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RESEARCH ARTICLE

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Effects of temperature, reaction time, atmosphere, and catalyst on hydrothermal liquefaction of Chlorella

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Abstract

Hydrothermal liquefaction (HTL) is the direct conversion of wet biomass into bio-oil at high temperature (200–400°C) and high pressure (10–25 MPa). In this work, we investigated HTL with 4.5 g of Chlorella and 45 ml of water/ethanol (1:1 vol. ratio) in a 100 ml reactor. Bio-oils produced are characterized via elemental analysis, thermogravimetric analysis, and gas chromatography–mass spectrometry (GC–MS). HTL of Chlorella was investigated at 240 and 250°C for 0 and 15 min under an air or H_2 atmosphere and with and without 5% zeolite Y. Temperature increased the bio-oil yield from 38.75% at 240°C to 43.04% at 250°C for 15 min reaction time. Longer reaction time increased the bio-oil yield at 250°C from 39.14% for 0 min to 43.04% for 15 min. The H_2 atmosphere had a significant effect for HTL at 240°C. Zeolite Y increased the bio-oil yield significantly from 32.03% to 43.06% at 250°C for 0 min. The carbon content of bio-oil increased with the temperature while the oxygen content decreased. The boiling point distribution of bio-oils in the range of 110–300°C varies with temperature, and atmosphere. At 240°C for 15 min, the 110–300°C range increased from 31.19% in air (240-15-air) to 39.25% in H_2 (240-15-H_2). The H_2 atmosphere increased the content of hydrocarbons, alcohols, and esters from 69.61% in air (240-0-air) to 82.83% in H_2 (240-0-H_2). Overall, temperature, reaction time, atmosphere, and catalyst all significantly influenced the yield and/or quality of bio-oils from HTL of Chlorella.

KEYWORDS
bio-oil, elemental analysis, HHV, HTL, zeolite Y

1 | INTRODUCTION

Recently, biofuels have drawn extensive research due to the increase in global population, the depletion of fossil fuels, fluctuating oil prices, and climate change. Biofuels are considered a suitable alternative to fossil fuels. Depending on the feedstock sources, biofuels can be classified into first, second, and third generations. The main source of first-generation biofuels were the crops corn, sugarcane, and soybean. The disadvantage of the first-generation biofuels is that they compete with food crops. The second generation of biofuels is obtained from wheat straw, rice husks, plant seeds, and animal fats. The disadvantage of the second-generation biofuels is that its production cost is high and harvesting process, storage, and transport systems are inadequate for the processing of biomass in, large scale.[1] The third-generation biofuels microalgae have several advantages, including shorter growth cycles, faster growth rate, higher lipid content, ability to sequester carbon dioxide, and the highest photosynthesis efficiency.[2]

The current focus of this study is directed to the conversion of biomass via hydrothermal liquefaction (HTL) due to its ability to deal with whole biomass or processing wastes without drying, which is energy intensive. In the HTL process, high temperature (200–400°C) and high pressure (10–25 MPa) are applied to convert wet biomass into bio-crude oil, gas, aqueous phase, and solid residue. HTL has many advantages, namely, (i) drying of the bio-mass is no longer needed[3]; (ii) the components of bio-mass, namely, lipids, proteins, and carbohydrates all undergo hydrolysis and decomposition[4]; (iii) water possesses high dielectric constant, high ionic product, and low viscosity in the reaction system[5]; (iv) the organic solvents, especially ethanol, can be used with water because ethanol have the ability to react with acidic components in the bio-oil and a lower dielectric constant, allowing better dissolution of high-molecular weight products derived from biomass[6]; and (v) the nutrients (e.g., N, P, Mg, and K) can easily be separated and recycled for microalgae cultivation.[7]

HTL can be carried out with or without a catalyst. HTL reactions can be classified into three categories: (i) hydrolysis of lipids, proteins, and carbohydrates; (ii) rearrangement of the hydrolyzed products through decarboxylation, deamination, and dehydration reactions; and (iii) combination of reactive fragments through different reactions such as polymerization, condensation, cyclization, and dehydration.[4,5,8] HTL-derived bio-crude composition is dependent on the biomass feedstock composition, the reaction condition, added catalyst or solvent, and the atmosphere (such as, air, nitrogen, hydrogen, etc.).[9]

The bio-oil quality can be improved by using catalysts, and two methods are followed to improve the quality; (i) direct introduction of catalysts to the HTL and (ii) introduction of catalysts to treat the bio-oil after HTL.[10] Duan and Savage[1] investigated the HTL of *Nannochloropsis* sp. with heterogeneous catalysts (Pd/C, Pt/C, Ru/C, Ni/SiO_2-Al_2O_3, and zeolite) in He and H_2 atmospheres at 350°C. Generally, the catalytic HTL yields a higher percentage of bio-oil than the noncatalytic HTL. Sometimes, catalysts had a negative effect on the bio-oil yield, but the bio-oil obtained exhibited a lighter colour and a reduced viscosity as compared to the non-catalytic HTL. Biller et al.[11] investigated the effect of Co/Mo/Al_2O_3 on HTL of *Chlorella vulgaris* and *Nannochloropsis oculata* at 350°C, at a pressure of 150–200 bar. They found that the catalyst improved the bio-oil quality, higher heating value (HHV), the level of deoxygenation, and the percent yield. Jena et al.[12] investigated the effect of $Ca_3(PO_4)_2$ and NiO on the HTL of *Spirulina platensis* at 350°C for 60 min. Both NiO and $Ca_3(PO_4)_2$ decreased the bio-oil yield and increased the gaseous products.

Reaction parameters, such as temperature, reaction time, and atmosphere, significantly affect the HTL process. Temperature is a critical parameter and plays a vital role in influencing HTL.[13] The role of temperature on HTL includes two competition reactions, hydrolysis, and re-polymerization. Below 220°C temperature hydrolysis reaction dominant and 375°C temperature favours the formation of gaseous products. Reaction time is defined as the period at a constant temperature for the liquefaction process.[14] Eboibi et al.[15] observed that *Tetraselmis* sp. HTL at 350°C produced 65 wt.% bio-oil within 5 min. During HTL, both water and ethanol served as hydrogen donors.[16,17] Replacing the air atmosphere with hydrogen should also favour hydrogen donation and minimize re-polymerization.

In this investigation, HTL of Chlorella was performed without and with a catalyst (zeolite Y) under different temperatures, reaction times, and atmospheres to investigate the yield and quality of the bio-oils. Detailed comparisons of the results of non-catalytic HTL and catalytic HTL are summarized and discussed below.

2 | MATERIALS AND METHODS

2.1 | Materials

The feedstock of Chlorella microalgae was purchased from Stakich Inc. The zeolite Y (with a SiO_2:Al_2O_3 molar ratio of 30:1 and a surface area of 780 m^2/g) was purchased from Alfa Aesar. Solvents, such as dichloromethane, were purchased from Acros Organics, USA., and absolute ethanol was purchased from VWR, USA. The water used for reactions was deionized. The ultra-high purity (UHP) H_2 and Ar gases were purchased from an Air Liquide company, Airgas. All other chemicals used for this project were of analytical grade.

2.2 | Hydrothermal liquefaction

The HTL method is described in our previous publication[18] Figure 1 outlines the experimental procedure for the separation of the HTL products.

The percentage of bio-oil yield is calculated by the following formula.

$$\text{Bio-oil yield}(\%) = \frac{\text{Mass of bio-oil}(\text{g})}{\text{Mass of dried microalgae}(\text{g})} * 100\%$$

2.3 | Bio-oil analysis

The CHNS content of the Chlorella and bio-oils was determined in Atlantic Microlab (6180 Atlantic Blvd # M,

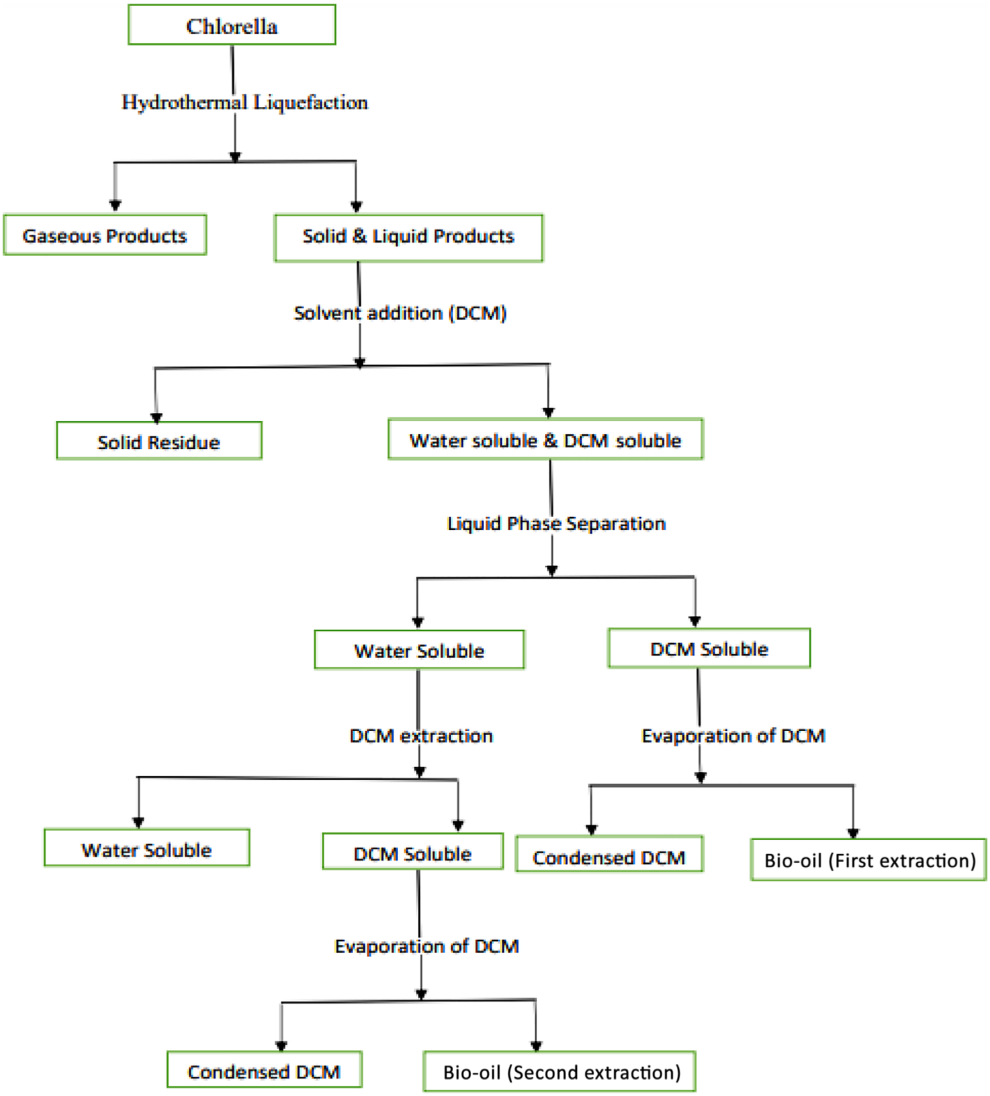


FIGURE 1 Product recovery and separation procedure of hydrothermal liquefaction (HTL) process. DCM, dichloromethane

Norcross, GA 30071), and O content was determined by difference from the sum of C, H, N, and S. The HHV was calculated using data from C, H, N, O, and S using Boie's equation.[19]

$$\mathrm{HHV}\,(\mathrm{MJ/kg}) = 0.3516^{*}\,\mathrm{C} + 1.16225^{*}\,\mathrm{H} - 0.1109^{*}\,\mathrm{O} + 0.0628^{*}\,\mathrm{N} + 0.10465^{*}\,\mathrm{S} \quad (1)$$

where C, H, O, N, and S are the percentages of elements in the bio-oils.

The energy of the bio-oils relative to the energy input of the Chlorella was studied in terms of energy recovery ratio (ERR).[20] The ERR was determined using the following equation:

$$\mathrm{ERR}\,(\%) = (\mathrm{Y}_{\mathrm{bio-oil}} \times \mathrm{HHV}_{\mathrm{bio-oil}})/\mathrm{HHV}_{\mathrm{feedstock}} \times 100\% \quad (2)$$

where $\mathrm{Y}_{\text{bio-oil}}$ and $\mathrm{HHV}_{\text{bio-oil}}$ are the bio-oil yield and HHV (MJ/kg) of bio-oils, respectively, and $\mathrm{HHV}_{\text{feedstock}}$ is HHV (MJ/kg) of Chlorella.

Thermogravimetric analysis (TGA) is a miniature distillation, and it measures the change in weight as a function of temperature or time. The TGA was determined using the TGA-Q500, a TA instrument, under N_2 flow (40 ml min^{-1}) from the ambient temperature to 800°C. The instrument's ramp was 10°C min^{-1}, and it was isothermal at 25°C for 5 min and at 800°C for 5 min.

The gas chromatography–mass spectrometry (GC–MS) was used for a detailed study of the bio-oils. A GC–MS (a Trace 1300 GC with an ISQ QD Single Quadrupole MS, Thermo Scientific, USA) was used with a 30 m long TG-5MS column (with inside diameter [ID] of 0.32 mm and film thickness of 0.25 μm) along with low polarity 5% diphenyl and 95% dimethyl polysiloxane) and a high purity helium gas, with a flow rate 1.5 ml min^{-1}. An

TABLE 1 Bio-oil yields from hydrothermal liquefaction (HTL) of Chlorella at different conditions; ZY: Zeolite Y, air: air atmosphere, H_2: H_2 atmosphere

HTL condition	First extraction (%)	Second extraction (%)	Total yield (%)	HTL condition	First extraction (%)	Second extraction (%)	Total yield (%)
240-0-air	35.81 ± 1.17	7.03 ± 0.42	42.84 ± 1.59	250-0-air	39.14 ± 0.64	9.97 ± 0.48	49.11 ± 1.12
240-0-H_2	36.41 ± 0.92	8.49 ± 0.17	44.90 ± 1.09	250-0-H_2	32.03 ± 0.82	16.23 ± 0.90	48.26 ± 1.72
240-0-air-ZY	35.53 ± 0.60	9.10 ± 0.10	44.63 ± 0.70	250-0-air-ZY	41.70 ± 0.31	6.90 ± 1.21	48.60 ± 1.52
240-0-H_2-ZY	36.37 ± 0.53	10.46 ± 0.95	46.83 ± 1.48	250-0-H_2-ZY	43.06 ± 1.35	7.18 ± 0.61	50.24 ± 1.96
240-15-air	38.75 ± 1.28	7.61 ± 0.54	46.36 ± 1.82	250-15-air	43.04 ± 0.98	8.05 ± 0.41	51.09 ± 1.39
240-15-H_2	43.02 ± 0.20	6.0.85 ± 0.66	49.87 ± 0.86	250-15-H_2	43.30 ± 0.51	6.98 ± 0.43	50.28 ± 0.94
240-15-air-ZY	43.03 ± 0.05	6.67 ± 1.15	49.70 ± 1.20	250-15-air-ZY	43.61 ± 0.53	6.69 ± 0.60	50.30 ± 1.13
240-15-H_2-ZY	45.03 ± 0.54	6.17 ± 0.85	51.20 ± 1.39	250-15-H_2-ZY	43.30 ± 0.51	6.98 ± 0.43	50.28 ± 0.94

automatic injector injected 0.5 μl of sample into the inlet port to vapourize at 300°C. The column temperature was programmed from 80 to 275°C, ramped to 3°C min^{-1}, and maintained at the final temperature for 10 min. GC–MS began analyzing after 2.5 min to avoid solvent peaks, with a scan mass range set for 50–550 amu for 0.2 s. The MS was used as a detector; split ratio was 3, and the NIST library was used to identify compounds.

3 | RESULTS

3.1 | Bio-oil yield

The factors influencing the HTL of Chlorella are reaction temperature, time, atmosphere, and catalyst. Both non-catalytic and catalytic HTL reaction are investigated under different temperatures, reaction times, and atmospheres. Bio-oil yield is the combination the of first and second extractions. Here, we focus mainly on the first extraction (organic layer) because more than 80% of bio-oil went to the organic layer. Table 1 shows the percentage of yield of bio-oils at different HTL conditions of Chlorella. Non-catalytic HTL evaluated at 240°C for 0 min in air is labelled as 240-0-air and catalytic HTL at 250°C for 15 min in H_2 and zeolite Y is labelled as 250-15-H_2-ZY. Bio-oil yields (%) at different HTL conditions are summarized in Table 1.

3.1.1 | Non-catalytic HTL of microalgae

The effects of temperature, time, and atmosphere on non-catalytic HTL are described and summarized as follows:

Effect of temperature

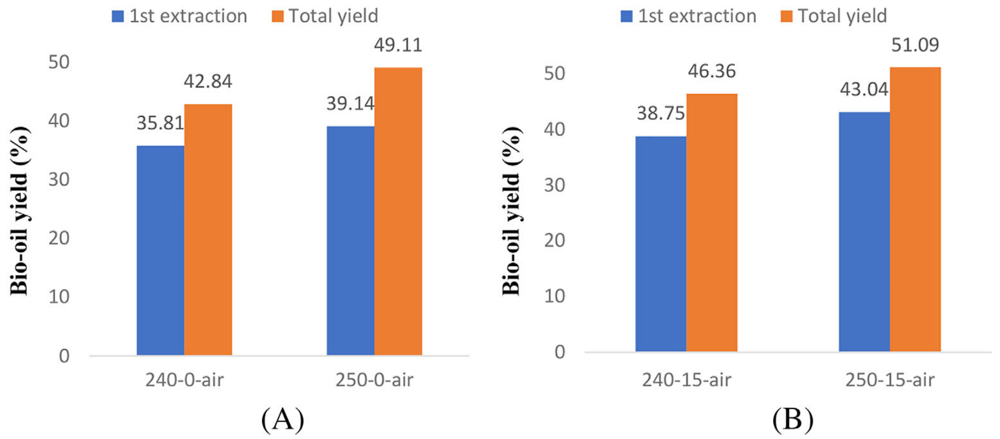
The effect of temperature on the bio-oil yield from HTL of Chlorella was evaluated at 240 and 250°C. Figure 2 illustrates the influence of reaction temperature on the yield of bio-oil in the air. As indicated in Figure 2A, the yield of bio-oil (first extraction) in the air atmosphere increased with the increase in temperature from 35.81% (total 42.84%) at 240°C to 39.14% (total 49.11%) at 250°C for 0 min reaction time, which represents $a\sim9\%$ increase. Figure 2Bb shows that the yield increases from 38.75% (total 46.36%) at 240°C for 15 min of reaction time to 43.04% (total 51.09%) at 250°C, $a\sim11\%$ increase. This is likely due to the fact that increase in temperature promotes the hydrolysis of biomass, leading to a higher bio-oil yield.[9]

Effect of reaction time

Figure 2 shows the bio-oil yields from HTL of Chlorella for 0 and 15 min at 240 and 250°C in the air atmosphere. As illustrated in Figure 3A, the bio-oil yield in the first extraction increases from 35.81% for 0 min to 38.75% for 15 min at 240°C, $a\sim8\%$ increase. At 250°C, as shown in Figure 3B, the yield increases from 39.14% for 0 min to 43.04% for 15 min, $a\sim10\%$ increase. Too long of a reaction time enhances the decomposition of bio-oil or polymerization forming high-molecular compounds as solids.[14,21]

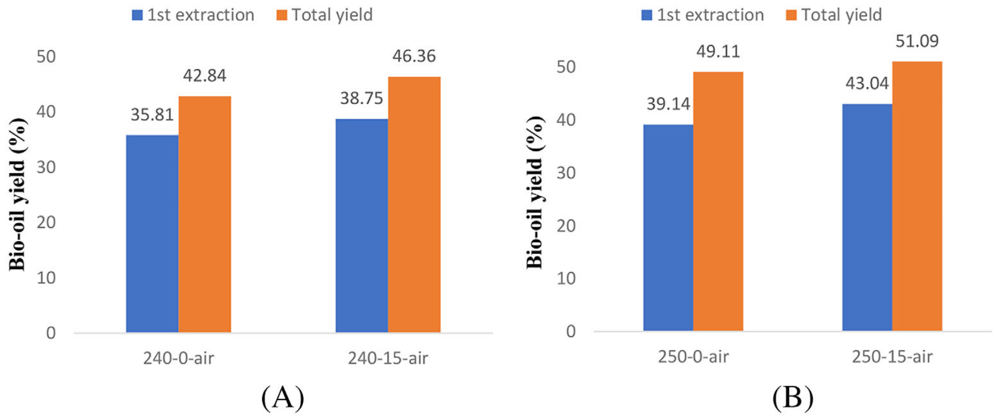
Effect of reaction atmosphere

In Figure 3, H_2 atmosphere at 240°C of 0 min slightly increased the bio-oil yield (first extraction, 36.41%) as compared to the air atmosphere (35.81%). But with 15 min at 240°C, the percentage of yield of bio-oil enhanced from 38.75% in air to 43.02% in hydrogen (Figure 4A). However, the opposite result was obtained at 250°C for 0 min (Figure 4B). It decreased from 39.14%



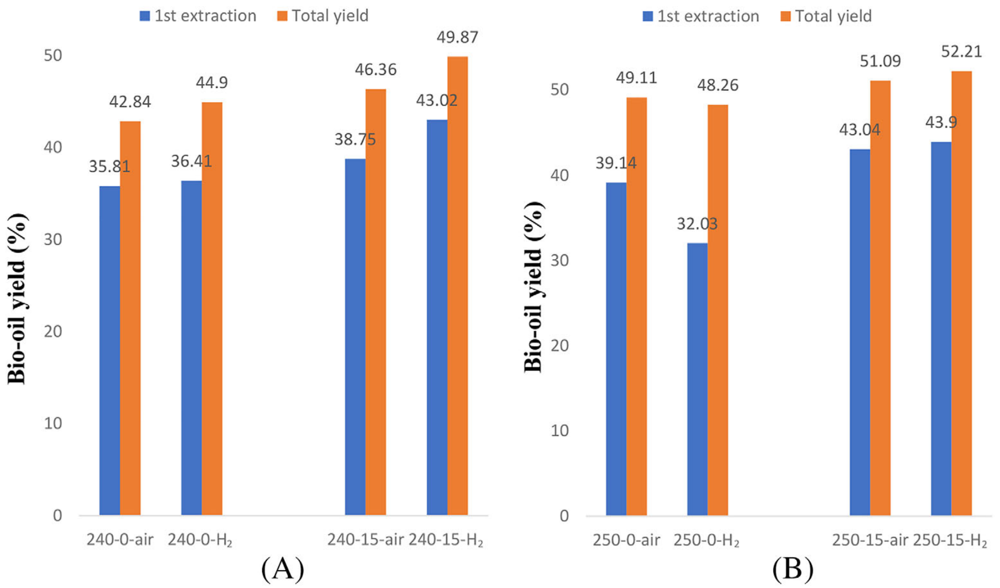
(A) (B)

FIGURE 2 Effect of temperature on the yield of bio-oils in the air atmosphere from non-catalytic hydrothermal liquefaction (HTL) of Chlorella for (A) 0 min and (B) 15 min



(A) (B)

FIGURE 3 Effects of reaction time on the bio-oil yield in the air atmosphere from non-catalytic hydrothermal liquefaction (HTL) of Chlorella at (A) 240°C and (B) 250°C



(A) (B)

FIGURE 4 Effect of atmosphere on the bio-oil yield from non-catalytic hydrothermal liquefaction (HTL) of Chlorella at (A) 240°C and (B) 250°C for 0 and 15 min

in air to 32.03% in H_2 at 250°C for 0 min. At 250°C for 15 min, H_2 atmosphere had a negligible effect from 43.04% to 43.90% (Figure 4B). This result indicates that hydrogen enhanced the stabilization of free radicals from the decomposition of microalgae and prevented retrogressive polymerization to form coke/char.[22] A similar result was observed in the previous study.[23] The highest yield bio-oil (first extraction: 43.90% and total:52.21%) was observed at 250°C for 15 min reaction time in hydrogen atmosphere (Figure 4B).

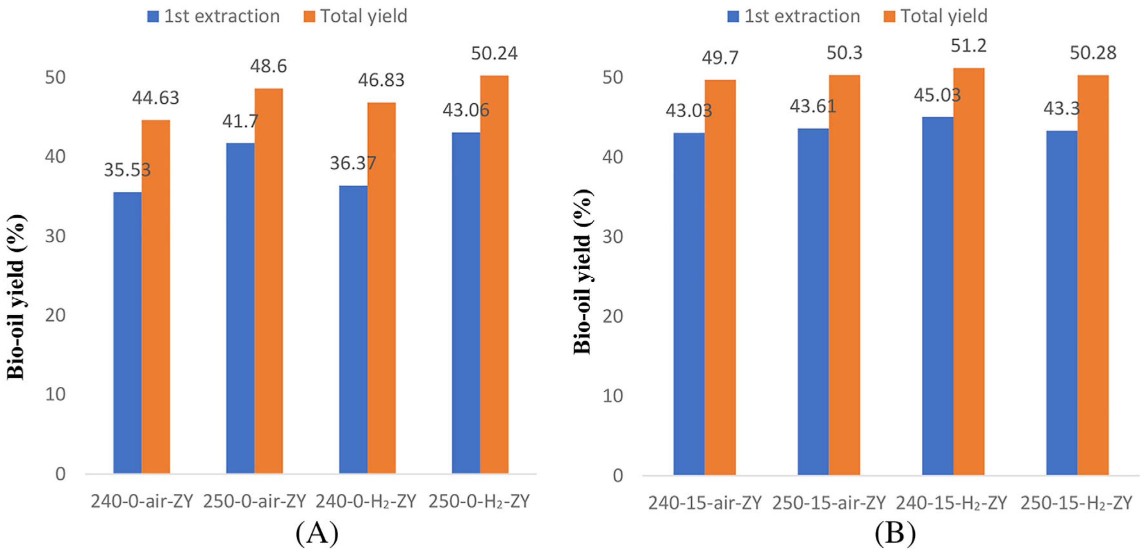


FIGURE 5 Effects of temperature on the bio-oil production in air and H_2 atmosphere from catalytic (Zeolite Y) hydrothermal liquefaction (HTL) of Chlorella at (A) 240°C and (B) 250°C

3.1.2 | Catalytic HTL of microalgae

The catalyst used in this study was zeolite Y. The catalyst influenced the bio-oil yield. Zeolite catalysts are known to promote the hydrocracking of larger molecules into smaller, more volatile molecules and can increase bio-oil yields under adequate conditions.[1]

Effect of temperature

As shown in Section 3.1.1 and our previous study,[18] temperature is one of the major factors that influence the HTL of microalgae. Temperature changes the dielectric constant of water during HTL, which affects the yield and quality of bio-oils.[9,24] The catalyst and temperature influence the bio-oil yield in HTL of microalgae.[25] As illustrated in Figure 5, the bio-oil yield (first extraction) increased with increasing temperature from 35.53% at 240°C to 41.7% at 250°C for 0 min in air and 36.37% at 240°C to 43.06% at 250°C for 0 min in H_2. Temperature had no significant effect for 15 min reaction time at both 240 and 250°C in air and H_2 (Figure 5B). A higher temperature could enhance zeolite Y for bond cessation and hydrolysis of biomass macromolecules, resulting in an increase in the bio-oil yield.[25] However, it's likely limited by a short reaction time since it will promote further cracking of bio-oil.

Effect of reaction time

Effects of reaction time on the bio-oil yield were explored for 0 min and 15 min at 240 and 250°C in both air and H_2 atmospheres. The bio-oil yield (first extraction) jumped with the increase in time from 35.53% for 0 min to 43.03% for 15 min in air at 240°C and 36.37% for 0 min to 45.03% for 15 min in H_2 at 240°C (Figure 6A). However, the yield of bio-oil was only slightly enhanced with increasing time from 41.70% for 0 min to 43.61% for 15 min in air at 250°C but was essentially with no change in the H_2 atmosphere (Figure 6B). This result is consistent with the previous study on the HTL of microalgae.[26] The reduced bio-oil yield at longer reaction time is due to the subsequent cracking or re-polymerization of HTL products. Faeth et al.[27] reported that rapid liquefaction of *Nannochloropsis* sp. resulted in a 66 wt.% bio-oil yield within 1 min, and the bio-oil has the same carbon content and a higher calorific value compared to the bio-oils obtained from the slow HTL.

Effect of reaction atmosphere

A reducing atmosphere can enhance the bio-oil yield from catalytic HTL as reported in the literature.[1,9] As mentioned in Section 1, the addition of hydrogen increases the bio-oil yield of HTL of *Nannochloropsis* sp. using zeolite as reported by Duan and Savage.[1] As indicated in Figure 7, the addition of 150 psi hydrogen to the reactor leads to a slightly higher bio-oil yield from 35.53% in air to 36.37% in H_2 at 240°C for 0 min and 43.03% in air to 45.03% in H_2 at 240°C for 15 min (Figure 7A). The yield of bio-oil increased with the addition of hydrogen from 41.70% in air to 43.06% in H_2 at 250°C for 0 min, but no significant effect was observed for 15 min (Figure 7B).

3.1.3 | Comparison of the yield of bio-oil of non-catalytic versus catalytic HTL

The results of catalytic and non-catalytic HTL are compared in Figure 8. As shown in Figure 8A, zeolite

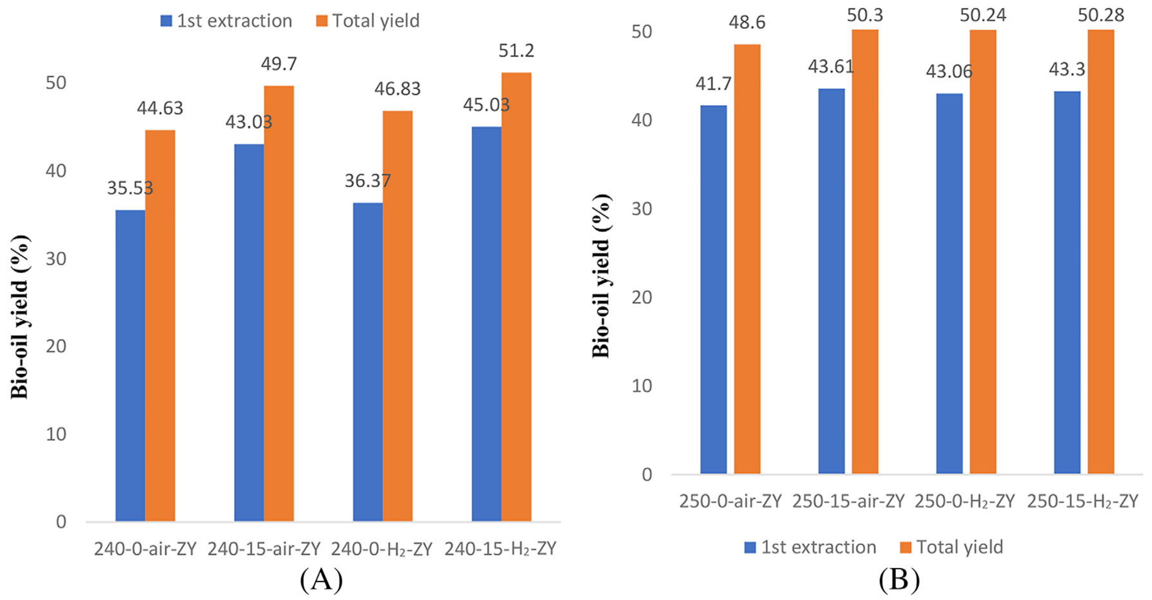


FIGURE 6 Effects of time on the bio-oil yield in air and H_2 atmospheres from catalytic hydrothermal liquefaction (HTL) of Chlorella at (A) 240°C and (B) 250°C

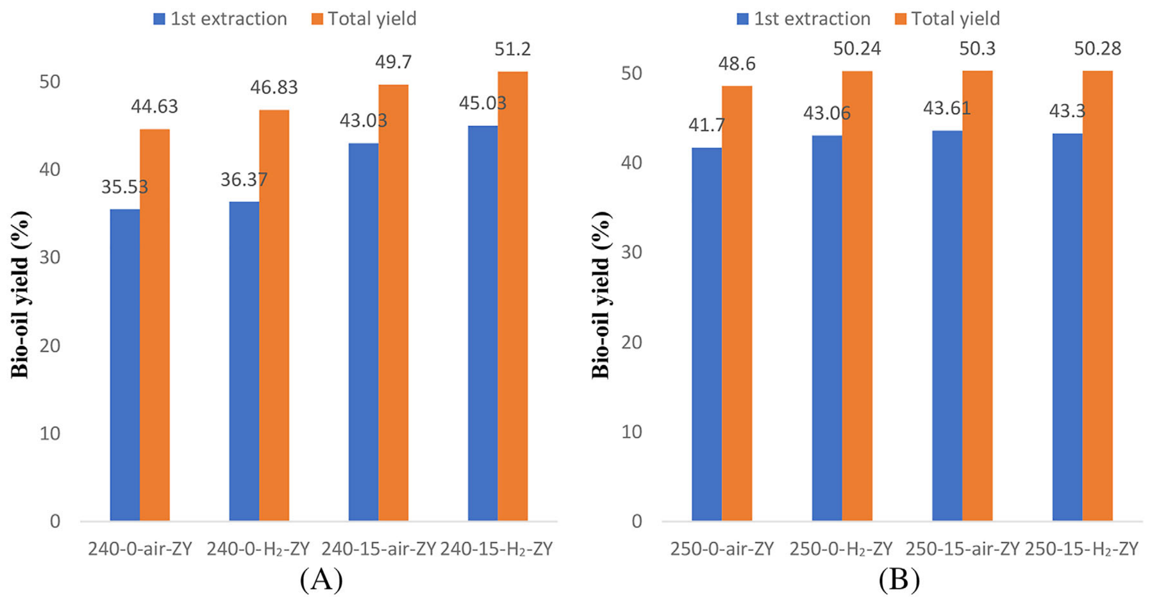


FIGURE 7 Effect of atmosphere on the bio-oil yield from catalytic hydrothermal liquefaction (HTL) of Chlorella at (A) 240°C and (B) 250°C for 0 and 15 min

Y showed a negligible effect at 240°C for 0 min, 35.35% to 35.53% and 36.41% to 36.37%, in air and H_2, respectively (Figure 8A). At 240°C for 15 min, the effect of zeolite Y is more significant, from 38.75% to 43.03% and 43.02% to 45.03% in air and H_2, respectively (Figure 8B). However, at 250°C for 0 min, the yield jumps from 32.03% to 43.06% with the addition of zeolite Y in H_2 (Figure 8C). On the other hand, zeolite Y had essentially no effect on yield at 250°C for 15 min in air or H_2 (Figure 8D). The catalyst effect is dependent on reaction temperature and time.

3.2 | Elemental analysis of bio-oil

CHNOS analysis results of the bio-oil are presented in Table 2. We consider the average value of the elemental analysis at different HTL conditions under the same

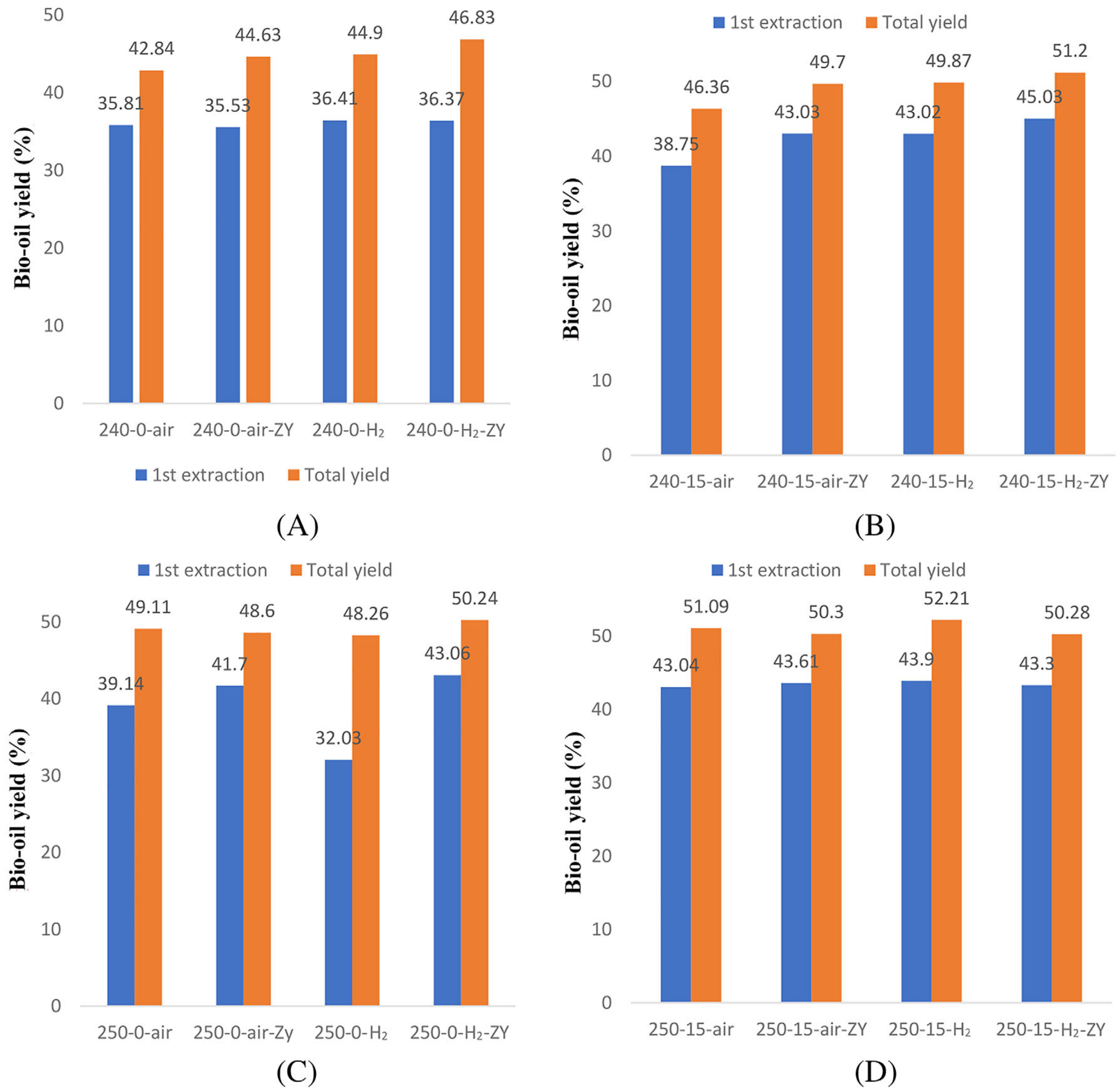


FIGURE 8 Effect of Zeolite Y on the bio-oil production from hydrothermal liquefaction (HTL) of Chlorella in air and H_2 atmospheres at (A) 240°C for 0 min, (B) 240°C for 15 min, (C) 250°C for 0 min, and (D) 250°C for 15 min

reaction temperature and time to explain the variation in CHNOS and its HHV. The elemental composition (CHNOS) of Chlorella is high in O and N and low in C and H. So, the HHV is low at 23.09 kJ/g and both the N/C and O/C ratios are high at 0.212 and 0.816, respectively. On the other hand, the elemental composition of bio-oils is different from that of biomass (Table 2), and therefore, their HHV and N/C and O/C ratios are different.

3.2.1 | Variation in CHNOS and HHV with temperature

The C content of the bio-oil increased with the increase in temperature and O content and decreased with the HTL reaction temperature in the air atmosphere. The C content of the bio-oils increases from 61% at 240°C for 0 min (240–0) to 63.97% at 250°C for 0 min (250–0) and from 61.29% at 240°C for 15 min (240–15) to 66.21% at 250°C for 15 min (250–15). The O content decreased from 22.42% (240–0) to 19.21% (250–0) and 22.05% (240–15) to 17.06% (250–15). The S content of the bio-oil had no significant temperature effect. Temperature has a small effect on the N content of the bio-oil, that is, N content slightly decreased with the increase in temperature (Table 2).

The ratios of H/C, N/C, and O/C slightly decreased with the increase in temperature from 240 to 250°C at a constant reaction time (Table 2). The HHV (kJ/g) had a relatively mild temperature effect. The HHV increased from 29.35 (240–0) to 30.45 (250–0) and 29.36 (240–15) to 31.88 (250–15). However, the energy recovery has a more

TABLE 2 CHNOS analysis and higher heating value (HHV) of bio-oils from non-catalytic and catalytic hydrothermal liquefaction (HTL) of Chlorella

		Elemental analysis (%)									
HTL condition	**Bio-oil yield (%)**	**C**	**H**	**N**	**S**	**O**	**H/C**	**N/C**	**O/C**	**HHV (kJ/g)**	**Energy recovery (%)**
Chlorella		51.34	7.29	9.35	0.57	31.45	1.7	0.212	0.816	23.09	
240-0-air	35.81(first)	65.6	8.23	7.73	0.62	17.82	1.51	0.137	0.362	31.71	49.18
240-0-H2-	36.41 (first)	59.96	8.28	7.74	0.46	23.56	1.66	0.151	0.524	28.63	45.15
240-0-air-ZY	35.53 (first)	56.49	8.61	7.22	0.45	27.23	1.83	0.149	0.642	27.35	42.09
240-0-H_2-ZY	36.37 (first)	61.98	8.33	8.19	0.45	21.05	1.61	0.154	0.453	29.7	46.78
Average	**36.03**	**61**	**8.36**	**7.72**	**0.495**	**22.42**	**1.65**	**0.148**	**0.495**	**29.35**	**45.8**
240-15-air	38.75(first)	59.75	8.59	7.63	0.46	23.58	1.73	0.149	0.526	28.89	48.48
240-15-H_2	43.02 (first)	62.49	8.54	7.92	0.34	20.71	1.64	0.215	0.441	30.14	56.16
240-15-air-ZY	43.03 (first)	59.72	8.79	7.42	0.39	23.68	1.64	0.145	0.529	28.2	52.55
240-15-H_2-ZY	45.03 (first)	63.19	8.35	7.89	0.34	20.23	1.59	0.146	0.427	30.22	58.93
Average	**42.46**	**61.29**	**8.57**	**7.72**	**0.383**	**22.05**	**1.65**	**0.164**	**0.481**	**29.36**	**54.03**
250-0-air	35.33 (first)	64.84	8.45	7.82	0.59	18.3	1.56	0.141	0.376	31.14	47.65
250-0-H_2	34.19 (first)	63.59	8.3	8.48	0.47	19.16	1.57	0.156	0.402	30.45	45.09
250-0-air-ZY	44.01 (first)	63.45	8.42	7.79	0.44	19.9	1.59	0.143	0.418	30.43	58
250-0-H_2-ZY	38.77 (first)	63.98	8.23	7.89	0.44	19.46	1.54	0.144	0.406	30.46	51.14
Average	**38.08**	**63.97**	**8.35**	**7.99**	**0.485**	**19.21**	**1.57**	**0.146**	**0.401**	**30.45**	**50.47**
250-15-air	33.34 (first)	65.1	8.46	7.51	0.38	18.55	1.56	0.135	0.38	31.17	43.66
250-15-H_2	42.1 (first)	67.03	8.58	7.67	0.4	16.32	1.54	0.133	0.324	32.25	58.8
250-15-air-ZY	37.92 (first)	67	8.59	8.15	0.39	15.87	1.54	0.142	0.316	32.34	53.11
250-15-H_2-ZY	42.79 (first)	65.69	8.67	7.82	0.34	17.48	1.58	0.139	0.355	31.77	58.88
Average	**39.04**	**66.21**	**8.58**	**7.79**	**0.378**	**17.06**	**1.56**	**0.137**	**0.344**	**31.88**	**53.61**

significant temperature effect, increasing from 45.8% (240–0) to 50.47% (250–0) (Table 2).

3.2.2 | Variation in CHNOS and HHV with reaction time

With HTL in air and H_2 atmosphere, a longer reaction time increased the contents of C and H in the bio-oil at a constant temperature. The C content largely increased from 63. 97% (250–0) to 66.21% (250–15) and H content slightly increased from 8.35% (250–0) to 8.58% (250–15). The S and O content of the bio-oil decreased with reaction time, but the reaction time had no effect on the N content. The S content reduced from 0.485% (250–0) to 0.378% (250–15) and the O content decreased from 19.21% (250–0) to 17.06% (250–15) (Table 2).

The ratios of H/C and N/C show no regular trend with reaction time, but O/C ratio decreased with reaction time. The O/C ratio decreased from 0.401 (250–0) to 0.344 (250–15). The HHV and ERR increased with reaction time. The ERR increased from 45.8 (240–0) to 54.03 (240–15) and 50.41 (250–0) to 53.61 (250–15) and HHV increased from 30.45 (250–0) to 31.88 (250–15) (Table 2).

3.2.3 | Variation in CHNOS and HHV with atmosphere

The C content of non-catalytic HTL decreases when changing from an air atmosphere to a H_2 atmosphere. For example, the yield at 240°C for 0 min decreases from 65.60% in air (240-0-air) to 59.96% in H_2 (240-0-H_2), and at 250°C for 0 min, it decreases from 64.84% in air (250-0-air) to 63.59% in H_2 (250-0-H_2). However, at 240°C for 15 min, the C content increases from 59.75% in the air atmosphere (240-15-air) to 62.49% in H_2 (240-15-H_2), and at 250°C for 15 min, it increases from 65.10% in the air (250-15-air) to 67.03% in H_2 (250-15-H_2).

On the other hand, the C content of catalytic HTL increases when changing from the air atmosphere to the H_2 atmosphere. At 240°C for 0 min, the C content increases from 56.49% in air (240-0-air-ZY) and 61.98% in

H_2 (240-0-H_2-ZY), and at 240°C for 15 min, it increases from 59.72% in air (240-15-air-ZY) to 63.19% in H_2 (240-15-H_2-ZY). But an opposite scenario was observed for 0 and 15 min at 250°C.

The N content of bio-oils from both non-catalytic and catalytic HTL decreases when changing from the air atmosphere to H_2 atmosphere, no matter what the reaction temperature (240 and 250°C) and reaction time (0 and 15 min) used. The S content also decreases (non-catalytic and catalytic HTL) from air to H_2 atmospheres at various HTL conditions. However, the O content only decreases in catalytic HTL when switching from the air atmosphere to H_2 atmosphere but not so for non-catalytic HTL.

The ratios of H/C and O/C (non-catalytic and catalytic HTL) decreased in the H_2 atmosphere versus the air atmosphere for 15 min at 240 and 250°C, but an opposite trend was observed for the N/C ratio. The HHV and ERR (non-catalytic and catalytic HTL) increases in the H_2 atmosphere for 0 and 15 min at 240 and 250°C.

3.2.4 | Effect of catalyst on CHNOS and HHV

As shown in Table 2, the C content increases by the addition of zeolite Y in the H_2 atmosphere at 240 and 250°C for 0 and 15 min. Zeolite Y in H_2 atmosphere decreases the content of O in comparison to the non-catalytic HTL in the H_2 atmosphere at 240 and 250°C for 0 and 15 min. S content was also decreased by zeolite Y in both air and H_2 atmospheres compared to non-catalytic HTL at different reaction times and temperatures. Zeolite Y decreases the N content at all HTL conditions, as mentioned in Section 3.2.3, in both air and H_2 atmospheres.

Zeolite Y in H_2 atmosphere decreases the H/C ratio compared to non-catalytic HTL but the ratio of N/C and O/C increases by zeolite Y in the air atmosphere than non-catalytic HTL for 0 and 15 min at 240 and 250°C.

Zeolite Y in air and H_2 atmosphere increases the ERR of bio-oils than the non-catalytic HTL for 0 and 15 min at 240 and 250°C. Zeolite Y has no significant effect on HHV.

3.3 | Thermal gravimetric analysis of bio-oil

TGA measures the boiling point distribution of bio-oils and is performed under the N_2 atmosphere from 25 to 800°C. One representative example of the boiling point distribution of bio-oils under different HTL conditions is shown in Table 3. The remaining information of the boiling point distribution of bio-oil is included in the supporting document (Tables S1 and S3).

We are especially interested in the distribution of the boiling point of bio-oil in the range of 110–300°C because it consists of gasoline, jet fuel, fuel for stoves, and diesel oil. The percentage of weight loss can be influenced by the reaction atmosphere and catalysts.

The H_2 atmosphere in non-catalytic HTL increased, in comparison to the air atmosphere, the percentage of bio-oil in the boiling point range of 110–300°C at 240°C (Figure 9A). The same portion increased from 31.19% (240-15-air) to 39.25% (240-15-H_2) at 240°C for 15 min when changing the atmosphere from air to H_2 (Figure 9B). At 240°C for 15 min, zeolite Y in the air increased the same portion of bio-oil from 31.19% (240-15-air) to 37.26% (240-15-air-ZY) (Figure 9B). Similarly, zeolite Y in air (37.26%, 240-15-air-ZY) performed better than zeolite Y in

TABLE 3 Boiling point distribution of bio-oils with non-catalytic and catalytic hydrothermal liquefaction (HTL) of Chlorella in different atmospheres at 240°C for 0 min

Molecule types	Temperature (°C)	240-0-air (wt.%)	240-0-H_2 (wt.%)	240-0-air-ZY (wt.%)	240-0-H_2-ZY (wt.%)
Yield of bio-oils (first extraction)	→	35.81 ± 1.17	36.41 ± 0.92	35.53 ± 0.60	36.37 ± 0.53
Bottle gas and chemicals	25–110	1.55	3.33	7.80	3.80
Gasoline	110–200	6.70	6.37	11.66	9.35
Jet fuel, fuel for stoves, and diesel oil	200–300	21.93	23.13	20.82	22.31
Lubricating oil for engines, fuel for ships, and machines	300–400	23.30	24.82	21.09	23.11
Lubricants and candles, fuel for ships	400–550	21.59	17.24	14.35	18.07
Fuel for ships, factories, and central heating	550–700	24.38	11.35	11.78	17.27
Asphalt and roofing	700–800	0.01	6.85	5.81	5.47
Boiling point range of interest	110–300	28.63	29.48	32.48	31.66

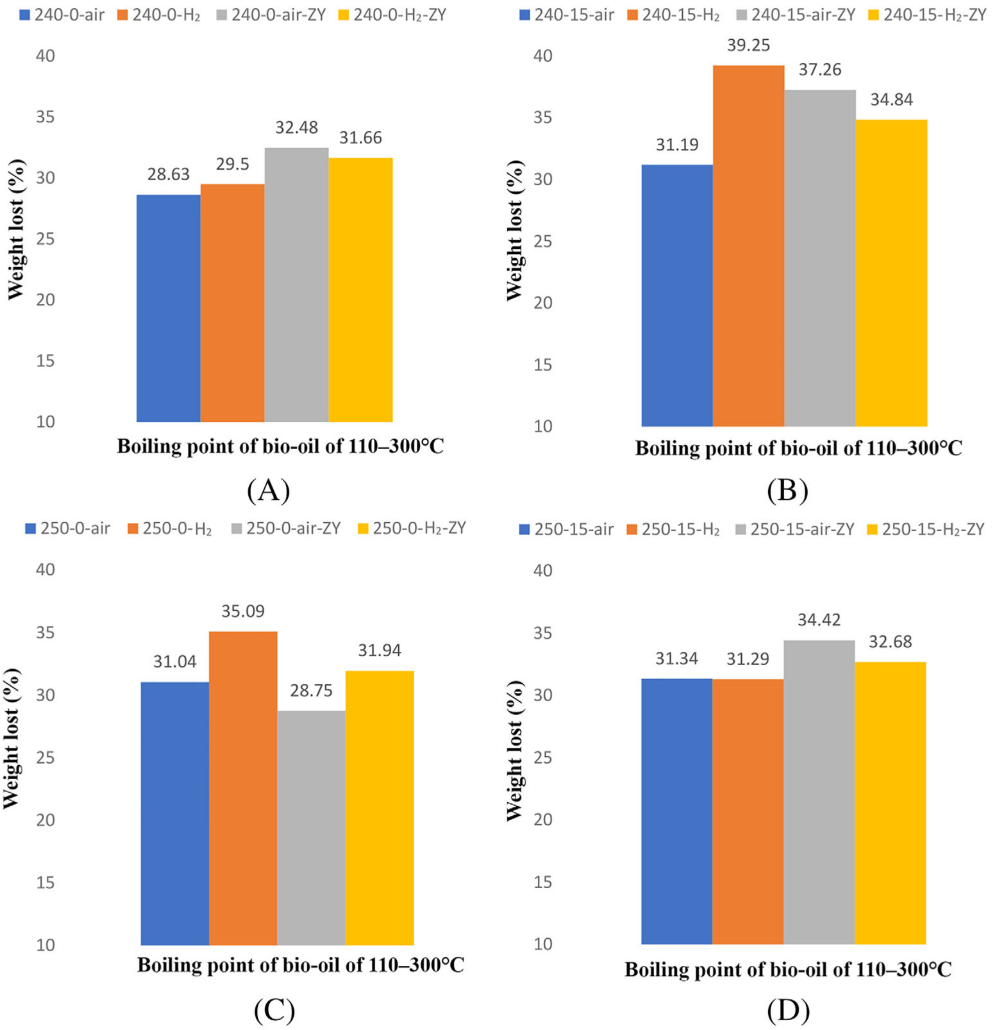


FIGURE 9 Effect of atmosphere and catalyst on the boiling point range of bio-oil of 110–300°C from HTL of Chlorella at 240 and 250°C for 0 and 15 min

H_2 (34.84%, 240-15-H_2-ZY) for the boiling point range of 110–300°C (Figure 9B).

3.4 | GC–MS analysis of bio-oil

The GC–MS analysis is used to identify the bio-oil components. The major components of the bio-oil were N-containing components (N-heterocyles, amides, amino acids, and N & S), which can be attributed to the high amount of protein (57.14%) in the Chlorella, and other functional groups are ketone, aldehyde, hydrocarbon, alcohol, ester, and fatty acid. Tables S4–S11 (see Appendix S1) provide retention time, peak name, and relative peak area from the GC–MS analysis.

3.4.1 | Variation in bio-oil components with temperature and reaction time

Figures S1–S3 (see Appendix S1) illustrate the variation in bio-oil components with reaction time and temperature. As indicated in Figure 10, the content of N-containing compounds slightly increased with the increase in temperature from 240 to 250°C. N-containing compounds increased from 26.4% at 240°C to 27.56% at 250°C for 0 min and 25.85% at 240°C to 28.49% at 250°C for 15 min. The content of fatty acids was unchanged for 0 min, but increased from 2.57% at 240°C to 6.5% at 250°C for 15 min. The content of hydrocarbons, alcohols, and esters decreased with increasing temperatures from 69.61% at 240°C to 66.35% at 250°C for 0 min and 69.45% at 240°C to 60.45% at 250°C for 15 min. O-containing compounds increased with the increase in temperatures from 3.15% at 240°C to 5.19% at 250°C for 0 min and 2.46% at 240°C to 6.29% at 250°C for 15 min.

3.4.2 | Variation in bio-oil components with reaction atmosphere and catalysts

Reaction time, atmosphere, temperature, and catalysts influenced the bio-oil components as determined by the GC–MS analysis. Figures S4–S7 (see Appendix S1)

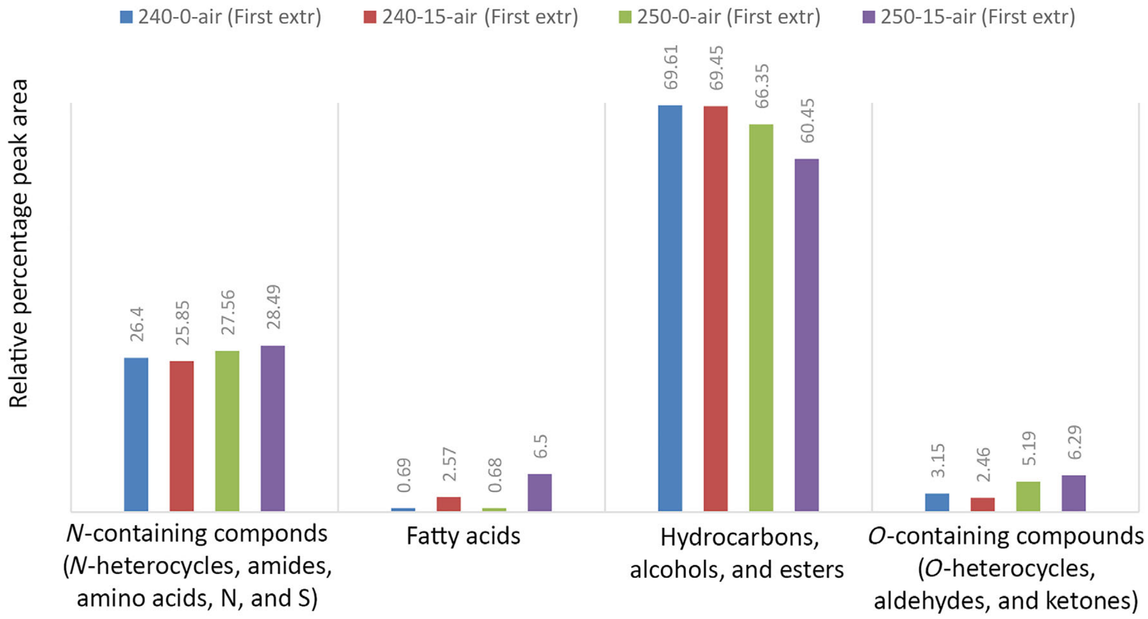


FIGURE 10 Variation in bio-oil (first extraction) components without catalyst in the air atmosphere at different times and temperatures

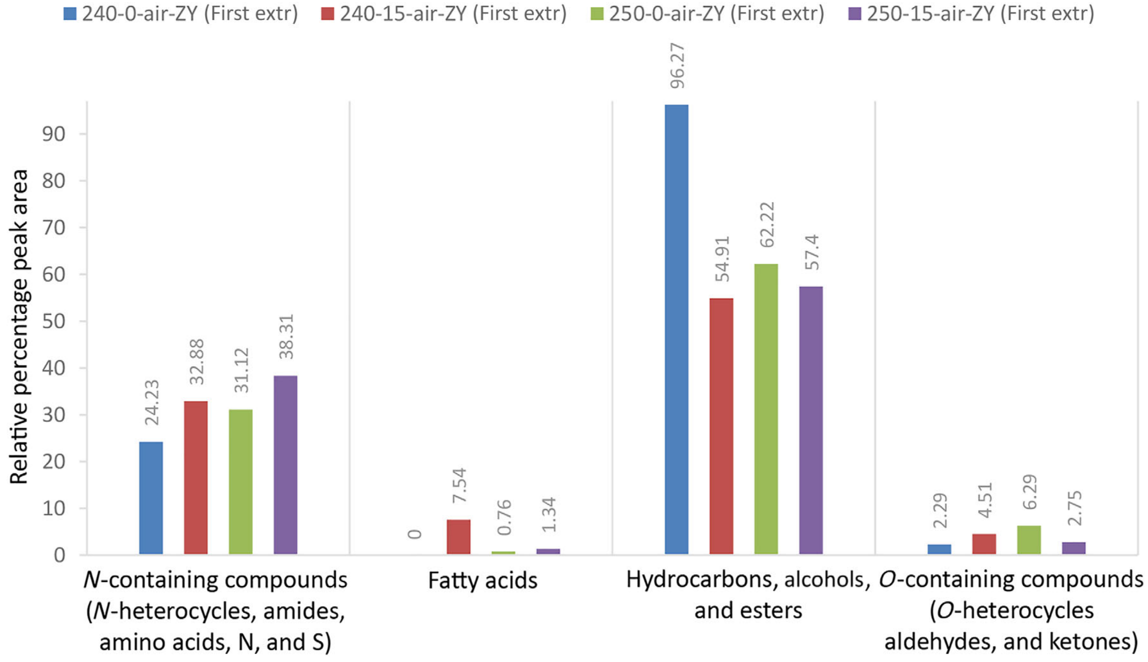


FIGURE 11 Variation in bio-oil (first extraction) components with Zeolite Y in the air atmosphere catalysts at 240 and 250°C

illustrate the variation in bio-oil components with catalysts and reaction atmosphere.

With zeolite Y in the air atmosphere, the N-containing compounds increased with the increase in temperature and reaction time (Figure 11). The percentages of hydrocarbons, alcohols, and esters were the highest, with 96.27% (240-0-air-ZY) and 62.22% (250-0-air-ZY) for 0 min at 240 and 250°C, respectively. O-containing compounds increased with the increase in reaction time from 2.29% (240-0-air-ZY) to 4.51% (240-15-air-ZY) at 240°C and decreased from 6.29% (250-0-air-ZY) to 2.75% (250-15-air-ZY) at 250°C.

At 240°C, the H_2 atmosphere decreased the N-containing compounds from 26.4% in air (240-0-air) to 15.31% in H_2 (240-0-H_2). But with zeolite Y, the H_2 atmosphere increased the N-containing compounds from 24.23% in air (240-0-air-ZY) to 29.42% in H_2 (240-0-H_2-ZY). On the other hand, the H_2 atmosphere (82.83%, 240-0-H_2) favours

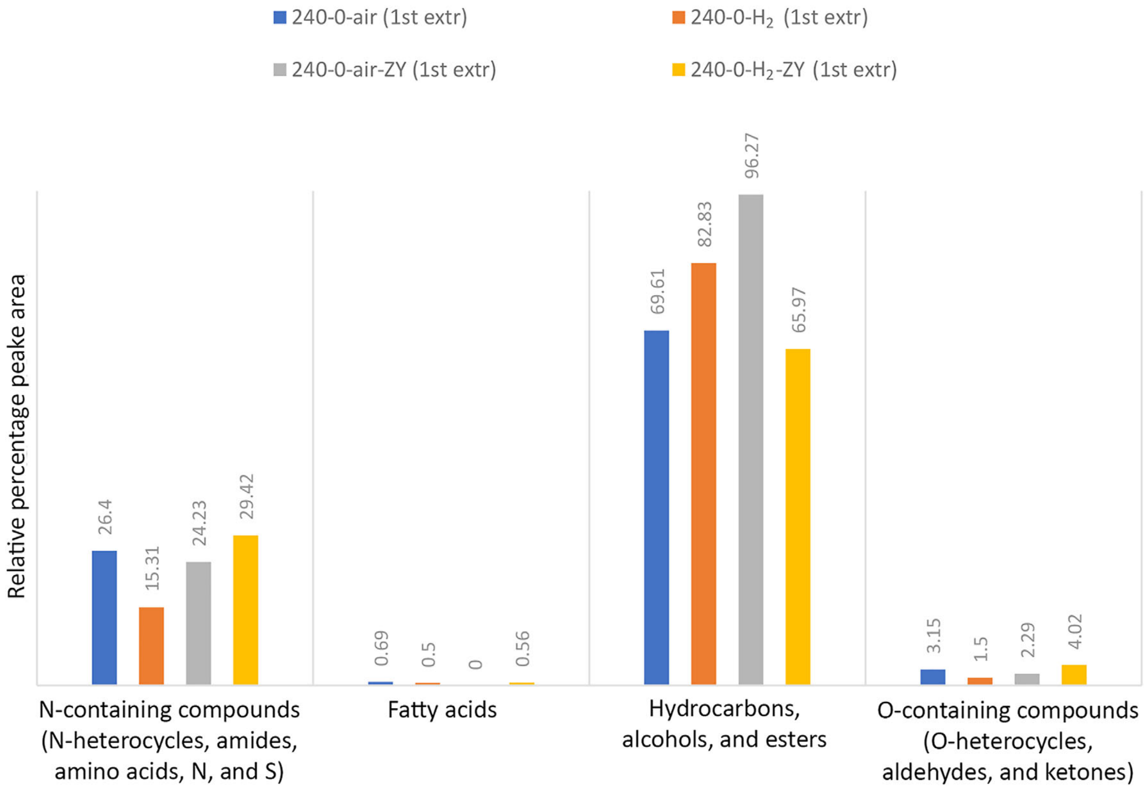


FIGURE 12 Variation in bio-oil (first extraction) components with different atmosphere at 240°C for 0 min

the content of hydrocarbons, alcohols, and esters over the air atmosphere (69.61%, 240-0-air). With zeolite Y, however, the air atmosphere (96.27%, 240-0-air-ZY) produced more content of hydrocarbons, alcohols, and esters than the H_2 atmosphere (65.97%, 240-0-H_2-ZY). As for O-containing compounds, the H_2 atmosphere decreased its portion in bio-oil, from 3.15% in air (240-0-air) to 1.5% in H_2 (240-0-H_2), but zeolite Y increased the O-containing compounds in the H_2 atmosphere (2.29%, 240-0-air-ZY) in comparison with the reaction in the air atmosphere (4.02%, 240-0-H_2-ZY) (Figure 12).

4 | DISCUSSION

HTL of Chlorella was performed in air and H_2 atmospheres at varying reaction times (0 and 15 min) and temperatures (240 and 250°C) in the absence of and in the presence of catalysts. The results are discussed in terms of non-catalytic HTL, catalytic HTL, and the quality of bio-oil below.

4.1 | Non-catalytic HTL

Non-catalytic HTL of Chlorella was influenced by temperature, reaction time, and reaction atmosphere in this study. The yield of bio-oil in air increased with the increase in temperature from 35.81% at 240°C to 39.14% at 250°C for 0 min, which represents *a*∼9% increase, and 38.75% at 240°C to 43.04% at 250°C for 15 min, which represents *a*∼11% increase. Reddy et al.[28] investigated the effect of temperature on HTL of *Nannochloropsis gaditana* and *Chlorella* sp. at 180 to 330°C for 30 min in N_2 atmosphere. Its yield of bio-oil from *Chlorella* sp. increased from 9.50% at 118°C to 29.70% at 250°C. A maximum 32.54% yield was observed at 300°C and a further increase in temperature slightly reduced the yield. The bio-oil yield of *Nannochloropsis* sp. increased from 16.85% at 180°C and stabilized at 25% at 250°C. Although a maximum yield of 47.5% was observed at 300°C, it required a much higher reaction temperature. Miao et al.[29] investigated the impacts of reaction condition on the production of bio-oil from *Chlorella sorokiniana* at 220–300°C for 60 min in the N_2 atmosphere. The yield of bio-oil increased with the increase in temperature from 15.9% at 220°C to 31% at 300°C for 60 min.

In our present study, we obtained better yield from the first extraction alone (39.14% at 250°C for 0 min in air and 43.04% at 250°C for 15 min) than the previous studies, which were investigated at higher temperatures and with longer reaction times. For the reaction time effect, the bio-oil yield in air increased with reaction time from 35.81% for 0 min to 38.75% for 15 min at 240°C, a~8% increase, and 39.14% for 0 min to 43.04% for 15 min at 250°C, a~10% increase. Alba et al.[23] studied the evaluation of HTL as the conversion method in an algae biorefinery concept: *Desmodesmus* sp. was used as biomass at 175–450°C for 5–60 min. They found that the HTL of *Desmodesmus* yielded 40.5 wt.% bio-oil within 5 min at 300°C as compared to the maximum yield of 46.6 wt.% at 60 min. Although it resulted in a slightly higher yield than that in our study, it required higher temperatures and longer reaction times. In this study, non-catalytic HTL of Chlorella in air resulted in better yields (39.14% for 0 min to 43.04% for 15 min at 250°C) than previous studies. Although these results were obtained with lower temperatures and shorter reaction times, changing atmosphere from air to H_2 increased the bio-oil yield even further. For example, at 240°C for 15 min, our result showed about a 11% increase, from 38.75% (in air) to 43.02% (in H_2). Similar enhancing effects of H_2 versus air as atmosphere were reported in the study of Akhtar and Amin[9] who reviewed the effects of temperature, atmosphere, residence time, etc. on the bio-oil yield and the quality of the product.

4.2 | Catalytic HTL

In catalytic HTL, zeolite Y plays a significant role in increasing the bio-oil yield. At 240°C for 15 min in air, the zeolite Y increased the bio-oil yield from 38.75% (240-15-air) to 43.03% (240-15-air-ZY), a~11% increase. In H_2, the increase was less, from 43.02% (240-15-H_2) to 45.03% (240-15-H_2-ZY), a~5% increase. However, at 250°C for 0 min in H_2, the yield jumps from 32.03% (250-0-H_2) to 43.06% (250-0-H_2-ZY) with the addition of zeolite Y. It increased by ~35%, the largest effect observed with zeolite Xu et al.[30] investigated the HTL of *Chlorella pyrenoidosa* catalyzed by Ce/HZSM-5 in the N_2 atmosphere at 300°C for 20 min. The bio-oil yield increased from 33.0% to 34.02% for HZSM-5 and 33.0% to 49.87% for Ce/HZSM-5. Ce/HZSM-5 produced more bio-oil than HZSM-5 because Ce enhanced the acidic properties of HZSM-5. The potential of Ce/HZSM-5 is good and will be investigated by our research group in the future. On the other hand, Zhang et al.[20] investigated five different zeolite catalysts (HZSM-22, HZSM-5, H beta, MCM-22, and SAPO-11) in the catalytic HTL of *Euglena* sp. at 280°C for 30 min. These zeolite catalysts slightly decreased the bio-oil yield but improved the bio-oil quality. Interestingly, much higher bio-oil yields of HTL of *C. pyrenoidosa* in sub- and supercritical ethanol with heterogeneous catalysts (Raney Ni and HZSM-5) in H_2 and N_2 for 30 min were reported by Zhang et al.[22] They reported that the tested catalysts had no significant effect on the bio-oil yield in the temperature range of 240–300°C in N_2 or H_2. Saber et al.[31] investigated HTL of N*annochloropsis* sp. using nano-Ni/SiO_2 and synthesized zeolite in the argon atmosphere at 250°C for 60 min. The bio-oil yields of nano-Ni/SiO_2 > analcime zeolite are 30% and 24.0%, respectively. However, none of them had a promotion effect comparable to Zeolite Y on Chlorella in H_2 in this study. Zeolite Y in this investigation performed better at a shorter reaction time than previous studies. Jena et al.[12] investigated the effects of $Ca_3(PO_4)_2$ and NiO on the HTL of *S. platensis* at 350°C for 60 min. Both NiO and $Ca_3(PO_4)_2$ decreased the bio-oil yield by 24.3% (from 39.9% to 30.2%) and 13.5% (from 39.9% to 34.5%), respectively. Chen et al.[32] studied catalytic HTL of *Dunaliella tertiolecta* over carbon nanotubes-supported Co to produce bio-oil at 320°C for 30 min. Co/CNTs increased the bio-oil yield from 37.4% to 40.25% at 320°C for 30 min. Zeolite Y as a catalyst in our present study performed better than any other zeolites used in the previous studies. In our study, temperature (from 240 to 250°C) had a significant effect on the bio-oil yield from catalytic HTL, both in H_2 and air. Zeolite Y in air enhanced bio-oil yield with the increase in temperature from 35.53% (240-0-air-ZY) to 41.70% (250-0-air-ZY) for 0 min, a~17% increase. Zeolite Y in H_2 increased the yield of bio-oil with increasing temperature from 36.37% (240-0-H_2-ZY) at 240°C to 43.06% (240-15-H_2-ZY) at 250°C for 0 min, a~18% increase. Reaction time (from 0 to 15 min) had a more significant effect on the bio-oil yield than temperature. Zeolite Y increased the bio-oil yield in air at 240°C with the increase in time from 35.53% for 0 min to 43.03% for 15 min, a~21% increase, and 36.37% for 0 min to 45.03% for 15 min in H_2 at 240°C, a~23% increase. Replacing air with hydrogen in the reactor led to a slightly higher bio-oil yield in the presence of zeolite Y from 35.53% to 36.37% at 240°C for 0 min and 43.03% to 45.03% at 240°C for 15 min. Duan and Savage[1] investigated HTL of *Nannochloropsis* sp. with heterogeneous catalysts (Pd/C, Pt/C, Ru/C, Ni/SiO_2-Al_2O_3, and zeolite) in He and H_2 atmospheres at 350°C. High-pressure H_2 increased the bio-oil yield for Pd/C and decreased the bio-oil yield for Pt/C, Ru/C, Ni/SiO_2-Al_2O_3, and zeolite. It appears that the H_2 atmosphere effect is catalyst specific and likely, biomass and HTL condition specific. In our present study, we investigated a different biomass (Chlorella) and different HTL conditions than Duan and Savage's study. In addition, we used ethanol as a co-solvent and at a much lower reaction temperature. Hence, upon the addition of H_2, the bio-oil yield slightly increased.

4.3 | Quality of bio-oils

The elemental composition of bio-oils was influenced by reaction time and temperature. For temperature, the C content increased from 61.21% at 240°C to 63.10% at 250°C for 0 min. The O content decreased with increasing temperature. It decreased from 21.72% at 240°C to 17.95% at 250°C for 15 min. Similar results were reported by Li and Savage[33] who studied bio-oil obtained from HTL of *Nannochloropsis* sp. over HZSM-5 catalyst at 400–500°C in H_2 for 0.5–4 h. They reported that the C content increased with increasing temperature and the O content reduced with increasing temperature. The O content of the bio-oil also decreased to about one-third (from 8.35% to 2.81%) by treatment with HZSM-5 at 400°C. The H content slightly increased with increasing reaction time from 8.34% for 0 min to 8.58% for 15 min at 250°C. Similar to O content, the N content in the bio-oil decreased with the increase in reaction time from 8.02% for 0 min to 7.78% for 15 min at 250°C. With an increase in C content and a decrease in O and N contents, the ratios of H/C, N/C, and O/C in the bio-oil decreased as the temperature increased from 240 to 250°C. Similarly, Li and Savage[33] reported that the ratios of H/C, N/C, and O/C decreased with the increase in temperature. The HHV of bio-oil increased with temperature from 29.40 kJ/g at 240°C to 30.17 kJ/g at 250°C for 0 min and 29.55 kJ/g at 240°C to 31.49 kJ/g at 250°C for 15 min. Reddy[28] reported that the HHV of bio-oil increased with temperature due to the deoxygenation of bio-oil at high temperature. The trend of HHV in our present study matched well with previous studies. As a result, energy recovery of the bio-oil increased with increasing reaction time from 48.90% for 0 min to 55.32% for 15 min at 240°C due to higher HHV of the bio-oil from a longer reaction time. Based on TGA results, H_2 atmosphere and plasma treated zeolite Y[18] increased the 110–300°C fraction of bio-oils from the HTL of Chlorella. The H_2 atmosphere (without catalyst) enhanced the 110–300°C fraction of bio-oil the most, from 31.19% (240-15-air) to 39.25% (240-15-H_2) at 240°C for 15 min, $a{\sim}26\%$ increase. Argon plasma mildly increased the 110–300°C fraction of zeolite Y[18] in H_2 from 31.94% (250-0-H_2-ZY) to 36.63% (250-0-H_2-ZY-AP) at 250°C for 0 min. H_2 plasma zeolite Y increased the 110–300°C fraction from 32.68% (250-15-H_2-ZY) to 38.43% (250-15-H_2-ZY-HP) at 250°C for 15 min, $a \sim 18\%$ increase. This aspect indicated that zeolite Y and plasma zeolite Y with acidic sites and large surface area could promote the cracking of heavier crude of bio-oils to the 110–300°C fraction. Zhang et al.[20] reported that zeolite catalysts (HZSM-5, H beta and SAPO-11) altered the boiling point distribution of the bio-oils of *Euglena* sp. The contents of gas oil components (180–410°C) with zeolite catalysts were reported to increase by 7%–23%. In our present study, we obtained a smaller catalytic effect using zeolite Y. However, H_2 plasma zeolite Y increased the 110–300°C fraction significantly at 250°C for 15 min in H_2, from 31.29% to 38.43%, $a{\sim}23\%$ increase. The components of bio-oil obtained from GC–MS showed that the portion of N- and O-containing compounds increased with temperature from 240 to 250°C. The portion of hydrocarbons, alcohols, and esters decreased with temperature. Gai et al.[34] investigated the reaction pathway of HTL using *C. pyrenoidosa* and *S. platensis* at 200 and 320°C. They also reported that the portions of N- and O-containing compounds in the bio-oil increased with the increase in temperature from 200 to 320°C. Higher temperatures enhance the repolymerization and recombination of the reaction intermediates of bio-oil.[35] Similar to our study, Gai et al.[34] reported that the portion of esters and alcohols of the bio-oil decreased with the increase in temperature. In addition, our study showed that the H_2 atmosphere (without catalyst), zeolite Y, and plasma zeolite Y decreased (with some exceptions) the portion of N-containing compounds in the bio-oil. The H_2 atmosphere (without catalyst) significantly decreased the portion of N-containing compounds almost to half from 26.4% (240-0-air) to 15.31% (240-0-H_2) at 240°C for 0 min, $a{\sim}42\%$ reduction. Zhang et al.[20] reported the portion of N-containing compounds (from *Euglena* sp. at 280°C for 30 min) decreased with H beta zeolite from 30.87% to 16.68%. It represented a 46% decrease. They reported that the acidity of zeolite causes the denitrification of bio-oils. Similar to the N-containing compounds, the portion of O-containing compounds decreased (with some exceptions) with H_2 atmosphere zeolite Y. O-containing compounds reduced with H_2 atmosphere by ~52% at 240°C for 0 min, 240-0-air versus 240-0-H_2. Under H_2 atmosphere, zeolite enhanced (with some exceptions) the portion of hydrocarbons, alcohols, and esters in the bio-oil for fuel purposes. The H_2 atmosphere (without a catalyst) increased the portion of hydrocarbons, alcohols, and esters at 250°C for 0 min by ~37%. Similar results were obtained by Zhang et al.,[20] who reported that H beta zeolite increased the hydrocarbons, alcohols, and esters (from *Euglena* sp. at 280°C for 30 min) in the bio-oil from 33.86% to 58.34%.

5 | CONCLUSIONS

Non-catalytic HTL of Chlorella is influenced by temperature, time, and the reaction atmosphere. The yield of bio-oil in air increased with temperature, from 35.81% at 240°C to 39.14% at 250°C for 0 min, which represented $a{\sim}9\%$ increase, and 38.75% at 240°C to 43.04% at 250°C for 15 min, which represented $a{\sim}11\%$ increase. The bio-oil yield in air increased with the increase in time, from 35.81% for 0 min to 38.75% for 15 min at 240°C, ~8% increase, and 39.14% for 0 min to 43.04% for 15 min at 250°C, ~10% increase. Using H_2 atmosphere instead of air during non-catalytic HTL also increased the bio-oil yield to about the same level.

The addition of zeolite Y plays a significant role in increasing the bio-oil yield. At 240°C for 15 min, the zeolite Y increased the bio-oil yield, by ~11% and ~5% in air and H_2, respectively. However, at 250°C for 0 min in H_2, the yield jumps significantly with the addition of zeolite. It increased by ~35% from 32.03% (250-0-H_2) to 43.06% (250-0-H_2-ZY). The temperature effect on bio-oil yield in the presence of zeolite Y in H_2 is relatively mild, ~18%. The reaction time effect in H_2 is larger, ~23%.

The elemental compositions of bio-oils were influenced by reaction time and temperature. As the temperature increased from 240 to 250°C, the C content increased, the O content and N content decreased, and the ratios of H/C, N/C, and O/C decreased. HHV and ERR increased with the increase in reaction time and temperature.

Overall, the introduction of H_2 atmosphere and zeolite Y in the HTL of Chlorella increased the bio-oil yield; reduced the N- and O-containing compounds; enhanced the content of hydrocarbons, alcohols, and esters; and increased the 110–300°C fraction of bio-oils.

AUTHOR CONTRIBUTIONS

Tarek Md. Anamul Haque: Conceptualization; data curation; formal analysis; investigation; methodology; resources; validation; writing – original draft; writing – review and editing. **Michael Brdecka:** Data curation; formal analysis; visualization. **Valeria Duran Salas:** Data curation; formal analysis; resources. **Ben Jang:** Funding acquisition; investigation; methodology; project administration; supervision; validation; writing – review and editing.

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PEER REVIEW

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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