthalene, 1,2-dihydro	C ₁₀ H ₁₀
14.124	Naphthalene	C ₁₀ H ₈
14.374	Benzene, 1-ethyl-1-propenyl	C ₁₁ H ₁₄
14.561	Dodecane	C ₁₂ H ₂₆
16.043	2-Ethyl-1-H-indene	C ₁₁ H ₁₂
16.554	1H-Indene, 2,3-dimethyl	C ₁₁ H ₁₂
17.254	Naphthalene, 1-methyl	C ₁₁ H ₁₀
17.378	Tridecane	C ₁₃ H ₂₈
17.715	Naphthalene, 2-methyl	C ₁₁ H ₁₀
20.038	Tetradecane	C ₁₄ H ₃₀
22.340	2-Naphthaleneethanol	C ₁₂ H ₁₂ O
22.596	Pentadecane	C ₁₅ H ₃₂
24.940	Hexadecane	C ₁₆ H ₃₄
29.373	Pentadecanenitrile	C ₁₅ H ₂₉ N
33.514	Heptadecanenitrile	C ₁₇ H ₃₃ N