

Characterization of bio-crude produced by graphene carbon tetranitrate catalyzed hydrothermal liquefaction and ultrasonication of *Ulva prolifera* mixed chicken waste

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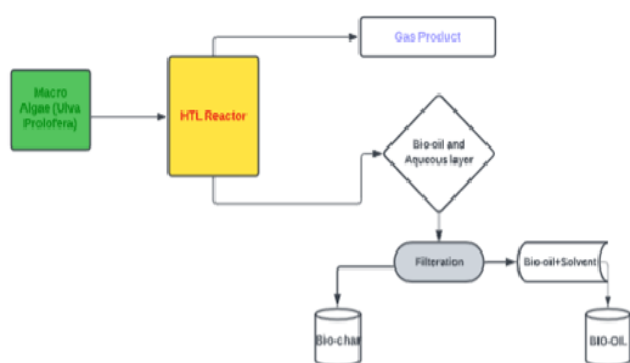
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Graphical abstract



Abstract

The utilization of macroalgae, specifically *Ulva prolifera*, for the manufacture of bio-crude demonstrates great potential as a viable alternative to conventional fossil fuels. This is mostly owing to its abundant availability and renewable characteristics, making it an optimal choice for bio-oil production. This study examined the synthesis of bio-crude through the Hydrothermal Liquefaction (HTL) method. The combination of Ultra-sonicated *Ulva prolifera*, Chicken Waste, and water facilitated the transformation of the moist biomass into Bio-crude. The study also examined the influence of process parameters, including the optimal operational temperature, retention time, and feedstock mixing ratio (275 °C, 30 minutes, and 1:4 ratio) for the graphene-C₃N₄ catalyst, KOH. The study's findings verified that a significant amount of bio-oil, specifically 23.5wt.% based on dry weight measurements, was successfully produced. Bio-oil mostly consists of alcohols, esters, phenols, ketones, and acidic chemicals. Furthermore, the bio-oil exhibited a significant heating value of 38.15 MJ/kg, which can be attributed to the presence of carboxylic acid groups and aliphatic hydrocarbons. Furthermore, the carbon content in the bio-oil was found to be double that of the macroalgae used as feedstock. Additionally, the heating value of the bio-oil was shown to be 2.5 times

greater than that of the macroalgae. Hydrothermal liquefaction may be used to efficiently create bio-oil from *Ulva prolifera*, a third-generation fuel that has great potential as an environmentally benign and sustainable energy source.

Keywords: Algae, bio-oil, bio-crude, hydrothermal, co-liquefaction, environment, marine waste, nano catalyst

1. Introduction

The increasing demand for the extraction and purification of conventional fossil fuels has resulted in substantial increases in prices and undesired ecological impacts. According to the Oil Market Report 2023, there will be substantial increase in the global demand for crude that could potentially reach one hundred and two million barrels per day. However, the annual petroleum production expected to decrease after 2022 by around three hundred thousand barrels every day (Faeth *et al.* 2013). Moreover, combusting fossil fuels results in the emission of alarming amounts of greenhouse gases into the atmosphere. This in turn will exacerbate the global warming problem, which may surpass historic preindustrial temperatures and cause other meteorological menaces such as sea level rise and desertification. which ultimately leads towards mass extinction and depletion of resources (Client earth communication, 2018). As the world progresses and the population grows at an unmatched pace, energy has become a crucial factor for development. This increasing demand for energy resources resulted in an exponential increase in the emission of GHGs.

Despite the progress in the shift from fossil fuel-based transportation system to electrical transportation, fossil fuels will remain to be the leading sources in the transportation and allied sectors. Nevertheless, extracting bio-oil from macroalgae appears a hopeful path towards generating sustainable energy because of their rapid growth and abundance and minimal resource requirement. Macroalgae are plentiful photosynthetic marine organisms obtainable in large quantities naturally or are cultivated in

ponds (Gardner, 2015, Jung *et al.* 2013, Liu *et al.* 2021, Van Hal *et al.* 2014).

Biochemical conversions often take significantly longer than thermochemical processes. Thermochemical reactions are frequently undertaken by heating biomass in a pressured oxygen-depleted environment, to enhance conversion and yield. Biomass conversion reactions, according to Gollakota *et al.* 2018, four are broadly classified into categories of combustion, gasification, pyrolysis, and hydrothermal processing. In the case of partial oxidation, the process known as gasification occurs at high temperatures to create gaseous fuel products, mainly syngas. Pyrolysis is the process of producing bio-oil, gases, and charcoal at medium to elevated temperatures in the absence of air. Among the four techniques listed above, the most promising technique that has garnered attention recently is hydrothermal liquefaction (HTL).

During the 1960s, the process of converting biomass into liquid form has made hydrothermal liquefaction a promising technology. A pilot plant was built in the following decade after engineers developed an approach called hydrothermal upgrading (HTU). Not long after this development, scientists proposed using hydrodeoxygenation as a method of converting bio-crude into fuel with greater efficiency sources. (Castello *et al.* 2018, Appell *et al.* 1975, Appell, 1971). In recent days, the world has focused on alternative biomass based renewable energy sources, mainly agricultural waste. among the common agricultural waste, Algae biomass has received a very high level of interest. Where algae as an eco-friendly medium for generating biofuel is gaining momentum. Algae's exceptional degree of photosynthetic productivity, fast growth rate and capacity to thrive in both freshwater and saltwater are all contributing factors towards its high demand. Both microalgae and macroalgae feedstocks can be used for producing biofuels because of abundance and potential to grow in fresh water without requiring land as any common agricultural biomass. Additionally, unlike other sources that primarily provide nutritional value, algae do not function so far as a main source of nourishment, which makes them more promising renewable energy alternatives out of them (Sayre, 2010, Jung *et al.* 2013, Huijgen and van Hal, 2014). Hydrothermal Liquefaction technology, which has considerable potential, transforms biomass into liquid biofuels. This process operates in the temperature range of 200-400°C pressure

range of 5-20 MPa in the presence of water as a reaction medium. Furthermore, HTL technology results in a high conversion and Yield of bio-oil and was observed to be economically viable and competitive compared to other biomass conversion technologies (Gollakota *et al.* 2018; Zhang *et al.* 2018; Zhu *et al.* 2017 and Elhassan *et al.* 2022).

Juntao Yang *et al.* (2023) conducted a complete study of the integration of several anaerobic digestion periods to create biogas, bio-oil, and biochar, as well as to improve energy recovery from the standpoint of energy flow. As the AD period grew from 3 to 15 days, the cumulative CH₄ yield increased from 33.23 to 249.20 mL/g VS. Pyrolysis of the solid digestate produced biochar ranging from 28.81 to 35.96%, whereas the bio-oil and pyrolysis gas gradually declined. The coupled system optimization reached the highest energy efficiency of 71.9% with a net energy gain of 2.0 MJ/kg wet biomass at a 12-day AD time, as recommended by the energy flow analysis. In addition, for the 2020 study, Gopinath K.P. and Arun J. examined the use of biochar as a cost-effective and environmentally friendly adsorbent for the removal of harmful colorants (dyes) from water. This review focuses on the many methods used for biochar production, including hydrothermal carbonization, pyrolysis, and hydrothermal liquefaction. Biochar, as an adsorbent, offers several benefits including its environmentally benign nature, affordability, and user-friendly application. It can be produced from a wide range of readily available materials, and it exhibits both recyclability potential and a better adsorption capacity compared to conventional adsorbents.

Furthermore, Bin Wang *et al.* (2021) investigated the performance of biochar-based catalysts on HTL using the low-lipid microalgae, *Spirulina platensis*, as a feedstock. The by-product of *spirulina platensis* HTL-solid residue was collected and activated to obtain biochar (BC). Then, the BC was used as the carrier to support Co, Ni and their oxides CoO_x and NiO to form Co/BC, Ni/BC, CoO_x/BC, NiO/BC catalysts. The results showed that the maximum yield of bio-oil catalyzed by BC was 35.80 wt% with 304°C, 34.7 min, and 0.32 g catalyst loading. BC catalyst displayed an improvement of bio-oil yield up to 4.00 wt% at low temperatures (260–280°C). The Ni/BC catalyst worked best for making bio-oil. It reached its highest level of 36.57 wt% at 280°C, 35.0 min, and 0.15 g of catalyst loading, which was 6.40 wt% higher than the case with no catalyst.

Table.1. Source of the Catalyst involved bio-oil study.

Materials	Catalyst and operating conditions	Sources
Marine macroalgae	Na ₂ CO ₃ 220–320 °C and 2 MPa	Zhou, D. et.al., (2010)
Woody biomass	Rb ₂ CO ₃ and CS ₂ CO ₃	Karagoz, S. et.al., (2004)
Woody biomass	NaOH and K ₂ CO ₃	Karagoz, S. et.al., (2004)
Marine macro algae (Ulwa Prolifera+ Chicken waste &g- g-C ₃ N ₄	KOH g-C ₃ N ₄ 270–320 °C and 20Mpa-30Mpa	Current research

According to Elliott *et al.* 2015; Stucki *et al.* 2009 experiments employed both subcritical liquid phase and super-critical vapor phase conditions, thus illustrating the

adaptability and potential of Hydrothermal liquefaction (HTL) technology to function both in subcritical and super critical conditions. The topic of algae-related hydrothermal

liquefaction (HTL) has garnered considerable attention that endeavors have been made to improve the performance in terms of bio-oil yield and quality from the HTL process. The introduction of Na_2CO_3 , Rb_2CO_3 and CS_2CO_3 , NaOH and K_2CO_3 result shown in **Table 1**.

The current research work attempted to use graphene Carbon tetranitride ($\text{g-C}_3\text{N}_4$) catalyzed Marine Macro algal biomass- chicken waste with water to investigate the effect of retention time, operational temperature, mixing ratio on the bio-oil yield of algal biomass processed in a hydrothermal liquefaction unit. Furthermore, the effect of ultrasonic cavitation treatment on the degradability of feed algal biomass has also been studied. The bio-crude yield and the physio-chemical characteristics of the product from the hydrothermal liquefaction (HTL) unit were investigated as well.

2. Materials and methods

2.1. Sample collection

The Marine Macroalgae (*Ulva prolifera*) samples were collected from the algal blooms in the nearby north Chennai beach area, India. The samples were washed and refrigerated at 4°C before further treatment and characterization tests were conducted on the sample. Physical and chemical characterization tests including identification of species and type of algae were carried out using an Olympus CX21 compound microscope at four hundred magnifications. Microscopic investigations were performed by measuring the presence of lipid-producing green macroalgae. The macroalgae species were also identified morphologically. It was confirmed the availability of significant amount of carbohydrates, proteins, lipids, and other compounds in the macroalgae investigated.

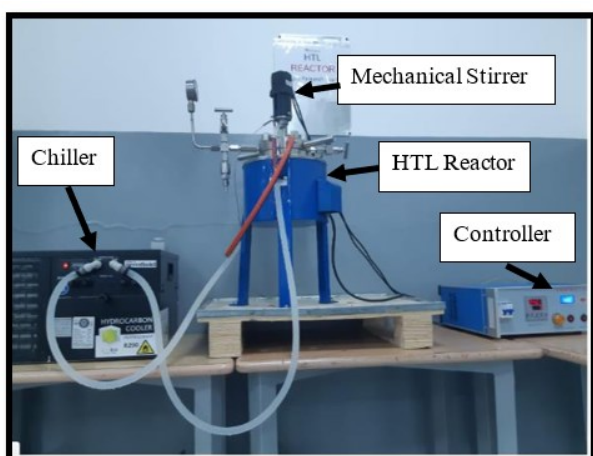


Figure 1. Hydrothermal Liquefaction Reactor (HTL) setup

Figure 1 shows a hydrothermal liquefaction reactor used for the experimental study. The apparatus used for experimentation has a capacity of half a liter (manufactured by ZZKD Machinery and Instrument Equipment with the model of CJF-0.5- Keda Machinery-China). An electric heating mechanism powered by the HTL temperature-raising function while temperature control with K-type thermocouples enabled enhanced accuracy. Furthermore, the pressure measurements ranging from 10

MPa to 30MPa were monitored constantly via sensor-equipped pressure gauge.

The HTL reactor is equipped with a magnetic coupling drive to agitate the slurry in, providing four distinct stirring velocities of 100, 150, 250, and 300 rpm. To prevent overheating, the magnet coupling was cooled using an Arm field hydrocarbon cooler. The Hydrothermal Liquefaction reactor (HTL) had two gas sampling ports and one liquid sampling line. The product line was equipped with a condenser also cooled by the chiller. Marine macroalgae (*Ulva prolifera*) with and without ultra sonicated feedstock, chicken waste, water, and Catalyst (KOH , $\text{g-C}_3\text{N}_4$) were infused into the Hydrothermal Liquefaction reactor (HTL). The blend ratio varied in accordance with each individual examination that was carried out. Subsequently, heat was administered to reach an optimal temperature, which it sustained for a pre-planned duration before shutting down completely. The sample is collected by both approaches by continuous condensation and cooling down by normal tap water. In case of high temperatures, the composition of bio-crude(bio-oil) contains less oxygen-containing species and more hydrocarbons and aromatic compounds.

2.2. Analytical study

In this work, the bio-oil is produced from a mixture of Marine algae, chicken waste and water used as feedstock in the presence of a catalyst. The amount of bio-oil produced by hydrothermal liquefaction (HTL) was quantified based on the weight percentage calculations. The retention time and temperature play an essential role in the HTL reactor performance. The residence time enhances the conversion of bio-crude composition of hydrocarbon as. The Aqueous phase analysis of the bio-oil from the HTL was carried out by measuring Total Organic Carbon Analyzer (TOC-L Shimadzu Analyzer), FTIR and GCMS graph confirms the functional group confirmation for the maximum bio-oil yield for the catalyzed Marine Macroalgae with Chicken waste mixed water. Biochar is formed in the bottom of the reactor; The bio-char surface morphological characteristics were investigated using scanning electron microscopy with a high magnification power. The research validates the surface properties and microstructure of biochar including distribution, size, and form of the pores on the surface of the biochar. The elemental composition of biochar was determined using EDX, which offers details on the type and concentrations of species found in the substance. SEM and EDX analyses together provide a comprehensive understanding of the physical and chemical characteristics of biochar.

3. Results and Discussion

3.1. Effect of Temperature on bio-oil yield

Temperature is the most important process parameter influencing the rate of reaction, yield, and quality of the bio-oil produced in the hydrothermal liquefaction (HTL) process. Experimental results showed the yield increased linearly with increasing temperature up to around 280°C , due to the thermal breakdown and enhanced conversion of the feedstock into bio-oil as shown in figure 2. Beyond the temperature of 280°C , the bio-oil yield started falling

sharply accompanied by excessive char formation or carbonation due to water deficient reactor environment. The percentage yield of bio-oil for untreated, ultrasonically treated, KOH treated and gC_3N_4 treated Marine Macroalgae biomass was found to be 17.5, 20.5, 22.5 and 23.5 respectively the experiment carried out using ultrasonically pretreated algal biomass and gC_3N_4 catalyst gave the best yield compared to the other experiments carried out with or without ultrasonication and with KOH. (Xu *et al.* 2014).

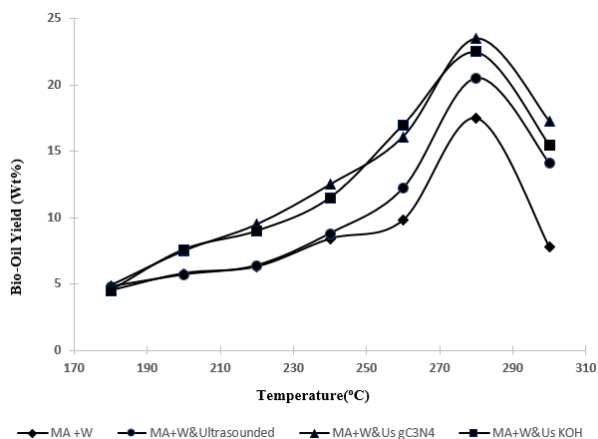


Figure 2. Temperature Vs Macroalgae Bio-Oil Yield

3.2. Effect of Retention period on Bio-oil yield

The effect of the retention period on the bio-oil yield was investigated by varying the retention period between 20 and 100 minutes, with the interval of 20 minutes at different temperatures of 240°C, 260°C, 280°C and 320°C. As shown in figure 3, the bio-oil yield increased until a retention duration of 80 minutes for the indicated temperatures. This is associated with higher retention time contributing to higher conversion of feedstock into bio-oil. The yield started declining beyond the retention time of 80 minutes. It can also be observed from figure 3 that the increase in temperature resulted in a steady increase in bio-oil yield up until the temperature reached 280 °C as reported in Figure.2 for gC_3N_4 treated biomass beyond this temperature the bio-oil yield started to decline. Similar trends were published by other researchers (Elliott *et al.* 2015). The declining yield at higher retention time is attributed to the degradation of bio-oil into bio-char due to carbonation of the organic mass in the HTL (Karagöz *et al.* 2004, Gao, 2017, Jung *et al.* 2013).

3.3. Effect of Ulva (Marine algae) to chicken waste mixing ratio on bio-oil yield

The concentration of macroalgae with chicken waste feedstock is another operating factor investigated in the HTL process, as the presence of other biomass as a co-liquefaction agent affects the density of the mixture and influences the reaction rate. This experimental work showed that higher feedstock concentrations led to lower yield (bio-oil), with a maximum production observed at a feedstock concentration of [13.3% to 75%]. Lower yield at higher feedstock concentrations may be due to the reduced surface area available for the reaction and the hinderance effect of the proteinaceous biomass from the

chicken on the degradation of the agal biomass (Baicha *et al.* 2016).

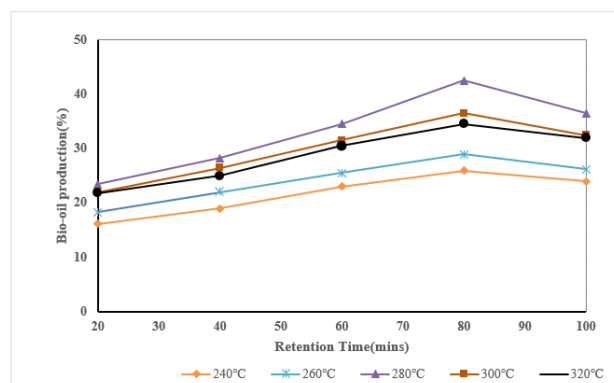


Figure 3. Retention time vs Bio-Oil production

The bio-oil yield increased from $16 \pm 2.5\%$ to $26 \pm 1\%$ when the solid loading rate was varied from 50% to 75%. The bio-oil from a 75% solid loading rate also showed a comparably higher density of 0.905 g/cm^3 with respect to all the other bio-oil samples.

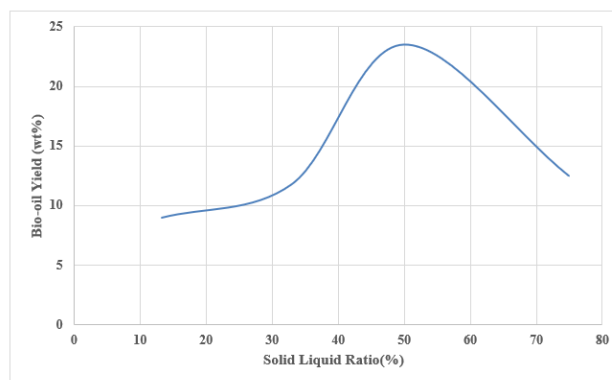


Figure 4. Solid-liquid Ratio vs Bio-oil production

3.4. Effect TOC

All the bio-oil samples in this experiment were analyzed using the Shimadzu-Total Organic Carbon Analyzer to measure the Total Organic Carbon present in the product. The total organic carbon and total nitrogen contents in the aqueous fraction were measured for the appropriate conditions as shown in Figure 5. The current investigation clearly confirms the feasibility of HTL technology for the efficient conversion of carbon available in the aqueous phase to bio-oil. The pure Macro algae with water (label 1) shows the highest TOC indicating the lowest bio oil yield, and sample 2 (MA+ Chicken waste +Catalyst and Water) gives the lowest TOC available in the aqueous phase compared to the other samples investigated in this study as shown in figure 5. The results reported in this study are compared to previously published literature (XU, Y., ZHENG, X., YU, H. & HU, X. 2014 Huijgen and van Hal, 2014) with the bio-oil yield. When water is used as a liquefaction solvent, the number of heteroatom compounds will be increased in the aqueous phase leading to higher TOC. The remaining charts are labeled as 3, 4, 5, 6, 8, 9, 10, and 11. This study presents the ratios of untreated macroalgae to water, both with and without catalyst mixes, that result in a reduced conversion of bio-oil production. This indicates a significant presence of total organic content. On the other

hand, the TN was higher in the alcoholic liquefaction aqueous phase (5000-4600 mg/ L) compared to the water liquefaction aqueous phase (2800 mg/L). This might be due to the N-heterocyclic compounds and fatty acid amides that are highly soluble in the aqueous phase when alcoholic solvents are used and this is in well agreement with GC-MS results.

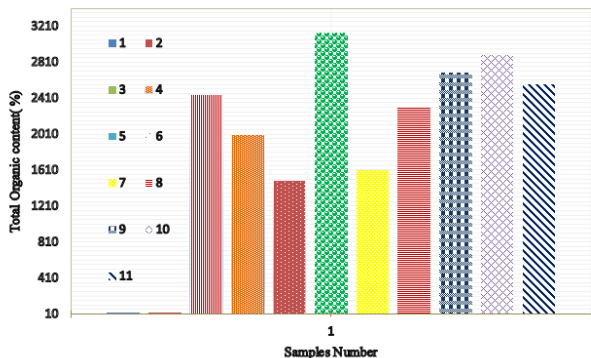


Figure 5. Total Organic Carbon at various conditions (1: Macro algae and water, 2: Ultrasonicated Macro Algae + Chicken waste and gC₃N₄, 7: MA+Water+Chicken waste and gC₃N₄)

3.5. FTIR analysis

The functional groups of compounds that are found in the compound can be fully understood from the FTIR spectrum. Figure 6 shows the FTIR spectra of bio-oil and chicken waste feedstock. The bio-oil peaks have higher transmittance at four different locations than the feedstock: 307 cm⁻¹, 2914 cm⁻¹, 2851 cm⁻¹, and 719 cm⁻¹.

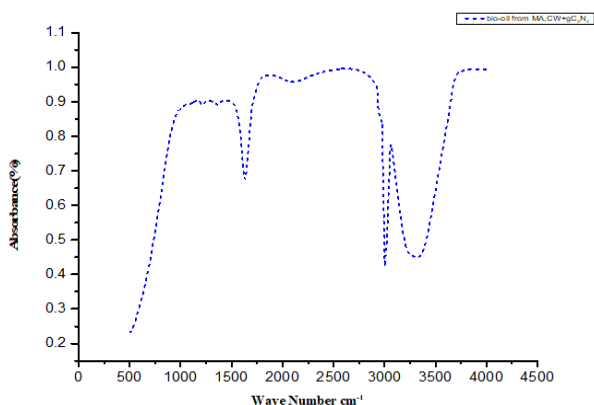


Figure 6. FTIR report of the Bio-oil composition

Figure 6 shows FTIR Results of the Ultrasonicated marine algae (Ulwa), Chicken waste produced bio-oil composition. The peaks at 1173 cm⁻¹ and 1097 cm⁻¹ correspond to the phenols and or alcohols. At 1709 cm⁻¹, C=O stretching vibrations indicate the presence of esters and acids; at 966 cm⁻¹, 1119 cm⁻¹, and 1240 cm⁻¹, Figure 6 also confirmed the amount of hydrocarbon present in the bio-oil mixture (Single trend attached for the references). The FTIR spectra of the bio-oils presented here are comparable to those of the biocrude extracted by HTL published by (Yan *et al.* 2019).

3.6. GC-MS

Gas chromatography-mass spectrometry was the technique of choice for the analysis of the produced bio-oil and HTL aqueous phase. The carbon dispersion in bio-oils that were produced from ultrasound Marine macro algae (*Ulva*) are shown in Figure 7. The chromatogram shown in Figure 7 was generated from the GC-MS for ultra-sonicated marine algae, chicken waste and water-produced bio-oil. A sizeable portion of the hydrocarbon-rich bio-oil was composed of straight-chain molecules (alkanes) in the C₇–C₂₁ range. Bio-oils have also been discovered to contain carbon molecules that are less common in the C₂-C₆ and above C₂₁ range. Due to the presence of aromatic hydrocarbons, the bio-oil's octane number has increased. The compounds identified under organic acids were hexadecenoic acid, hexadecenoic acid methyl ester etc. Hexadecenoic acid is one of the major frequent components found in bio-oil synthesized from algae (Chen *et al.* 2012, Akhtar and Amin, 2011, Xu *et al.* 2014).

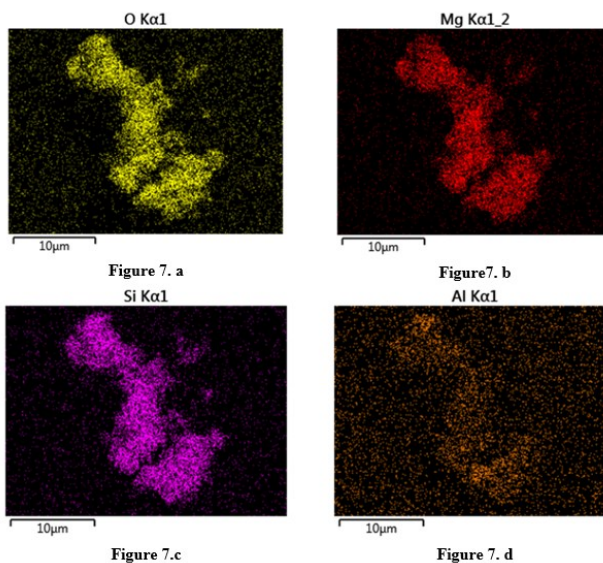
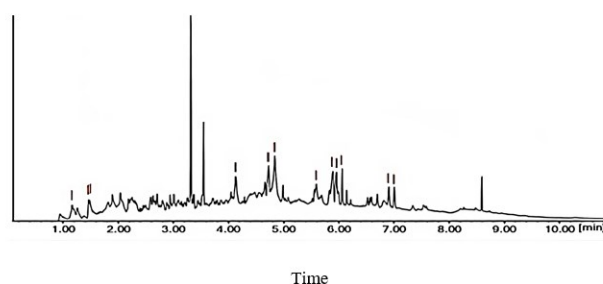


Figure 7. GC-MS Graph for ultra sonicated marine algae, chicken waste with water produced Bio-oil with the temperature 280 °C with 80min

3.7. Morphological Modification in SEM for Biochar

During the hydrothermal liquefaction process, the feedstock's shape changed, as seen in the SEM images. The detailed surface structure of the macroalgae can be observed in the feedstock diagram. These structures are broken down into tiny, permeability-enhancing fragments following hydrothermal treatment. The degradation of biochar occurs most quickly at a higher temperature of (280°C), based on the comparison made against other published literature in terms of its performance at various

temperatures. The *Ulva* marine algae were used as feedstocks and biochar source.

3.7.1. HTL influences on elemental composition

Light and transmission electron microscopy was used to examine the morphology of the biomass and biochar from the *Ulva prolifera* species. Scanning electron microscopy was used to investigate surface morphology (SEM) as shown in Figure 8. Biochar comprises carbon and ash its elemental composition varies based on the feed stock composition and Hydrothermal Liquefaction reactor conditions. Biochar contains Micro pore Miso pore and Macro pore structure. The Microporous structure in biochar is responsible for high absorptive capacity and surface area. Mostly Mesopore is vital for liquid-solid adsorption processes, while Macro pores are essential for bulk soil structure, hydrology, aeration, and movements of roots its nearer to the past literature studies (Freddo *et al.* 2012).

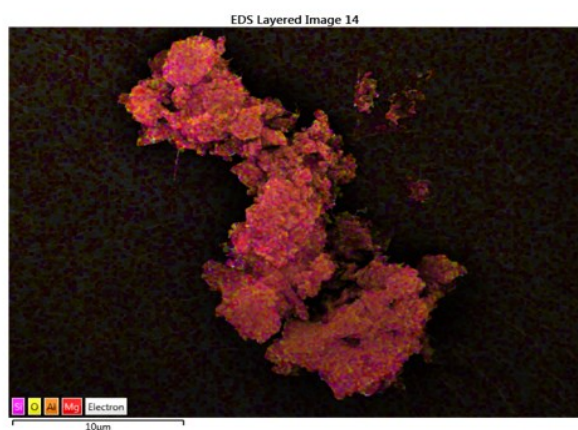


Figure 8 SEM Image of Bio-char composition MA with $g\text{-C}_3\text{N}_4$ catalyst

Figure.8 shows the elemental component distribution of the biochar composition of Marine Macroalgae (*Ulwa*) with Chicken waste with ultra sonication and without ultra sonication catalyzed samples are examined. Based on the investigation on the micronutrient binding on biochar and their exchange mechanism can lower the intake of harmful heavy metals. Bio-char surface comprises many chemically active groups, it includes ketone diols and carboxylic many

Table 2. Elemental Composition of *Ulwa* plus Chicken waste mixture and Bio-oil mixture

Composition	C	H	N	S	O	HHV(MJ/kg)
Ultra sonicated <i>Ulwa</i> Algae	32.4	6.72	7.97	4.1	31.51	15.2
Bio-oil @280°C	62.72	7.49	9.18	0	20.16	37.9±0.25

4. Conclusions

This study focuses on the enhancement of production of bio-crude oil from macro algae by hydrothermal liquefaction process in the presence of another biomass chicken waste and a catalyst $g\text{-C}_3\text{N}_4$. This research shows that the Ultra sonicated marine Macro algae mixture with chicken waste gave better bio-oil yield., It was confirmed that the optimal temperature and optimal retention time for the optimum bio-oil yield are at 280°C and 80 minutes respectively.

others, which produce the vast potential for adsorption of noxious elements such as manganese, aluminum in acid soils and Cadmium, Arsenic, Nickle, and Cadmium in heavy metal polluted soil. It has numerous benefits of biochar including improved soil structure, increased water retention, pH regulation, carbon sequestration, and retention of nutrients. The pH of biochar can range from neutral to alkaline. Biochar can assist buffer pH levels when added to acidic growth media, resulting in a more stable environment for the growth of marine algae. Biochar will improve soil fertility. These fundings in agreement with previous studies (Ahmad *et al.* 2018, Wild and Jones, 2009)

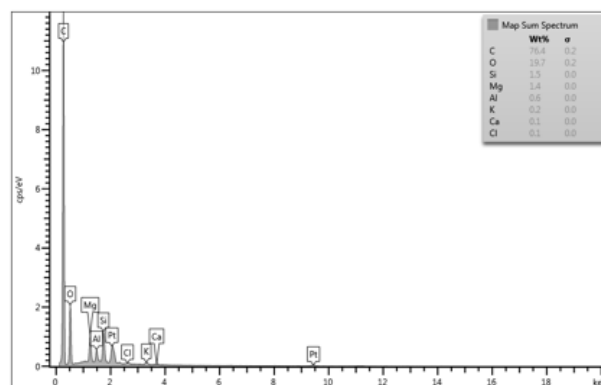


Figure 9. EDX graphical image of Biochar produced by HTL

Additionally, energy dispersive X-ray spectroscopy (EDXs) was also used to determine the elemental composition of the collected biochar samples. Figure 8 shows the results of an EDXs analysis used to identify the elemental composition (Xu *et al.* 2018, Ahmad *et al.* 2018, Hossain *et al.* 2022, Li *et al.* 2018, B-H. Jeon, 2013). The SEM mesoporous structure improved soil structure, increased water retention, pH regulation, carbon sequestration, and retention of nutrients **Table 2** clearly shows that, the composition of carbon in the bio oil was twice the amount in the feed macroalgae as it was stated in the GC-MS chromatogram due to the presence of aromatic hydrocarbons, the bio-oil's octane number has increased and the heating value for the bio oil was measured to be 2.5 times higher that of the macroalgae.

The utilization of the Nobel catalyst $g\text{-C}_3\text{N}_4$ in this study led to the attainment of the greatest yield of 23.5wt dry mass basis. The bio-oil composition is mostly characterized by alcohols, esters, phenols, ketones, and acidic chemicals. Furthermore, the heating value of the substance was determined to be 37.29 MJ/kg, mostly attributed to the prevalence of carboxylic acids rather than aliphatic hydrocarbons.

Furthermore, the increased conversion to bio-crude from the aqueous combination was validated by the examination of total organic carbon. On the other hand,

the results of the SEM and EDX investigations revealed that the amount of carbon present in the bio-oil was twice as much as the amount found in the feed macroalgae. Furthermore, the heating value of the bio-oil was measured to be 2.5 times higher than that of the macroalgae, which was also confirmed by the GC-MS chromatogram. This was due to the presence of aromatic hydrocarbons.

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