Enhanced Bio-Oil Production from *Nannochloropsis* Algae *via* Catalytic Liquefaction: Synthesis and Application of Iron-based Magnetically Recoverable Catalysts

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Magnetically recoverable iron-based catalysts were developed, with the goal of being cost-effective, reusable, and environmentally friendly. The use of iron-based magnetically recoverable catalyst enhances the catalytic process efficiency for the enhanced bio-oil yield and quality compared to non-catalytic and conventional catalytic methods. The present study aimed to evaluate the hydrothermal liquefaction (HTL) of *Nannochloropsis* sp. in the presence of Fe_3O_4 nanostructures for enhanced bio-oil production. The use of a magnetic-supported catalyst that is low-cost, safe, and can be reused many times without requiring a regeneration step (by retrieving it magnetically from the solid material) can serve as a novel strategy to be used at an industrial scale. The maximum bio-oil yield 31.4% was obtained with a Fe_3O_4 catalyst dosage of 0.3 g at temperatures of 300 °C and biomass to solvent ratio of 100 g/L, respectively. The compositional analysis of the produced bio-oil was performed and showed notable characteristics for biofuel application. The synthesized Fe_3O_4 catalyst was recyclable for up to five repeated cycles and a fluctuated bio yield was achieved for the last three cycles of procreation capability for HTL of *Nannochloropsis* sp. Further improvisation in designing the next generation magnetically recoverable catalyst with improved stability, efficiency will pay wave way for cost–effective and scalable bio-oil production systems.

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INTRODUCTION

For many years, the energy demands of the globe have been met by conventional fossil fuels such as coal and petroleum. Global population growth and urbanization are contributing to the ongoing depletion of fossil resources (Zhang *et al.* 2022). To lessen the usage of fossil fuels, researchers have looked at several different renewable biomass sources (Pandit *et al.* 2017). In recent decades, the atmosphere has experienced increased emissions of greenhouse gas due to the exhaustion of fossil fuels. Bhutto *et al.* (2016) predicts an approximate 80% surge in energy demand by 2030 due to modernization. Consequently, bioenergy has emerged as a promising solution to address current and future global energy needs (Gundupalli and Bhattacharyya 2021). Researchers worldwide are exploring various methods to harness valuable bioenergy from a range of biomass sources, including algal biomass (Prestigiacomo *et al.* 2019; Venkatachalam *et al.* 2023), agricultural resources (Zhang *et al.* 2023), and sludge (Ellersdorfer 2020; Zhang *et al.* 2023).

Biomass is an efficient and sustainable alternative energy source. A variety of biomasses, including wood biomass, sludge, microalgae, and macroalgae, can be used to produce biofuels as bioenergy. The three liquid biofuels that are most frequently created by researchers worldwide are bio-ethanol, biodiesel, and bio-oil (Ni *et al.* 2022; Fan *et al.* 2023). Liquid biofuels, especially ethanol and methanol, have significantly higher-octane number (~108 to 113) while compared to fossil-based gasolines octane number (~91 to 98), which helps the biofuel to be more efficient in high performance engines, where they exhibit smoother combustion with reduced knocking. Likewise, biodiesel and renewable diesel have higher cetane number (~75 to 85) compared to the conventional diesel cetane number (~40 to 55), which ensures better ignition performance, reduced engine noise, and smooth operations (Husam AI *et al*. 2017). Liquid biofuels have significantly less sulfur content (<10 ppm) in comparison to fossil fuels (~15 to 500 ppm), which means that they are more environmentally friendly. Therefore, compared to current fossil fuels, liquid biofuels have a higher octane/cetane number, a lower sulfur content, and may be used in engines already in use with little to no modification. When turned into biofuels, microalgae are an environmentally friendly biomass that lower carbon dioxide (CO_2) emissions compared to fossil-derived fuels. Microalgae cultivation is considered to be cost-effective, as recent studies have witnessed that the production costs of microalgae-based biofuels, while higher than conventional diesel (approximately $0.72/liter), are repeatedly decreasing with advances in technology and economics of scale, competitiveness with fossil fuels in certain regions (Rafa *et al.* 2021). Furthermore, microalgae require minimal amount of land resources. For instance, a suitable facility built on non-arable land with an area as small as 1 hectare can yield up to 25000 liters of bio-oil annually under optimized conditions (Nayana *et al.* 2023). Additionally, microalgae can utilize the organic contaminants in wastewater as nutrients, which further enhances their economic and environmental sustainability. These factors highlight the potential of microalgae biofuels, which can be a substitute for conventional fossil fuels. CO_2 is drawn from the atmosphere by microalgae and transformed into useful bioenergy products. Produced from microalgae biomass, the recommended biofuels are bio-ethanol, biodiesel, and bio-oil (Naumann *et al.* 2013). Moreover, algae offer several other benefits, such as high lipid productivity, quick development, high photosynthetic efficiency, accurate yield, and minimal land usage. Microalgae has significantly higher lipid content of about 20 to 50% compared to conventional biomass sources such as soybeans (20%), palm oil (30 to 50%. This makes microalgae especially advantageous for biofuel production. Microalgae have a faster growth cycle compared to other biomass sources such as corn and sugarcane which requires more than a month to grow. Microalgae also have a higher photosynthetic efficiency of around 6 to 8% which is higher than terrestrial plants such as corn, sugarcane, *etc.* Microalgae can be grown in non-aerable land, wastewater, unlike crops like soy, sugarcane, or corn that require fertile agricultural land. In this way, reliance on microalgae can reduce the competition with food production and minimizes the environmental impact of land use. Upon comparison of this microalgae and other biomass sources, the microalgae take more advantages with respect to sustainability, productivity, and scalability (Wang *et al.* 2023). The problem of eutrophication contamination in water can also be resolved by the usage of algae, which are able to reduce the nutrient pollution, sequester carbon dioxide, reduce overall greenhouse gas emissions, prevent harmful algal blooms, and restore the aquatic ecosystem (Basar *et al.* 2021; Naaz *et al.* 2023).

The two primary components of algal biomass are lipid and protein. Microalgal biomass is more suited for biofuel than lignocellulose materials due to its high caloric value, low viscosity, and low density when compared to plant biofuel (Xia *et al.* 2022).

Microalgae can be grown on non-arable land and wastewater, it is a sustainable and renewable energy source that lessens competition for resources with food production (Beuckels *et al.* 2015). Second, because bio-oil made from microalgae has a high energy density of about 30 to 40 MJ/kg while compared to the crude oil energy density of about 42 to 45 MJ/kg, it can be used in place of fossil fuels in a variety of applications, such as power generation and transportation. This microalgal bio-oil has the potential to become a competitive and sustainable alternative to conventional crude oil. In addition, compared to traditional fossil fuels, bio-oil has a smaller carbon footprint, which helps to cut greenhouse gas emissions (De Caprariis *et al.* 2017; Arun *et al.* 2018).

Microalgae are photosynthetic organisms. Examples include *Nannochloropsis* sp., *Chlorella* sp., and *Botryococcus* sp., which holds a high amount of lipid content that can act as a feedstock for biofuel applications (Xu *et al.* 2018; Prestigiacomo *et al.* 2019). The hydrothermal liquefaction process tends to be a thermochemical liquefaction process that helps to extract the bio-oil from the algal biomass (Bo Zhang *et al.* 2018; (Mukundan *et al.* 2023). In the hydrothermal liquefaction process, the biomass is heated at a higher temperature (250 to 400 °C) and high pressure (10 to 25 MPa) in a closed reactor. The liquefaction process becomes more effective when a recoverable catalyst is used to facilitate the process of breaking down of complex organic compounds present in the microalgae. The liquefaction process tends to facilitate the process of depolymerization and deoxygenation of biomass and produce the bio-oil (Arun *et al.* 2020a). Through the process of magnetic separation techniques, the catalyst used during the liquefaction process can be recovered from the produced bio-oil, which in turn lowers the cost of the catalyst. To maximize the bio-oil yield from the algal biomass, the process conditions, such as temperature, residence time, and pressure, need to be optimized (Brown *et al.* 2010; Younas *et al.* 2017). The hydrothermal liquefaction of microalgae using magnetically recoverable catalyst for the production of bio-oil from the microalgae biomass was found to be a sustainable and promising resource utilization technique (Ding *et al.* 2019; Vickram *et al.* 2023). The use of magnetically recoverable catalysts are reusability, efficient recovery, and high catalytic performance by making them ideal for bio-oil production and its upgrading. This approach has potential to significantly improvise the economic and environmental viability of bio-oil as a renewable energy source, which ends up in circular energy systems. This hydrothermal liquefaction process was found to be a suitable and environmentally friendly technique for future developments. In the present study, the microalgae *Nannochloropsis sp* were examined for enhanced bio-oil production through catalytic liquefaction process using iron-based magnetically recoverable catalyst in the hydrothermal reactor. The iron based magnetically recoverable catalyst was synthesized using FeOx *via* simple wetness impregnation technique, and characterized and subjected to bio-oil production from *Nannochloropsis sp*.

EXPERIMENTAL

Algae Cultivation and Biomass Generation

The microalgae *Nannochloropsis* sp. biomass was chosen to cultivate in the photobioreactor having the white light intensity of about 200 W/m^2. The growth of the microalgae biomass was measured at 680 nm using UV spectrophotometer (Mettler Toledo model UV5, Switzerland). The cultivated biomass from the photobioreactors (PBRs) was separated using a settling process. The biomass along with the medium was poured into a separating funnel and allowed to settle for 8 to 9 h based on density. The *Nannochloropsis* sp. biomass collected from the separating funnel was dried at 105 °C for 3 h to remove excess of moisture.

Biomass Characterization

The recovered algae samples were dried for 24 h at 105 °C after being ground and sieved to a particle size of less than 60 µm. The proximate analysis of the dried biomass includes moisture, ash, volatile compounds, and fixed carbon contents were analyzed as per ASTM D3174-89 (Mythili *et al.* 2013). The CHNS analyzer (Perkin-Elmer 2400 series CHNS analyzer) was used to determine the Elemental analysis (Carbon, Hydrogen, Nitrogen, and Sulfur) of dried biomass. The elemental analysis of the dried biomass were estimated before the liquefaction experiment (Arun *et al.* 2021). The pyrolytic behavior of *Nannochloropsis* sp. biomass was estimated using a thermogravimetric analyzer (TGA; model TGA Q500 V6.7Build 203) under a nitrogen environment. The higher heating value of biomass depends upon the moisture content of the biomass. Increase in moisture content decreases the HHV value (Demirbas *et al.* 2007). The Higher Heating Value (HHV) was calculated using Eq. 1.

$$HHV\left(\frac{MJ}{Kg}\right) = 0.338 * C + 1.428 * (H - O/8) \quad (1)$$

Catalyst Synthesis and Characterization

The Fe oxide-supported activated carbon catalysts (FeOx/C) were prepared by simple wetness impregnation technique and had an active metal loading of 7.5 wt%. The activated carbon support was heated up for a whole night at 70 °C to dry it out before usage. The dried activated carbon support was filled with the appropriate volume of the Fe precursor of aqueous solution, and it was agitated for 8 h at room temperature. After that, water was extracted using a rotary evaporator at 50 °C. Then heat treated for 5 h at 550 °C in a tube furnace with a 30 mL min^{-1} of N_2 flow and dried for an additional night at 100 °C. The prepared catalyst was analyzed *via* scanning electron microscopy (SEM) (Hitachi S-3400 model, Tokyo, Japan) and Brunauer-Emmett-Teller (BET) surface area analysis (Arun *et al.* 2020b; Cronmiller *et al.* 2023).

Catalytic Liquefaction Experiments

The hydrothermal liquefaction reactions (HTL) were conducted in a stainless-steel closed Parr reactor with a capacity of 5 L at a varying temperature of 240 to 340 °C after reaching the set-point temperature for 1 h under nitrogen environment (20 bar). Algal biomass (25 g to 125 g /L dry weight) and deionized water as a solvent (1 L) were added to the reactor to be able to evaluate the effect of solvent-to-biomass ratio on bio-oil yield. Meanwhile, 0.1 to 0.5 wt% of FeO_x/C was used in the catalyst studies. Figure 1 highlights the workflow of bio-oil production process from microalgae biomass. The catalysts were employed directly from the synthesized state, without undergoing the conventional reduction process. As soon as the reaction was complete, the reactor was allowed to cool down for product recovery.

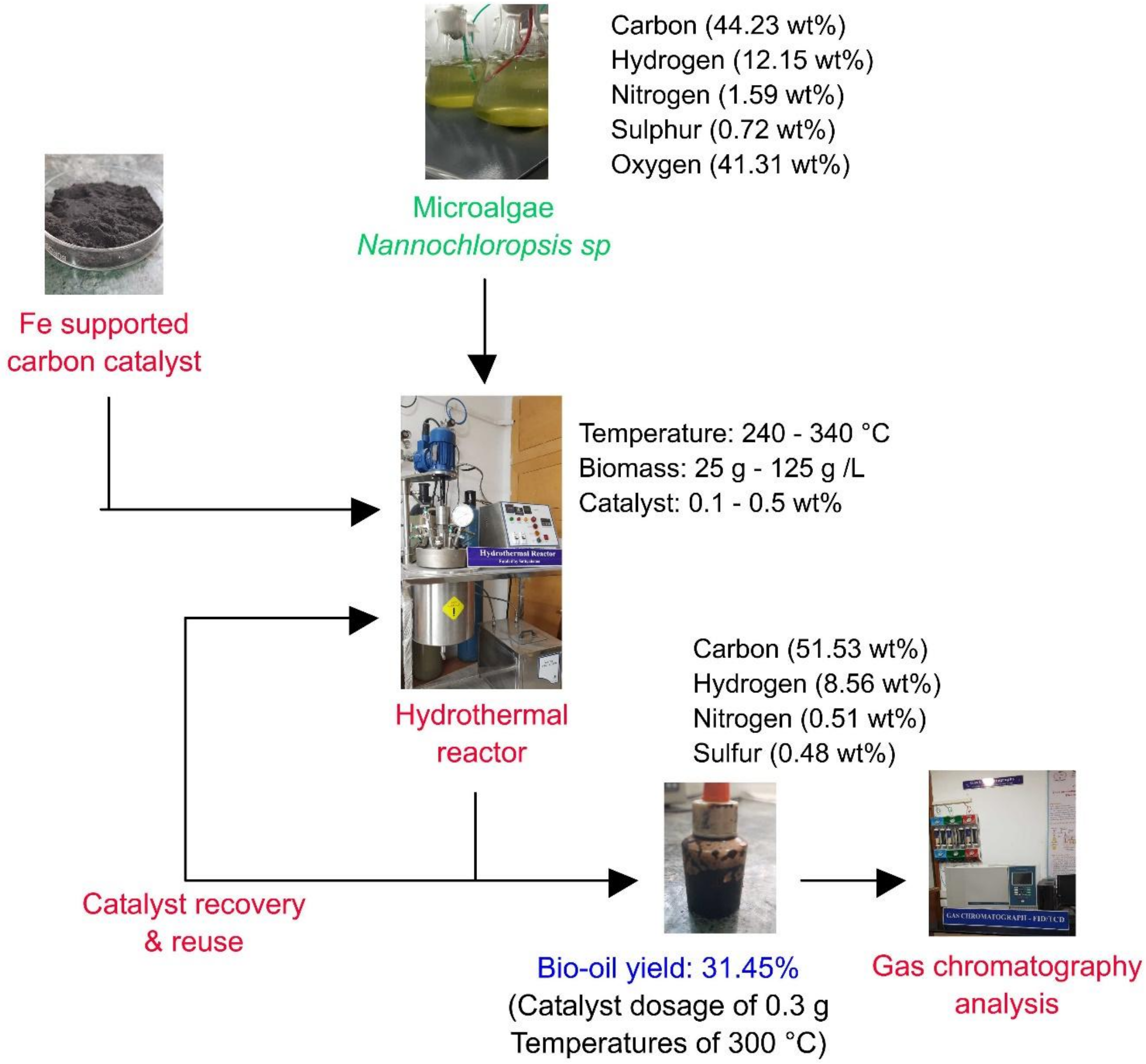

Fig. 1. Experimental flow of bio-oil production from Hydrothermal process from microalgae biomass

HTL Products Recovery and Analysis

The gas phase from the reactor was collected from the exhaust valve using airtight bags. It was subjected to gas compositional analysis to determine the different gas products distributed in it. Highly viscous dark brown slurry was recovered from the flush valve and subjected to liquid-liquid extraction process. An equal amount of dichloromethane (DCM) was added as solvent. The mixture was stirred vigorously and allowed to settle down in a separating funnel for phase separation. Three different products (solid residue, aqueous phase, and organic phase) were collected from the separating funnel. The unreacted DCM solvent was removed using a rotary evaporator at a temperature of 45 °C. Bio-oil and gas phase yields are estimated as per Eqs. (2 and 3):

$$Bio - oil\ yield\ (wt\%) = \frac{Mass\ of\ bio{-}oil\ (g)}{Mass\ of\ biomass\ (g)} \times 100 \tag{2}$$

$$Gas\ phase\ yield\ (wt\%) = 100 - (Bio - oil + Aqueous\ phase + Biochar) \tag{3}$$

Catalyst Recovery Studies

Recovery of the catalyst was done with the components first suspended in DCM, then extensively agitated using a vortex (Grant instrument PV-1), and centrifuged at 3000 RPM to recover the catalysts. After separating the supernatant, the particles were re-suspended in deionized water and oven-dried for an hour at 70 °C. The catalyst was then recovered using a magnetic bar. Before being utilized for the reusability tests, the recovered catalyst was dried for an entire night at 70 °C. For repeatability investigations, the recovered catalyst was used for other HTL experiments. However, the authors need to address the few inevitable losses incurred during catalyst filtering and recovery.

Gas Chromatography-Flame Ionization Detector analysis

A SPB-1 column (30 × 0.25 × 0.25) and a YL Clarity 6500 were used to evaluate components present in the bio-oil produced from HTL (Nagappan *et al.* 2021). Using a split ratio of 50.0, the injection temperature was 220 °C. Following a 5-min hold at 50 °C, the temperature was ramped up to 250 °C at a rate of 15 °C min^{-1}, held for 1 min, and then elevated to 300 °C at a rate of 5 °C min^{-1}, and held for 1 min.

RESULTS AND DISCUSSION

Algae Biomass Growth Profile

The growth profile of microalgal biomass in the photobioreactor is shown in Figure 2. Growing the microalgae at closed culture conditions plays a vital role in growth curve and population growth (Naumann *et al.* 2013). Figure 2 illustrates the growth of the microalgae population for a period of 20 days and the resulting biomass yield (g/L). The biomass concentration began to increase from 0.5 to 1.49 g/L during the adaptation period, day 10. The concentration of the biomass seemed to increase gradually due to the lack of adaptation of the biomass to the newly provided environment. During the course of growth period, the biomass tends to utilize the nutrients provided for their growth and multiply themselves to the maximum, which is evident from the biomass concentration increase from 1.49 to 1.91 g/L. Similar biomass growth curve studies have been carried out on the *Chlorella vulgaris* sp. and reported by Minh *et al.* (2021) and Bajwa *et al.* (2017).

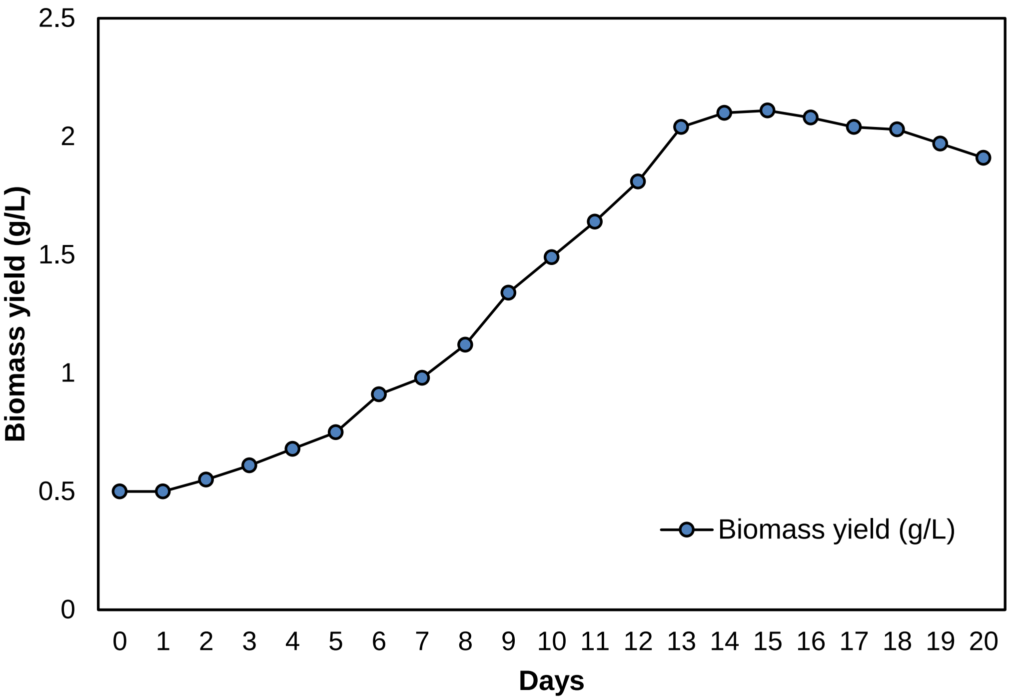

Fig. 2. Growth rate profile of *Nannochloropsis* sp. biomass cultivated in photo bioreactor

Algae Biomass Recovery

Similar growth conditions were followed for the microalgal cultures throughout all the studies (Tandon and Jin 2017). These conditions included room temperature and exposure to white light of 200 W/m^2. The suspended culture was run on a 12/12 h dark/light cycle, similar to the biofilm culture in the carrier test of the microalgae culture in the rotating photobioreactor portion. To monitor the biomass, the method used was to harvest the suspended biomass and concentrate it in a separation process using a gravity settling process (SIGMA, High-Speed Refrigerated Centrifuge, 3-30KS). During this period, algae cells underwent rapid division, increasing their biomass yield to a maximum of 2.11 g/L on the 15th day of the cultivation cycle. Beyond this, a slight reduction and saturation were seen in the biomass yield. This was due to the unavailability of nutrients in the medium and the penetration of light into the medium solution.

Biomass Characterization

The *Nannochloropsis* sp. biomass was harvested from the PBRs by a separation process at room temperature. The harvested biomasses were subjected to proximate and ultimate analysis as per ASTM D570-98 (2010). The moisture, ash, volatile matter, and fixed carbon of the *Nannochloropsis* sp. biomass were determined to be 14.8 wt%, 6.28 wt%, 54.3 wt%, and 24.6 wt%, respectively. The elemental analysis of biomass was determined to be Carbon (44.2 wt%), Hydrogen (12.2 wt%), Nitrogen (1.59 wt%), Sulphur (0.72 wt%), and Oxygen (41.3 wt%); the higher heating value (HHV) (24.9 MJ/kg), H/C (3.29), and O/C (0.70) of biomass were also determined. A recent study reported the proximate and ultimate analysis of *Nannochloropsis* sp., revealing a high lipid content, which is beneficial for biodiesel production. The proximate analysis indicated significant moisture, ash, volatile matter, and fixed carbon, providing insights into the biomass composition. The ultimate analysis showed substantial levels of carbon and hydrogen, essential for energy yield, while nitrogen and sulfur content were evaluated for their impact on fuel quality. Overall, the study highlighted the potential of *Nannochloropsis* sp. as a sustainable source for biofuels and nutraceutical applications. These findings support the feasibility of using microalgae in renewable energy production (Brown *et al.* 2010). The presence of a higher amount of volatile matter content in the biomass depicts the presence of biochemical components in the biomass.

Catalyst Analysis

Catalyst was supported in the food waste-based activated carbon, which has a surface area of 745 m^2/g, pore volume of 0.52 cm^3/g, and pore size of 4.81 nm. From the current study, the deposition or supporting of iron oxide into the activated carbon reduced the surface area to 586 m^2/g, pore volume of 0.42 cm^3/g, and pore size of 2.89 nm respectively. The SEM analysis of the activated carbon showed the presence of mesoporous structure for effective catalytic activity (Figure. 3). A similar kind of mesoporosity of the carbonaceous material of ZnCl activated carbon from food waste has been reported by Santhosh and Dawn (2021). Figure 4 displays the surface morphology of the synthesized catalyst under a distinct process. The result showed carbon surface was covered in an uneven layer of iron and oxygen groups. The catalyst precursor aggregated and the carbon was unevenly distributed on the carbon catalyst surface because the surface of the fibers was smooth and had low wettability to the catalyst precursor. In a study, the activated carbon prepared without a catalyst has less width and intensity than activated carbon made using a catalyst (Yassin and Abdulrazzak 2019). The elemental compositions of the aforementioned nanomaterial were determined using energy-dispersive X-ray (EDS) analysis (JEOL JSM-6330F, JEOL Ltd., Akishima, Tokyo, Japan) (Figure. 5a). They correlate to the presence of elements like C and O, in the synthesized catalyst as seen. Figure 5b demonstrates the oxygen content resulting from the iron oxide (Fe_3O_4) present in the activated carbon. The amount of carbon is observed because of the synthetic catalyst of carbon content (Figure. 5c). Similarly in a study by Derikvand and Azadbakht (2017) the EDS data of CNTs/GO/Fe_3O_4 was reported with a similar amount of carbon content.

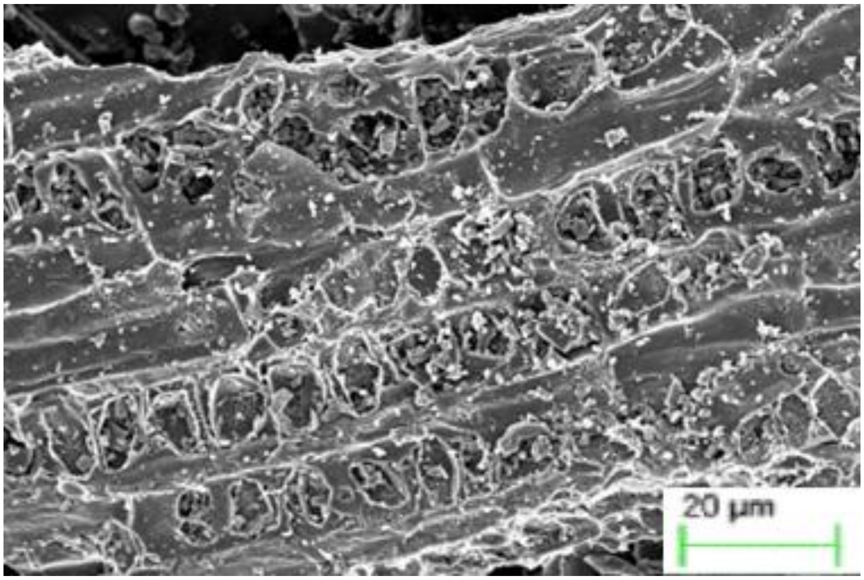

Fig. 3. Scanning electron microscopy image of synthesized activated carbon

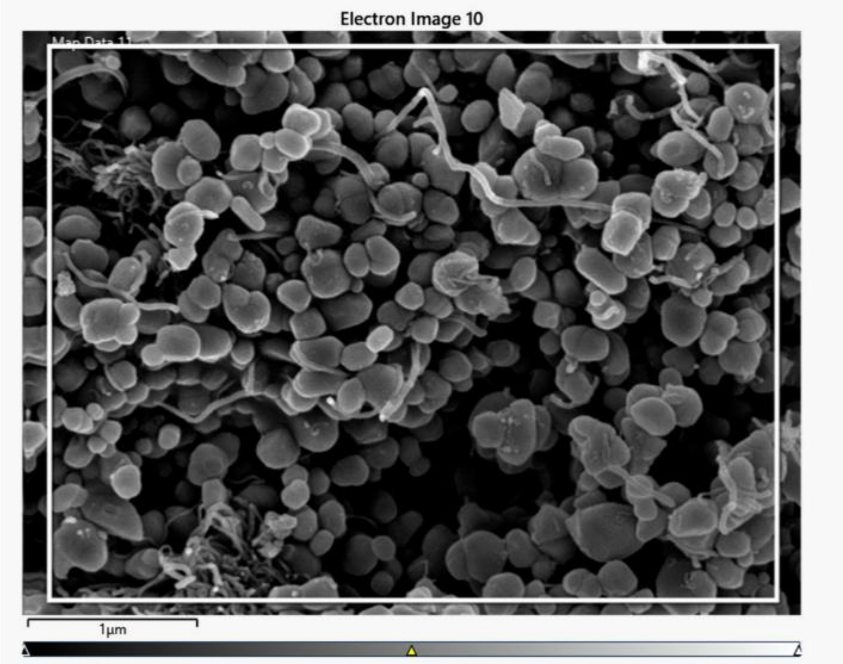

Fig. 4. Scanning electron microscopy image of synthesized catalyst

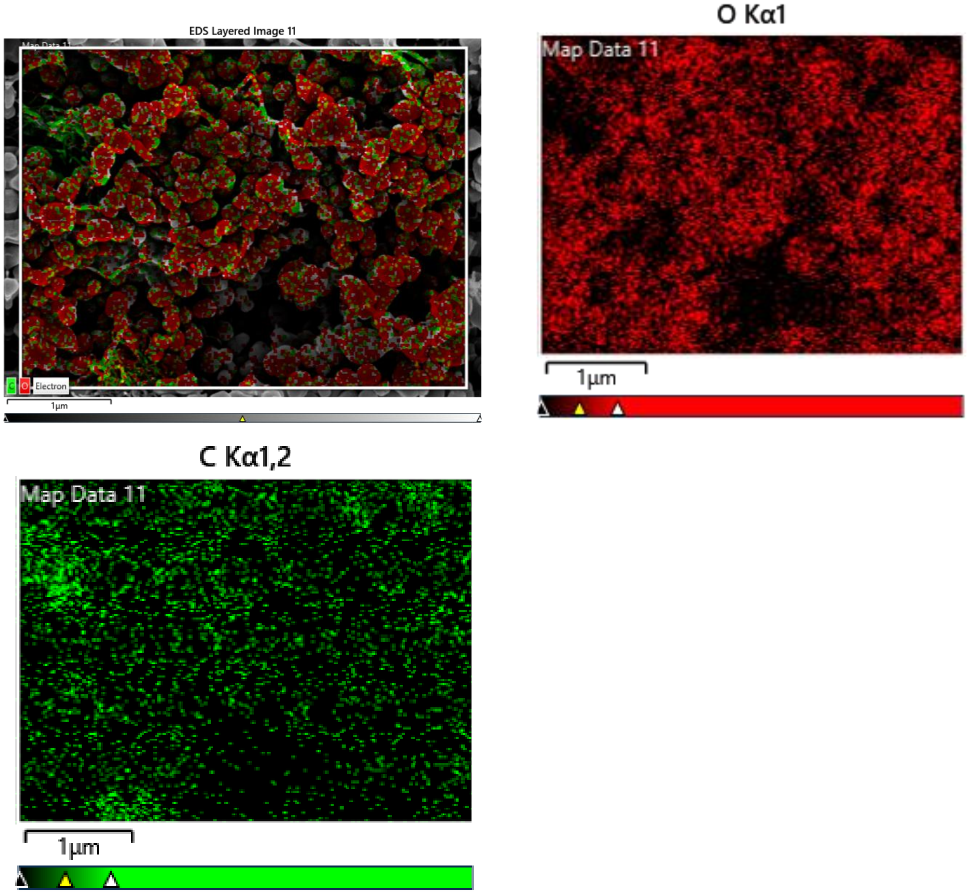

Fig. 5. a) EDS image of synthesized catalyst, b) Oxygen content of synthesized catalyst from EDS analysis, and c) Carbon content of synthesized catalyst from EDS analysis

LIQUEFACTION EXPERIMENTS

Effect of Temperature

In HTL, the quantity and quality of the products are notably influenced by temperature. Every product can have a certain ideal temperature. This section examined the bio-oil yield from the HTL process. Experiments were conducted at temperatures ranging from 240 to 340 °C for 60 min to investigate the effects of temperature on bio-oil yield. Figure 6 shows that the maximum yield (23.9%) of bio-oil was obtained at 300 °C. Additionally, biochar, gaseous phase, and aqueous phase yields were 14.1%, 34.11%, and 27.9%, respectively. A recent study on HTL of *Scenedesmus* sp. showed a bio-oil yield of 38.3% (Arun *et al.* 2020a). Decrease in bio-oil yield at higher temperature was due to the formation of gaseous products, which would have resulted from the oxidation reactions occurred within the reactor (Saber *et al.* 2018). The increase in temperature results in increased formation of gaseous products due to the conversion of low molecular weight compounds present in the bio-oil to less desirable by-products.

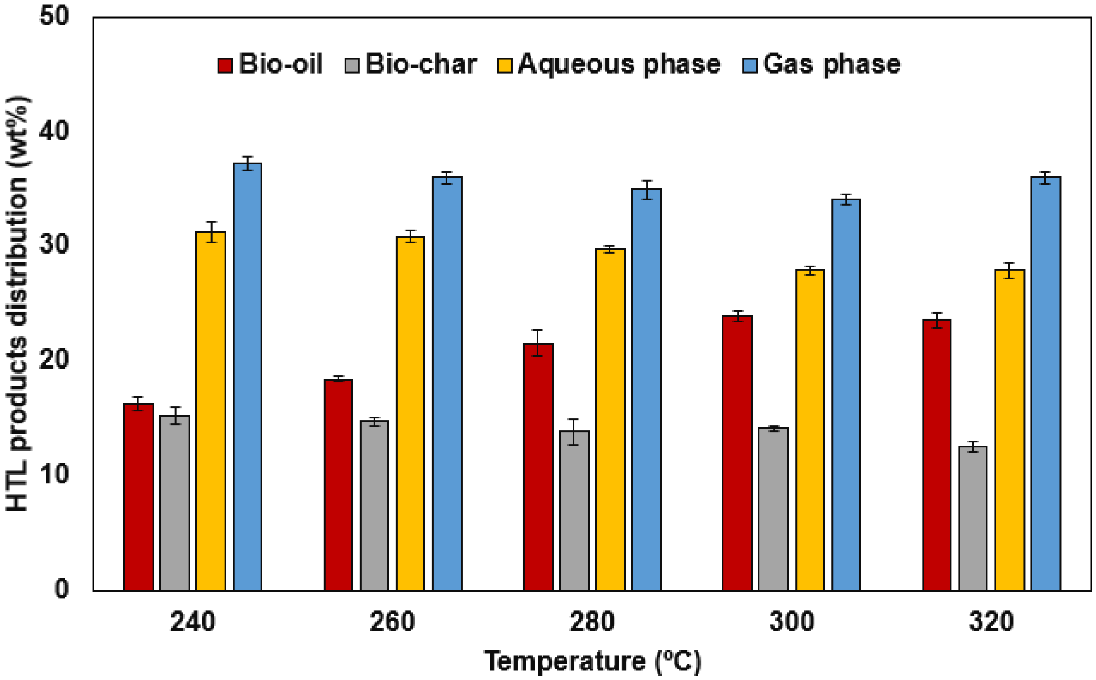

Fig. 6. Effect of temperature on HTL products distribution

Effect of Solvent to Biomass Ratio

The results illustrate the product yield of catalytic hydrothermal liquefaction that was achieved by varying the amount of microalgae biomass in relation to solvent. Because a denser solvent medium enhances extraction, using a lot of water often results in higher yields of liquids and gases. The results of experiments in this study were compiled to comprehend the effective recovery of biochar and bio-oil as products utilizing a range of biomass to solvent ratios. When compared to other compositions, the bio-oil output is higher due to the 125 g/L biomass to solvent ratio. Figure 7 depicts the maximum yield of bio-oil at 300 °C, which was 24.1 wt%. Meanwhile, gaseous product, biochar, and aqueous phase are composed of the remaining HTL byproducts under same condition, which have been found in amounts of 33.5 wt%, 12.4 wt%, and 30 wt%, respectively. According to a similar study (Yousefzadeh *et al.* 2024), the highest yield of bio-oil produced from *Nannochloropsis* sp. was 18.8 wt%. The increase in carbon content at higher solvent to biomass ratio would have been due to the unavailability of solvent system in the reaction process. This indirectly influences the formation of other HTL products to quite an extent. An optimum solvent to biomass ratio is the most crucial factor which defines the bio-oil yield since this influences the degree of biomass solubilization and effective breakdown process (Zeb *et al.* 2024).

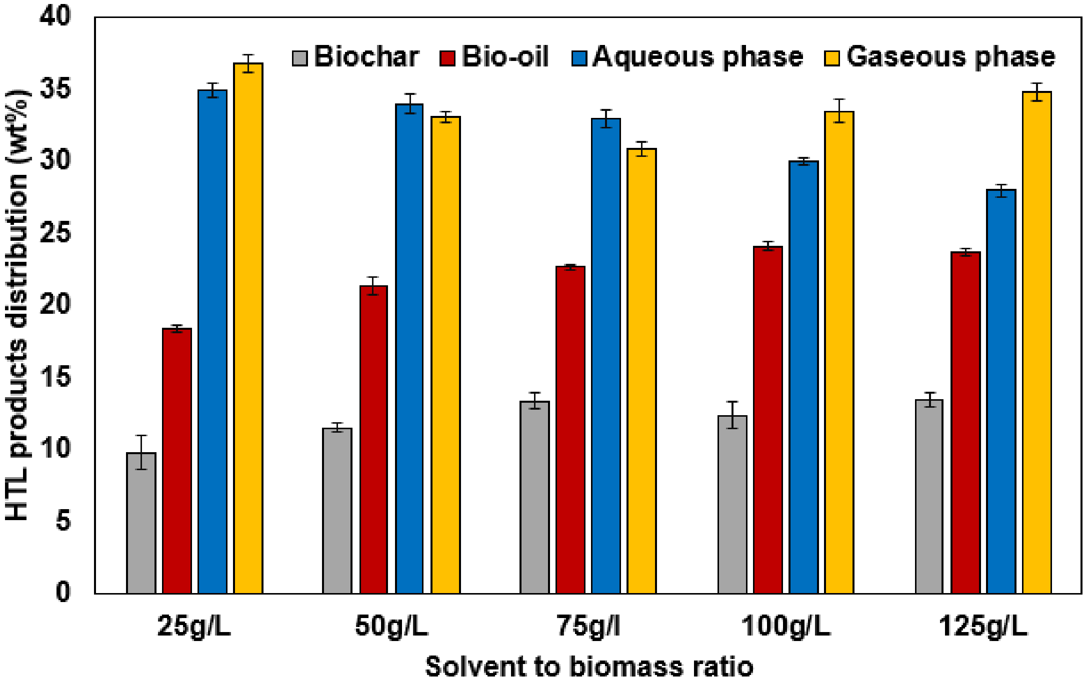

Fig. 7. Solvent to biomass on HTL products distribution

Catalyst Load on Bio-oil Yield

The effect of catalyst on bio-oil yield was investigated at 300 °C for 75 g of biomass and different catalyst loads (0.1 to 0.5 wt%). The catalyst load has a notable effect on bio-oil yield at 300 °C, as depicted in Figure. 8. The highest amount of bio-oil obtained was 31.4 wt% at a catalyst load of 0.3 wt% and further increase catalyst load decreased the production of bio-oil to 31.2 wt%. Addition of catalyst influences the bio-oil formation due to enhanced biomass breakdown and facilitating efficient depolymerization reactions (Silva *et al.* 2024). Further catalyst addition can reduce the activation energy required for chemical reactions to breakdown the complex molecules in the biomass. The decrease in bio-oil yield and increase in biochar formation at higher catalyst load was attributed to the unavailability of effective solid to biomass ratio in the reactor system. Catalyst is added mainly to increase the rate of reaction and with increasing the yield of our desired product. However, the used catalyst must have the potential to be recovered, reused, and refabricated to address the sustainable development goals (SDGs). To this extent the used catalyst was fabricated and synthesized in a way to be magnetically recovered and be reused in the further experiments. Table 1 highlights the various magnetic based catalysts used in the HTL process for bio-oil production. It can be seen that different kind of biomasses were studied in the magnetic catalytic HTL process.

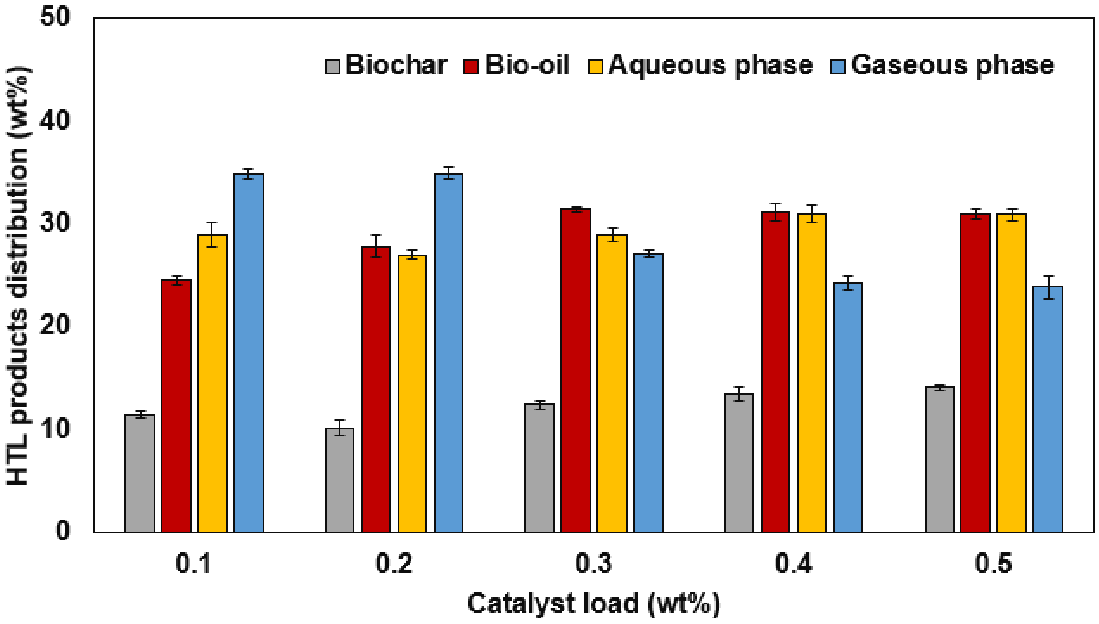

Fig. 8. Effect of catalyst load on HTL products distribution

Table 1. Comparative Literature Notes on Bio-oil Yield from HTL Studies with Magnetic Catalysts

Biomass Name	HTL Experimental Conditions (Temperature, Time, Pressure)	Bio-Oil Yield (%)	Magnetic Catalyst (dosage)	References
Rice Straw	300 °C, 120 min	30.4	NiO	(Younas *et al.* 2017)
Pine and Spruce Mix	250 °C, 105 min, 80 bar	47	Iron Oxide Nano-Catalysts (0.25g)	(Remón *et al.* 2019)
Brewers spent grains	320 °C, 60 min,	19.7	FeO_x/C (1:20)	(Mukundan *et al.* 2023)
Food Waste	300 °C, 60 min, 16 MPa	65	Iron-Oxide Nano-Catalysts	(Ebrahim *et al*. 2025)
Spirulina platensis	320 °C, 37 min	32.33	Fe_3O_4 nanostructure (0.75 g)	(Kandasamy *et al.* 2019)
Rice husk	260 C, 60 min, 10 bar	36.8	Hybrid magnetic nanocomposites	(Siddiqui *et al.* 2021)
Castor Residue	300 °C, 60 min, 10 MPa	21.20	K_2CO_3 (0.5M)	(Kaur *et al.* 2020)
***Nannochloropsis* sp**	**300 °C, 60 min, 20 bar**	**31.45**	**Fe_3O_4 nanostructure**	**In this study**

HTL PRODUCTS ANALYSIS

Bio-oil Characterization

The bio-oil (0.3 wt% and 3rd cycle) from HTL had carbon (51.53 and 51.56 wt%), hydrogen (8.56 wt and 9.41 wt%), nitrogen (0.51 and 0.62 wt%), and sulfur (0.48 and 0.59 wt%). The higher heating value (HHV) was (22.69 and 24.11 MJ/Kg), H/C of (1.99 and

2.19), and O/C of (0.56 and 0.55). Energy and carbon recovery were 36.6% and 28.6% for 0.3 wt% catalytic bio-oil. Table 2 provides a detailed note on the properties of bio-oil produced from different catalyst load and catalyst recycle studies. A recent study has reported a similar characterization of bio-oil from marine microalgae and *Nannochloropsis* sp. (Xia *et al.* 2022; EswaryDevi *et al.* 2023).

Table 2. Properties of Bio-oil Produced in Presence and Absence of Magnetically Reusable Catalyst

Bio-oil with Catalyst (wt%)	C	H	N	S	O	HHV (MJ/Kg)	H/C	O/C	Carbon Recovery (%)	Energy Recovery (%)
0.1	46.23	10.23	1.02	0.53	41.99	22.73	2.65	0.68	25.67	22.41
0.2	47.52	9.56	0.94	0.38	41.6	22.28	2.41	0.65	29.96	24.94
0.3	51.53	8.56	0.51	0.48	38.92	22.69	1.99	0.56	36.64	28.64
0.4	49.52	8.81	1.04	0.57	40.06	22.16	2.13	0.60	34.93	27.75
0.5	47.82	9.75	0.75	0.49	41.19	22.73	2.44	0.64	33.51	28.28
Non-catalytic	40.12	11	0.72	0.81	47.35	20.81	3.29	0.88	21.67	19.95
1st cycle	49.52	10.56	0.49	0.37	39.06	24.84	2.55	0.59	29.55	26.32
2nd cycle	50.23	11.24	0.74	0.41	37.38	26.35	2.68	0.55	29.98	27.92
3rd cycle	51.56	9.41	0.62	0.59	37.82	24.11	2.19	0.55	26.22	21.77
4th cycle	49.73	10.42	0.81	0.61	38.43	24.82	2.51	0.57	22.93	20.32
5th cycle	48.91	8.94	0.46	0.57	41.12	21.95	2.19	0.63	16.47	13.12

GC-FID Analysis

The HTL product was analyzed by the GC-FID analyzer to predict the major components present in the bio-oil, as illustrated in Figure. 9. The majority of the components were classified into hydrocarbons, furfurals, carboxylic acid, and aldehydes. Hydrocarbons were the predominant product class in the bio-oil at all temperatures, which made the fuel appropriate for use as diesel fuel (Arun *et al.* 2018). The percentage of hydrocarbon in the bio-oil increased from 54 wt% at 0.1 wt% of the catalyst load to 58 wt% at 0.3 wt% of the catalyst load. Further, there was a 56 wt% reduction in the hydrocarbon percentage in the bio-oil when the catalyst load was raised to 0.5 wt%. However, when the catalyst load was increased from 0.3 wt% to 0.5 wt%, the percentage of the hydrocarbons, furfurals, carboxylic acid, and aldehydes in the bio-oil was decreased, as per Figure. 9. The substances that fall under the classification of organic acids include methyl ester of hexadecanoic acid, as well as other similar compounds. Hexadecanoic acid is one of the primary and most prevalent ingredients in bio-oil that is produced from algae. Bio-oil from microalgae has number of compounds such as organic acids, oxygenated chemical, phenolic derivatives, nitrogenated chemicals, and hydrocarbons. Because of the presence of these compounds, the bio-oil produced from microalgae is found to be eligible for the thermochemical liquefaction process (Kumar *et al.* 2018).

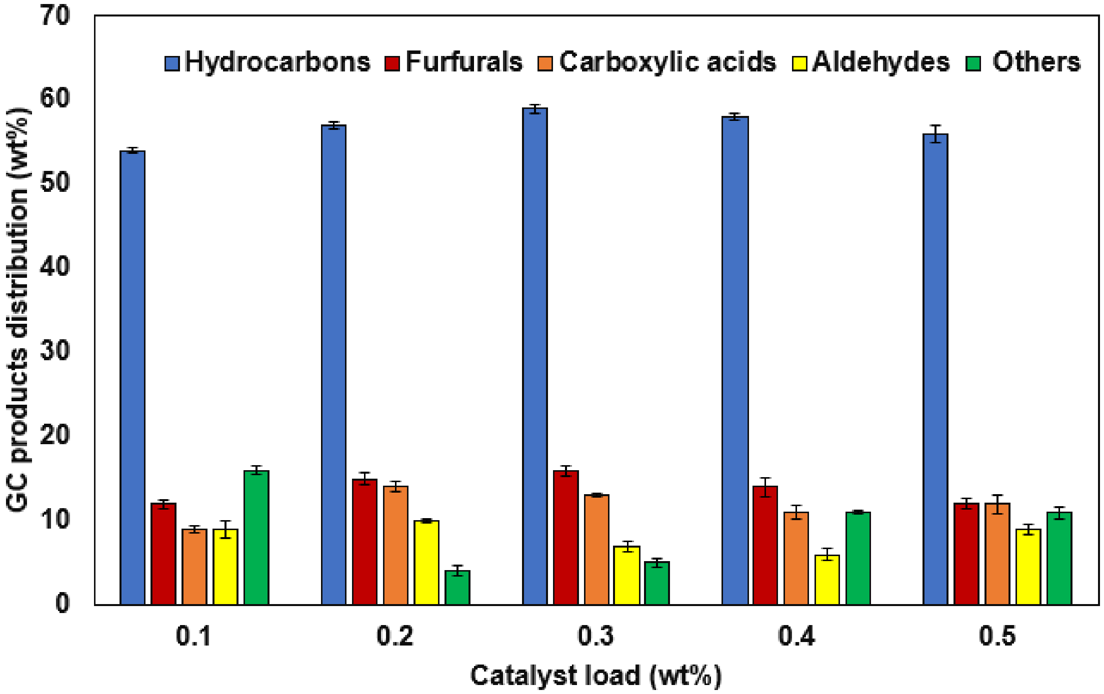

Fig. 9. Gas chromatogram profile of bio-oil with varying concentration of catalyst

CATALYST RECOVERY FEASIBILITY STUDIES

The reusability of the FeOx/C catalyst was examined with five reaction cycles of HTL with *Nannochloropsis* sp. biomass. Recovery and reuse of the catalyst influence the overall economy and efficiency of the process on an industrial scale. The catalyst recovery ranged from 72% to 83% from the above-mentioned different HTL experiments. The recovered catalyst was used in the next set of experiments with the same amount of prementioned catalyst load for ease of comparison studies. From Figure. 10, the third cycle consisted of 35 wt% aqueous phase, 20.4 wt% bio-oil, and 17.1 wt% bio-char. After this cycle, the production of biochar and aqueous phase increased while the yield of bio-oil declined. The aqueous and gas yields during the reusability tests did not differ notably.

Future Prospects

Hydrothermal liquefaction of algae biomass in the presence of a catalyst for sustainable biofuel production provides the ability to convert moisture biomass into high value bio-oil. Future research should focus on scalability towards efficiency and economics. Integrating carbon capture techniques and algae biomass can improve the sustainability. Value addition of byproducts biochar, aqueous phase and gas products can enhance the economic viability. Collaborative efforts between academia and industry will be a crucial factor to define the commercial viability of the study.

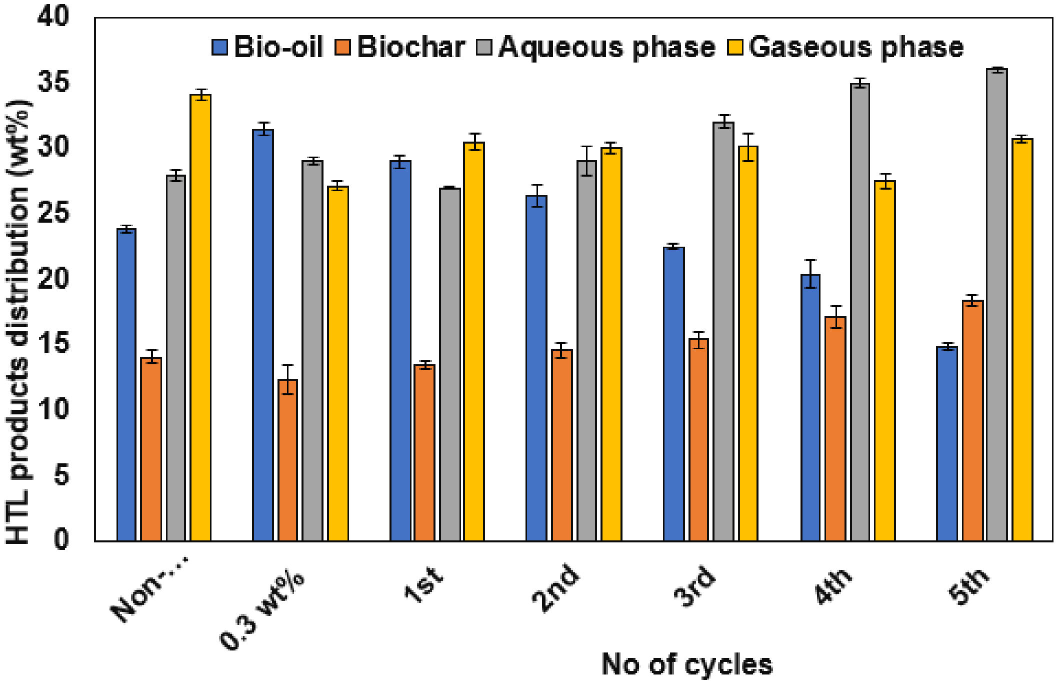

Fig. 10. Catalyst reusability study in HTL experiments in comparison with non-catalytic studies

CONCLUSIONS

1. A safe, non-expensive, stable, and magnetically separable Fe_3O_4 catalyst supported on activated carbon was developed to produce bio-oil from a microalgae *Nannochloropsis* sp. using a thermochemical liquefication process of HTL.
2. The developed catalyst increased the bio-oil production to a maximum of 31.4% with a catalyst dosage of 0.3 g at temperatures of 300 °C. After the liquefaction reaction, the synthesized catalyst was recovered and reused up to 5 times and achieved the bio-oil yield concentration of a maximum of 29% in the first cycle.
3. The decrease in bio-oil yield percentage tended to decrease in the next repeated cycles of the used catalyst was observed. Thus, in the 5th cycle, 15% of bio-oil yield was obtained while using the synthesized catalyst.
4. Further, the research can be focused on optimizing catalyst design, process integration and scaling up operations for industrial applications.

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Data Availability Statement

Data are available on request from the authors.

Declaration of Conflicting Interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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