Effects of plasma modification and atmosphere on catalytic hydrothermal liquefaction of Chlorella.

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ABSTRACT: The development of third generation biofuels from microalgae has seen extensive researched over the last few years. Hydrothermal liquefaction (HTL) is a promising route for producing of bio-oils from wet algae. The major drawback in HTL is the high temperature and high pressure which result in high capital cost of the process. To make HTL an economical process for bio-oil production, the temperature and pressure should be reduced and can be achieved by adding alcohol to water for HTL. The efficiency of the HTL process can also be improved by using a suitable heterogeneous catalyst with additional modifications. In this work, we investigated the effect of dielectric barrier discharge (DBD) plasma (argon and hydrogen plasma) modified zeolite Y as catalysts on the yield and quality of bio-oils produced in hydrogen atmosphere versus air at different reaction times (0 min and 15 min) and temperatures (240 °C and 250 °C). The mixture of solvents (50 vol. % water & 50 vol. % ethanol) was used in HTL to increase the yield and quality of bio-oils. Two sequential extractions were used to extract bio-oils from HTL products using dichloromethane. Different analytical techniques, such as thermal gravimetric analysis, elemental analysis, and gas chromatography-mass spectrometry, were used to understand the physicochemical properties of the bio-oils and for the determination of higher heating value (HHV). The introduction of DBD plasma to modify zeolite Y improved the bio-oil quality and yield from HTL processes. H_2 plasma modified catalyst enhanced the bio-oil yield at 240℃ from 46.83±1.48% (240-0-H_2-ZY) to 50.04±0.88% (240-0-H_2-ZY-HP) and from 50.24±1.96% (250-0-H_2-ZY) to 53.01±0.73% (250-0-H_2-ZY-HP) at 250 °C. Argon plasma modified catalyst reduced N-containing compounds from 29.42 % (240-0-H_2-ZY) to 2.94 % (240-0-H_2-ZY-AP) and decreased O-containing compounds from 4.02 % (240-0-H_2-ZY) to 1.38 % (240-0-H_2-ZY-AP) at 240℃.

1.0 INTRODUCTION

The global economy and population are growing rapidly. The traditional fossil fuels are aggressively depleted and cause environmental pollution. Hence an alternative of fossil fuel must be developed. Biofuels may be an excellent alternative of fossil fuel. Microalgae have been addressed as a source of the third-generation biofuels. Microalgae has several advantages including faster growth rate, highest photosynthesis efficiency [1], shorter growth cycles, higher lipid content and ability to sequester carbon dioxide. Moreover, algae production can occur in wastewater, marginal lands, saline water, and this has less impact on food supply with significant environmental benefits [2, 3].

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. Biomass can be converted into 'bio-crude' or 'bio-oil' with water at high temperature and high pressure via hydrothermal liquefaction. The process is generally carried out at temperature between 200-400°C and the pressure ranging between 10-25 MPa with or without catalyst in a high temperature high pressure (HTHP) reactor [4, 5]. These reaction conditions are sufficient to hydrolyze and decompose the proteins, carbohydrates, and lipids found in the biomass into smaller molecules which make up the bio-oil [5]. The feedstock characteristics of the biomass and various operating conditions (e. g. temperature, residence time, microalgae/solvent ratio, catalyst, and solvent etc.) determine the properties and product distribution of the bio-oils [6].

Biofuels obtained from HTL contain high percentage of nitrogen and oxygen. The high percentage of nitrogen and oxygen reduces the fuel efficiency of bio-oils and produces pollutants when burned. Catalysts can play an important role to improve the bio-oils quality and yield. Some acids (HCOOH, CH_3COOH) and alkali ($Na_2CO_3$and KOH) are widely used as homogeneous catalysts in HTL [7]. The homogeneous catalyst Na_2CO_3 can efficiently liquefy the algae which contain high amount of carbohydrate, but not so for algae containing high amount of proteins [8].

The heterogeneous catalysts are more desirable than homogeneous catalysts because (i) homogeneous catalysts may not be stable at severe conditions but heterogeneous catalysts sustain in the drastic condition (ii) separation of heterogeneous catalysts from reaction products can be

done easily. Zeolite catalysts exhibited excellent catalytic effects during HTL of microalgae. Xu *et al.* [9] first studied the impact of two zeolites (HZSM-5, Ce/HZSM-5) on HTL of *Chlorella pyrenoidosa* in N_2 atmosphere at 300 °C for 20 min. Active acidic sites, large surface area and channel structure of zeolites enhance the cracking reaction of bio-oils [10]. Widayanto *et al.* [11] investigated four high-silica zeolites namely HSZ-385, 890, 960, 990 in HTL processes and found that all zeolites enhanced the bio-oil deoxygenation and HSZ-960 (beta) exhibited a unique selectivity for hydrocarbons. Duan *et al*. [12] studied the effect of nine types of zeolites in H_2 atmosphere in HTL and observed that all zeolites due to the presence of acid sites enhance the denitrification and deoxygenation of the bio-oil. Wu *et al.* [13] 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. The best catalytic performance was exhibited by H beta zeolite. The zeolite catalysts slightly decreased the bio-oil yield but improved the bio-oil quality. Li and Savage [14] studied bio-oil obtained from HTL of *Nannochloropsis* sp. over HZSM-5 catalyst at 400-500 °C in H_2 for 0.5-4h. HZSM-5 greatly reduced the content of N, S, O in the bio-oil and decreased the bio-oil yield at 500 °C.

The overall aim of this project is to inspect the effect of Dielectric Barrier Discharge (DBD) plasma modified zeolite catalyst (zeolite Y) for the production of bio-oils and improve the bio-oils quality from microalgae (*Chlorella*) through hydrothermal liquefaction. Meanwhile, no research work has been noticed on the application of DBD plasma modified zeolite Y in the HTL process. DBD plasma works at atmospheric pressure and produce a low temperature plasma. The operating parameters of plasma such as supplied power, treatment time, used gases and their flow rate play an important role for the modification of material surfaces [15, 16]. A lot of details have been summarized in the review by Liu et al. [17] Catalyst Preparation with Plasmas: How Does It Work?

2.0 EXPERIMENTAL SECTION

2.1 Materials. *Chlorella* was used as a biomass purchased from Stakich Inc. The Zeolite Y purchased from Alfa Aesar having surface area 780 m^2/g, 30:1 mole ratio of SiO_2:Al_2O_3. For ethanol reactions, 200 proof absolute purity ethanol purchased from VWR U.S. and dichloromethane from Acros Organics, U.S.A. Deionized water was used for water reactions. The UHP argon and H_2 gases were purchased from Airgas, an Air Liquide Company. All other chemicals and equipment used for this experiment were lab grade.

2.2 DBD Plasma Modification of Catalyst. The dielectric barrier discharge (DBD) plasma used for modifying zeolite catalysts (Zeolite Y, hydrogen or argon) is a CTP-2000 K, plasma generator with a primary voltage difference of 80 V and frequency of 1.1–1.2 kHz, the same as the one in the literature [18,19]. The discharge is generated between two plane electrodes that is covered by 3mm thick Pyrex glass dielectric plates. The distance between the two glass dielectric plates is 12 mm. Plasmas were generated using H_2 gas and argon gas. The flow rate of UHP argon/H_2 with 30mL/min used in the plasma. The DBD plasmas run for 30 min to modify the catalyst.

2.3 Hydrothermal Liquefaction. The hydrothermal liquefaction will be carried out in a 100 mL batch reactor equipped with an auto-mated stirrer, an electric heater, a temperature controller, and a sample tube. 4.5 g of dried algae introduced into the sample tube of the reactor followed by adding 22.5 g deionized water and 17.75 g ethanol. In experimental runs including catalyst, 0.225 g catalyst (5 wt. %) is also loaded into the sample tube. Hydrothermal liquefaction (HTL) of *Chlorella* run under air atmosphere and hydrogen atmosphere. During the HTL in hydrogen atmosphere, hydrogen gas purged into the reactor to a pressure of 150 psi. Hydrogen gas purged five times to expel the air from the reactor. The reactor heated from the ambient temperature to the desired temperature, 240 °C or 250 °C with a temperature ramp at 6 °C/min. The automated stirrer used at a constant stirring rate to keep the temperature uniform inside the sample tube. After reaching the 240 °C or 250 °C temperature, the holding time of the sample was 0 and 15 min. HTL reaction condition is denoted such as 240-0-air for reaction at 240 °C in air atmosphere for 0 min reaction time and 250-15-H_2-ZY-HP represented reaction at 250 °C in H_2 atmosphere for 15 min reaction time and H_2 plasma modified zeolite Y act as a catalyst. Once the holding time is completed, the temperature set to the ambient temperature to cool down the reactor using fan.

After cooling down at ~ 40 °C, the reactor was depressurized before opening. Two extractions were carried out for bio-oil from the final product. In the first extraction, 25 mL of dichloromethane (DCM) mixed with final product. The aim of adding DCM is the extraction of organic components from both liquid and solid products. The mixture then filtered by Buchner funnel connected to a vacuum pump and the filter paper used in filtration was a medium mesh size. Two immiscible liquid phases (organic solvent soluble, water soluble) kept in separation funnel

overnight. After extraction of first phase bio-oil, same method followed by adding 25 mL of dichloromethane (DCM) with the residue left (aqueous phase) in the separation funnel. This is called the 2nd extraction. The DCM evaporated by using a rotary evaporator under a vacuum at 45°C for 20 min. and ethanol evaporated at 78 °C for 40 min. The bio-oil obtained after the evaporation of organic and has a dark color and high viscosity. During the evaporation of DCM, some light components of the bio-oil are lost which is reported to be less than 3% of the total mass of the bio-oil [20]. The percentage of yield of bio-oil calculated by the following formula.

$$Bio\text{-}oil\ Yield\ (\%) = \frac{Mass\ of\ Bio\text{-}oil\ (g)}{Mass\ of\ Dried\ Microalgae\ (g)} * 100\%$$

2.4 Bio-oil Analysis. The elemental composition of the bio-oil analyzed in Atlantic Microlab (6180 Atlantic Blvd # M, Norcross, GA 30071) to determine C, H, S, N and O content determined by difference (100-C-H-N-S). The higher heating value calculated via Boie's formula [21].

HHV (MJ/Kg) = 0.3516*C + 1.16225*H – 0.1109*O + 0.0628*N + 0.10465*S…… (1)

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

The energy recovery ratio (ERR) was used to study the energy of the bio-oils relative to the energy input of the microalgae [13]. The energy recovery was calculated as follows:

$ERR\ (\%) = (Y_{bio\text{-}oil} \times HHV_{bio\text{-}oil})/HHV_{feedstock} \times 100\ \%$..... (2)

Where, $Y_{bio\text{-}oil}$, $HHV_{bio\text{-}oil}$ and $HHV_{feedstock}$ were the bio-oil yield and HHV (MJ/Kg) of bio-oils and *Chlorella* respectively.

Bio-oil analyzed by using Gas Chromatography-Mass Spectrometry (a Trace 1300 GC with an ISQ QD Single Quadrupole MS, Thermo Scientific, U.S.A). A 0.5 µL sample injected using an automatic injector into the inlet port where it was vaporized at 300°C. The sample carried through a TG-5MS column with 30 m long, ID 0.32 mm and film thickness 0.25 µm and low polarity 5 % diphenyl and 95 % dimethyl polysiloxane with 1.5 ml/min helium. The column heated from 80°C, ramped 3°C/min, to 275°C and held for 10 min. The transfer line set to 250°C and ion source with an electron energy of 70 eV. Scan mass range set for 50-550 amu for 0.2sec and begun analyzing after 2.5min to avoid solvent peak. The MS used as a detector and split ratio was 3.

Compounds were identified according to the NIST library.

Thermal Gravitational Analysis (TGA) is an analytical technique that measures the change of weight as a function of temperature or time. Using a sample pan connected to a microbalance and exposed to heat up to 800°C, small mass changes can be observed [22]. Through this technique, we plan to use it as a miniature "distillation" by observing the boiling point distribution of the bio-oil and comparing it to crude oil [23]. The TGA carried out (TGA-Q500, TA Instrument) from the ambient temperature to 800°C under 40 mL min^{-1} nitrogen flow. The temperature raised from the ambient temperature to 800 °C ramp at 10 °C min^{-1} and isothermal at 25 °C for 5 min and at 800 °C for 5 min.

3.0 RESULTS

3.1 Bio-oil Yield

Hydrothermal liquefaction (HTL) of *Chlorella* were run under different conditions (temperature, time, atmosphere, and catalyst) to investigate the influence of these factors on the bio-oil yield. We classify the reactions as catalytic HTL and plasma modified catalytic HTL. We emphasized on the 1st extraction of the bio-oil yield because this is mainly coming from the organic layer and more than 80% of total yield of bio-oil is from the organic layer. Table 1 shows the percentages of yield of bio-oil at different HTL conditions of *Chlorella*. HTL condition presented including 4 conditions air-ZY, H_2-ZY, H_2-ZY-AP and H_2-ZY-HP at 240-0, 240-15, 250-0 and 250-15.

3.2 Effect of Plasma on the Bio-oil Yield

Plasma treatment induces changes on the surfaces of the catalysts. Argon and hydrogen plasma were used for the modification of zeolite Y. Plasma treatment modifies the acidity of zeolite catalysts. The aim of utilizing catalysts is to improve the yield and/or the quality of bio-oil. Catalytic HTL of microalgae has been reported to increase the bio-oil yield up to 50% in comparison to non-catalytic HTL [24].

In this study, plasma increased the bio-oil yield from 36.37 % with zeolite Y to 43. 76 % with H_2 plasma modified zeolite Y at 240 °C for 0 min. At 240 °C for 0 min, H_2 plasma modified

zeolite Y was more effective than argon plasma modified zeolite Y. H_2 plasma treatment leads to a higher degree of surface functionalization (partial dealumination of the Zeolite Y and thereby to an increase the number of acidic sites) of the catalyst and results in the increase of the bio-oil yield [25]. Both H_2 and argon plasma treatments had no significant effect on the yield of bio-oil for 15 min at 240 °C and at 250 °C for 0 min. On the other hand, the bio-oil yield increased from 43.3 % with zeolite Y to 45.04 % with argon plasma modified zeolite Y for 15 min at 250 °C. At 250 °C for 15 min, argon plasma modified zeolite Y was more effective than H_2 plasma modified zeolite Y.

Table 1: The percentages of yield of bio-oil from HTL of Chlorella at different HTL conditions-ZY-Zeolite Y, AP-Argon plasma, HP-Hydrogen plasma, air-Air atmosphere, H_2-Hydrogen atmosphere.

HTL condition	1st extraction (%)	2nd Extraction (%)	Total Yield (%)	HTL condition	1st extraction (%)	2nd Extraction (%)	Total Yield (%)
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
240-0-H_2-ZY-AP	42.53±0.35	5.43±0.31	47.96±0.66	250-0-H_2-ZY-AP	40.42±0.16	8.86±0.42	49.28±0.58
240-0-H_2-ZY-HP	43.76±0.74	6.28±0.14	50.04±0.88	250-0-H_2-ZY-HP	43.82±0.61	9.19±0.12	53.01±0.73
240-15-air-ZY	43.03±0.05	6.67±1.15	49.7±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	51.2±1.39	250-15-H_2-ZY	43.30±0.51	6.98±0.43	50.28±0.94
240-15-H_2-ZY-AP	44.09±0.03	5.65±0.39	49.74±0.42	250-15-H_2-ZY-AP	45.04±0.58	7.22±0.18	52.26±0.76
240-15-H_2-ZY-HP	45.20±0.17	6.58±0.12	51.78±0.29	250-15-H_2-ZY-HP	44.73±0.07	6.73±0.76	51.46±0.83

3.3 Elemental Analysis of Bio-oil

CHNOS analysis results of the bio-oils are presented in Table 2. We consider average percentage of (bolded rows in Table 2) the elements at different HTL condition to explain the variation of CHNOS and its high heating value (HHV) with reaction time and temperature. 18 samples of the 1st extraction of bio-oil placed at the top of Table 2 and 6 samples of the 2nd extraction of bio-oil placed at the bottom of Table 2.

The C and H contents in the bio-oils are higher than those of the biomass, whereas the decreased O and N contents lead much higher HHVs of the biomass (Table 2). The elemental analysis shows that the C content of the bio-oils increase with temperature for 0 min and 15 min

reaction times. The C content in the 1st extraction (61.83 % at 240 ºC, 15 min) bio-oil is higher than that of the 2nd extraction (60.71 % at 240 ºC, 15 min). The N content of the 1st extraction bio-oil increase with temperature as well for 0 min and 15 min reaction times. Nitrogen compounds are polar and tend to be more easily found in the 2nd extraction bio-oil (from the aqueous phase). Therefore, the N content of the 2nd extraction (10.84 % at 240 ºC for 15 min) is higher than in the 1st extraction (7.76% at 240 ºC for 15 min). However, the N content of the bio-oils from HTL of *chlorella* is much higher (7-8 wt. %) than that of petroleum (0-0.8 wt. %) [26]. Further refining is necessary for fuel purposes. The O content of bio-oils decreased steadily with the increase of temperature. Temperature is a vital factor which can influence the oxygen removal of bio-oil, especially in the presence of zeolite catalysts [27]. In general, the O content of 1st extraction bio-oils is slightly higher than the one of the 2nd extraction, for example 21.52 % vs 20.24 % at 240 ºC for 15 min.

As shown in Table 2, the contents of C and-, H in the 1st extraction increase with the increase of reaction time (0 min to 15 min) and N and-, O contents decrease with the reaction time (0 min to 15 min). The reduction of N and O content in the bio-oils during HTL reactions are typically via dehydration, decarboxylation, and deamination [28, 29]. Longer reaction time and higher temperature promote the dehydration, decarboxylation and deamination reactions and improve the bio-oil quality.

The ratios of H/C, O/C and N/C in the 1st extraction bio-oils decrease with increasing temperature from 240 ºC to 250 °C. On the other hand, under the same HTL condition, such as 240 ºC for 15 min the O/C and-, H/C ratios in the 2nd extraction are lower than the 1st extraction, but the N/C ratio is higher in the 2nd extraction.

The high heating value (HHV) in the 1st extraction bio-oils increase with increasing reaction time and temperature. The HHV of the 2nd extraction bio-oil at 240 ºC for 15 min (28.94 kJ/g) is lower than the 1st extraction under the same HTL condition (30.02 kJ/g for 15 min at 240 ºC). The bio-oil with the highest HHV (31.49 kJ/g) due to the lowest O and N contents is obtained under HTL at 250 ºC for 15 min. Energy recovery increase with increasing reaction time from 0 min to 15 min. Temperature had a significant effect on energy recovery for 0 min reactions, but not for 15 min reactions.

The best reaction condition in terms of energy recovery and quality of bio-oils in this study is at 250 ºC for 15 min. These high heating values are significantly higher than that of the dry microalgal feedstock (~19 kJ/g) but lower than that of petroleum crude oil (43 kJ/g) [22].

Table 2: Elemental analysis and HHV of the 1st and 2nd extraction bio-oil obtained from HTL of *Chlorella.*

HTL condition	1st extraction Bio-oil yield (%)	Elemental analysis (%)							HHV (MJ/g)	Energy recovery (%)
		C	H	N	O	H/C	N/C	O/C		
Chlorella		51.34	7.29	9.35	31.45	1.7	0.212	0.816	23.09	
240-0-air-ZY	35.53 (1st)	56.49	8.61	7.22	27.23	1.83	0.149	0.642	27.35	42.09
240-0-H_2-ZY	36.37 (1st)	61.98	8.33	8.19	21.05	1.61	0.154	0.453	29.7	46.78
240-0-H_2-ZY-AP	42.53 (1st)	62.21	8.44	7.93	21.42	1.63	0.149	0.459	29.8	54.89
240-0-H_2-ZY-HP	43.76 (1st)	61.02	8.4	7.82	22.76	1.65	0.15	0.497	29.18	55.3
Average	**38.4**	**60.43**	**8.45**	**7.79**	**23.12**	**1.68**	**0.15**	**0.513**	**29**	**49.77**
240-15-air-ZY	43.03 (1st)	59.72	8.79	7.42	23.68	1.64	0.145	0.529	28.2	52.55
240-15-H_2-ZY	45.03 (1st)	63.19	8.35	7.89	20.23	1.59	0.146	0.427	30.22	58.93
240-15-H_2-ZY-AP	44.09 (1st)	62.06	8.48	7.84	21.24	1.63	0.147	0.456	29.85	56.99
240-15-H_2-ZY-HP	45.20 (1st)	62.32	8.52	7.88	20.93	1.64	0.148	0.448	30.02	58.77
Average	**44.34**	**61.83**	**8.54**	**7.76**	**21.52**	**1.63**	**0.147**	**0.465**	**29.58**	**56.81**
250-0-air-ZY	44.01 (1st)	63.45	8.42	7.79	19.9	1.59	0.143	0.418	30.43	58
250-0-H_2-ZY	38.77 (1st)	63.98	8.23	7.89	19.46	1.54	0.144	0.406	30.46	51.14
250-0-H_2-ZY-AP	44.98 (1st)	60.92	8.36	8.02	22.7	1.65	0.144	0.497	29.12	56.73
250-0-H_2-ZY-HP	44.30 (1st)	61.8	8.26	8.09	21.85	1.6	0.153	0.471	29.42	56.44
Average	**40.26**	**62.54**	**8.32**	**7.92**	**20.98**	**1.59**	**0.146**	**0.448**	**29.86**	**55.58**
250-15-air-ZY	37.92 (1st)	67	8.59	8.15	15.87	1.54	0.142	0.316	32.34	53.11
250-15-H_2-ZY	42.79 (1st)	65.69	8.67	7.82	17.48	1.58	0.139	0.355	31.77	58.88
250-15-H_2-ZY-AP	44.46 (1st)	62.63	8.62	7.58	21.17	1.65	0.141	0.372	30.17	58.09
250-15-H_2-ZY-HP	44.80 (1st)	64.99	8.53	8.18	18.3	1.58	0.147	0.375	31.24	60.61
Average	**40.74**	**65.08**	**8.6**	**7.93**	**18.21**	**1.58**	**0.142**	**0.354**	**31.38**	**57.67**

HTL condition	2nd extraction	Elemental analysis (%)	HHV (kJ/g)	Energy recovery (%)

	Bio-oil yield (%)	C	H	N	O	H/C	N/C	O/C		
240-15-air	8.45 (2nd)	61.8	7.81	10.54	19.45	1.52	0.199	0.42	29.35	10.74
240-15-H_2	6.19 (2nd)	60.74	7.92	10.86	20.13	1.56	0.209	0.442	29.06	7.79
240-15-air-ZY	5.51 (2nd)	61.55	7.87	10.88	19.31	1.53	0.206	0.418	29.37	7
240-15-H_2-ZY	5.32 (2nd)	61.13	7.94	10.77	19.76	1.56	0.206	0.431	29.25	6.74
240-15-H_2-ZY-AP	5.65 (2nd)	59.3	7.74	11.17	21.4	1.57	0.22	0.481	28.22	6.91
240-15-H_2-ZY-HP	6.58 (2nd)	59.71	7.78	10.82	21.36	1.56	0.211	0.477	28.38	8.09
Average	**6.28**	**60.71**	**7.84**	**10.84**	**20.24**	**1.55**	**0.208**	**0.445**	**28.94**	**7.88**

3.4 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) in N_2 has been used to estimate the boiling point distribution of bio-oils. TGA performed under N_2 atmosphere from 25 °C to 800 °C resulted in a percentage of weight loss about >95 %. Figure 1 shows TGA results the 1st extraction of bio-oil from catalytic HTL of *Chlorella* at 240 °C. It is revealed from the TGA graph, including weight loss and derivative of weight loss versus temperature, that highest four peaks are at 110.64 °C, 271.47 °C, 397.43 °C, 563.02 °C. The first peak at 110.64 °C can be corresponding to the boiling point ranges of both 25-110℃ of bottle gas and chemicals and 110-200 °C of gasoline. The second peak at 271.47 °C corresponds to the boiling point range of 200-300 °C of jet fuel, fuel for stoves, and diesel oil. The third peak at 397.43 °C corresponds to the boiling point range of 300-400 °C of lubricating oil for engines, fuel for ships, and machines. The fourth peak at 563.02 °C corresponds to the boiling point range of 550-700 °C of fuel for ships, factories, and central heating.

We emphasized the distillation of bio-oils in the boiling point range 110-300 °C as it consists of gasoline, jet fuel, fuel for stoves and diesel oil. Boiling point distribution of bio-oils with catalysts in different atmospheres at 240 °C and 250 °C for 0 min and 15 min (see Tables 1-4 in supporting information). The percentage of weight loss can be influenced by the reaction atmosphere and plasma treatments. Figures 2 presents the effect of reaction atmosphere and plasma

treatments on the boiling point range of 110-300 °C of bio-oils obtained at 240 °C and 250 °C for 0 min and 15 min.

Plasma modified zeolite Y performed better than zeolite Y without plasma treatments in terms of producing the boiling point range of 110-300 °C in bio-oils from HTL reactions at 250 °C, including- Argon plasma modified zeolite Y at 250 °C for 0 min and H_2 plasma modified zeolite Y at 250 °C for 15 min. Argon plasma modified zeolite Y at 250 °C for 0 min increased the 110-300℃ range of bio-oil from 31.94 % (250-0-H_2-ZY) to 36.63 % (250-0-H_2-ZY-AP). H_2 plasma modified zeolite Y at 250 °C for 15 min increased the 110-300℃ range from 32.68 % (250-15-H_2-ZY) to 38.43 % (250-15-H_2-ZY-HP). The results indicate that using H_2 plasma modified zeolite Y for HTL in H_2 atmosphere at 250 °C for 15 min can produce the most fuels in bio-oils with the 110-300℃ boiling range.

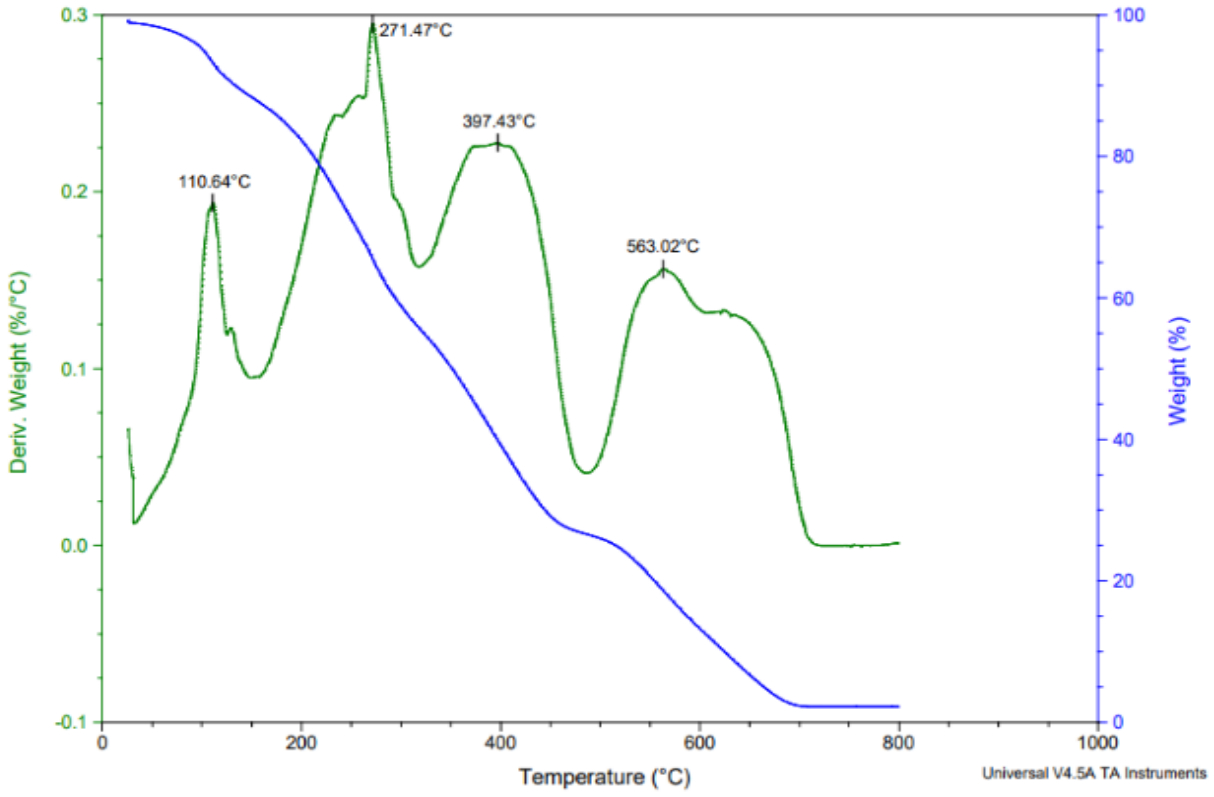
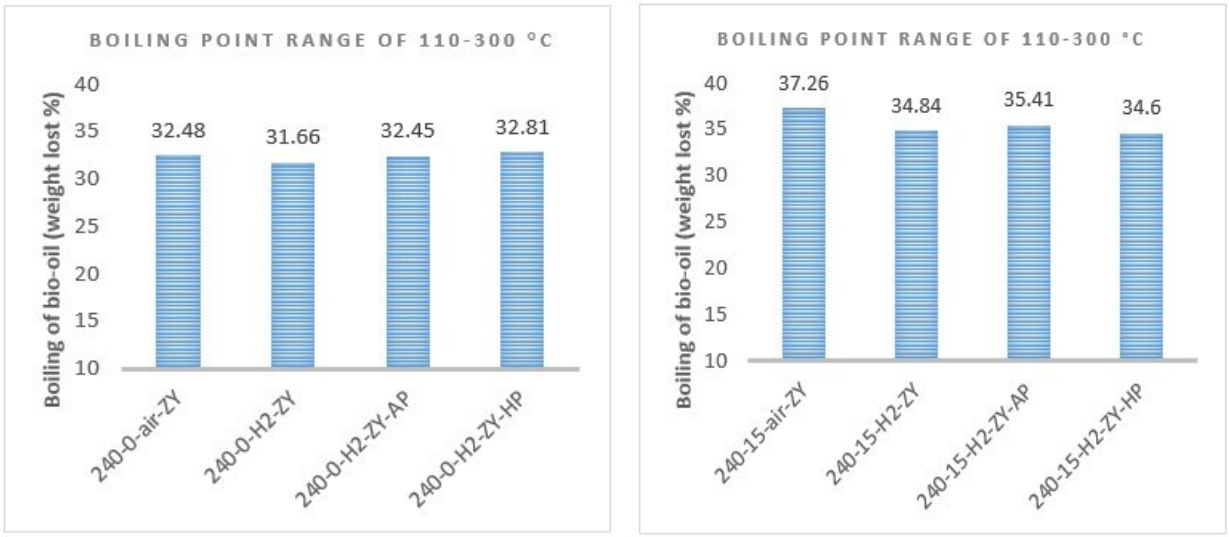
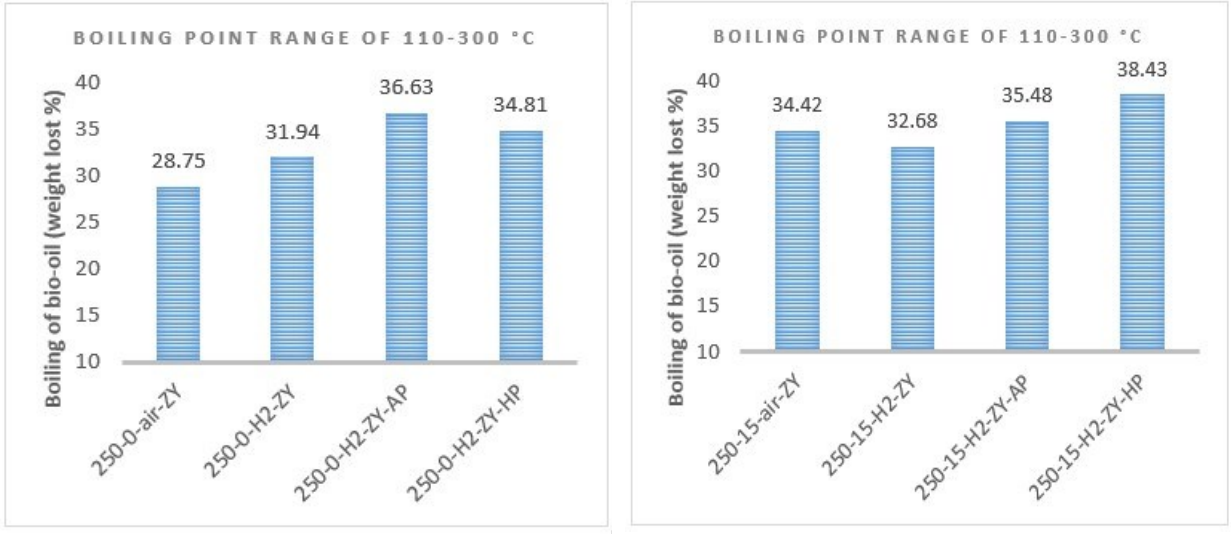


Figure 1: TGA Graph of Bio-Oil from H_2 Plasma modified Zeolite Y in H_2 Atmosphere at 240 ºc for 15 Min.



(a) (b)



(C) (d)

Figure 2: Effect of plasma modified Zeolite Y on bio-oil in the boiling point range of 110-300 °C from HTL of *Chlorella* (a) at 240 °C for 0 min reaction time, (b) at 240 °C for 15 min, (c) at 250 °C for 0 min, and (d) 250 °C for 15 min.

3.5 GC-MS Analysis

The detailed components of the bio-oils from catalytic HTL of *Chlorella* were identified by GC-MS analysis. Not all the components of the bio-oils cannot be characterized through GC-MS because (i) low molecular weight compounds might be lost during the solvent evaporation process for bio-oil recovery (ii) high molecular weight compounds with much higher boiling points could not elute from the GC column with the maximum column programmed temperature of 275°C [30]. The components of the bio-oil were grouped into different categories based on their functional groups such as amide, N-heterocycle, amino acid, ketone, aldehyde, hydrocarbon, N & S, O-heterocycle, alcohol, ester, and fatty acid. The major components of the bio-oil were N-containing compounds (N-heterocycle, amides, amino acids, and N & S) which can be attributed to the high amount of protein (57.14%) in the *Chlorella*. Previous studies have shown similar results [31, 32]. More than 70% of the N-containing compounds went to the aqueous phase which could be present in the 2nd extraction bio-oils of this study.

Catalysts influenced the bio-oil components as determined by the GC-MS analysis. The retention time, peak name, and relative peak area of the bio-oil components obtained from the GC-MS analysis and the type of compounds present in the bio-oil components (see Tables 5-12 in supporting information). For the 1st extraction bio-oil at 240 °C for 0 min, argon plasma zeolite Y reduced the N-containing compounds very efficiently from ~24% to ~3% (Figure 3). However, plasma modified zeolite Y did not show significant effect on the reduction of N-containing compounds in the 2nd extraction bio-oils. The catalyst causes denitrification of the bio-oil due to the presence of acidic sites and inhibited the Maillard reaction or the self-condensation of the amino acids [13]. The content of fatty acid is lower with zeolite Y than with plasma modified zeolite Y. Plasma modified zeolite Y enhanced the content of hydrocarbons, alcohols and esters at 240 °C for 15 min and at 250 °C for 0 min. Plasma modified zeolite Y performed better in the 1st extraction than the 2nd extraction for enhancing contents of hydrocarbons, alcohols and esters in the bio-oils. The content of O-containing compounds effectively reduced with plasma modified zeolite Y in the 1st extraction bio-oils at 240 °C for 0 min (see Figures 1-7 in supporting information).

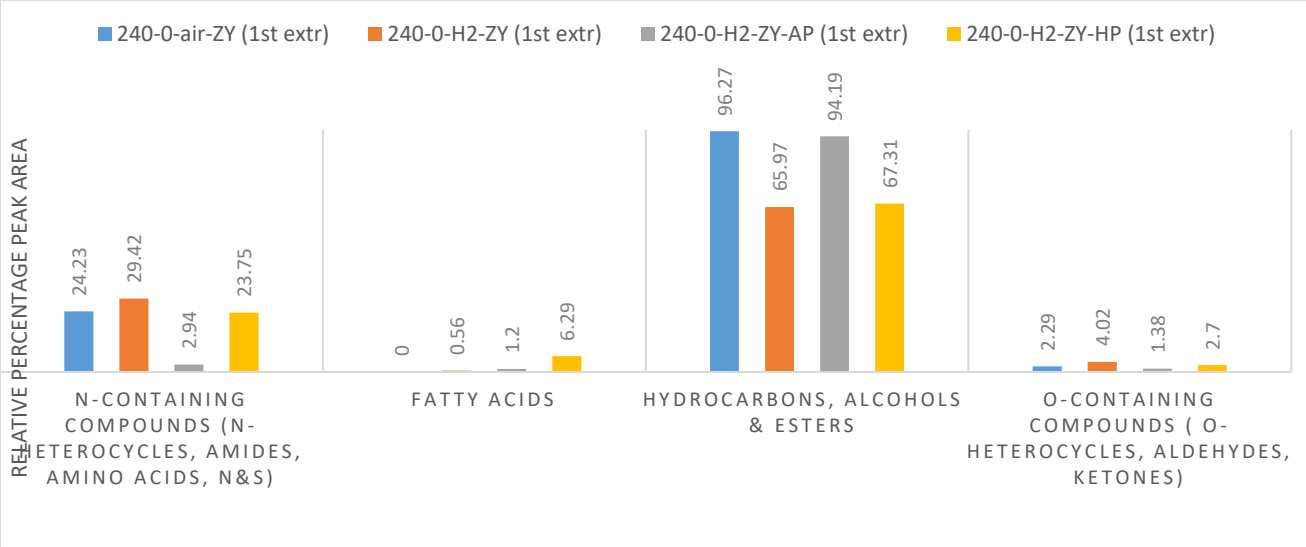


Figure 3: Variation of bio-oil components (1st extraction) with zeolite Y and plasma modified zeolite Y at 240 °C for 0 min reaction time.

4.0 DISCUSSION

HTL is an efficient method to produce bio-oils from microalgae. HTL reaction offers rapid conversion of algae to bio-oil and convert polysaccharides and proteins into an energy dense bio-oil. HTL of *Chlorella* was investigated with zeolite Y in air and H_2 atmospheres and using H_2 plasma and argon plasma modified zeolite Y in H_2 atmosphere for 0 & 15 min at 240 °C & 250 °C.

Based on our knowledge, there is no prior study using non-thermal plasmas to modify catalysts for HTL of algae. The surface properties of the materials can be modified with plasma treatments. The plasma treatment has the advantages of short treatment time and leading to a restructuring of the surface of the materials. It's likely that DBD plasmas modified the acid/base properties of zeolite Y and enhanced its catalytic HTL activity. The hydrophobic and hydrophilic properties of the surface of zeolite Y can also be significantly changed with the plasma treatment. Plasma-based processes are known to modify natural zeolites to increase their adsorption capacity and to reduce metal ions to its metal form [17], which could also happen to the zeolite Y used in this investigation. In this very first study, the results showed that plasma treatments had a very significant effect on zeolite Y for bio-oil yield from HTL. Argon plasma modified zeolite Y increased the bio-oil yield in H_2 from 36.37 % (240-0-H_2-ZY) to 42.53 % (240-0-H_2-ZY-AP) at 240 °C for 0 min. It represents an increase of ~17 %. H_2 plasma modified zeolite Y enhanced the

bio-oil yield from 36.37 % (240-0-H_2-ZY) to 43.76 % (240-0-H_2-ZY-HP) at 240 °C for 0 min. It increased by ~20 % (Table 1).

The elemental composition of bio-oils was influenced by reaction time and temperature. For temperature, the C content increased from 60.43 % at 240 °C to 62.54 % at 250 °C for 0 min. On the other hand, the O content decreased with increasing temperature. It decreased from 21.52 % at 240 ºC to 18.21 % at 250 ºC for 15 min (Table 2). Similar results were reported by Li and Savage [14] who studied bio-oil obtained from HTL of *Nannochloropsis* sp. over HZSM-5 catalyst at 400-500 °C in H_2 for 0.5-4h. They reported that the content of C increased with increasing temperature and O reduced with increasing temperature. O content of the bio-oil reduced to about one-third (from 8.35 % to 2.81 %) by treatment with HZSM-5 at 400 ºC. Much higher reductions are likely due to much higher reaction temperatures used.

With the increase of C content and decrease of 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 °C to 250 °C (Table 2). Similarly, Li and Savage [14] reported that the ratios of H/C, N/C and O/C decreased with the increase of temperature.

The HHV of bio-oil increased with temperature from 29.58 kJ/g at 240 ºC to 31.38 kJ/g at 250 ºC for 15 min (Table 2). Reddy [33] 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 49.77 % for 0 min to 56.81 % for 15 min at 240 ºC due to higher HHV of bio-oil from a longer reaction time (Table 2).

Based on TGA results, argon plasma mildly increased the110-300 °C fraction 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 modified 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 ºC for 15 min, a ~18% increase (Figure 2). This aspect indicates that plasma modified 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. Wu *et al.* [13] 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 7-23 %.

The components of bio-oil obtained from GC-MS shows that plasma modified zeolite Y is effective to reduce the N-containing compounds in H_2 atmosphere. Argon plasma decreased the N-containing compounds from 29.42 % (240-0-H_2-ZY) to 2.94 % (240-0-H_2-ZY-AP) at 240 °C for 0 min. It decreased by ~90 % (Figure 3). However, the effect of H_2 plasma modified zeolite Y is not as dramatic, which decreased the N-containing compounds from 29.42 % (240-0-H_2-ZY) to 23.75 % (240-0-H_2-ZY-HP) at 240 °C for 0 min, about ~19 % (Figure 3). Wu *et al.* [13] 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. Our study shows that argon plasma modified zeolite Y decreased the N-containing compounds by 90 % and H_2 plasma modified zeolite Y by 19 % which are comparable to the H beta zeolite activity.

Similar to the N-containing compounds, the portion of O-containing compounds decreased with plasma modified zeolite Y in the bio-oil. Argon plasma is better than H_2 plasma to modify zeolite Y in reducing the O-containing compounds at 240 °C for 0 min, by ~66 %, 240-0-H_2-ZY vs 240-0-H_2-ZY-AP (Figure 3). This is likely due to significant deoxygenation function of plasma modified zeolite Y as reported by Wu *et al.* [13].

Plasma modified zeolite Y enhanced (with some exceptions) the portion of hydrocarbons, alcohols, and esters in the bio-oil for fuel purposes. Argon plasma modified zeolite Y increased the portion even more. It increased by ~43 % at 240 ºC for 0 min in H_2, 240-0-H_2-ZY vs 240-0-H_2-ZY-AP (Figure 3). Similar results were obtained Wu *et al* [13] 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 %.

General Reaction Network of Bio-oil Components from HTL of Microalgae

Hydrothermal liquefaction involves the hydrolysis, depolymerization, and repolymerization of microalgae. Zhang *et al* [34] summarized the general reaction network of HTL process based on the experimental results and previous studies. Figure 4 shows the general reaction network of bio-oil components from HTL of microalgae and can be applied to *Chlorella* in this study.

The bio-oil contained an abundance of N-heterocycle compounds which can be formed through the self-condensation of amino acids or Maillard reaction between amino acids and reducing sugars obtained from the hydrolysis of proteins and carbohydrates [35]. N-heterocycle compounds consist of pyrazine ring, piperidine ring, piperazinedione ring, pyrrolo ring. N-heterocycle compounds observed in the GC-MS analysis were Pyrazine, 2-ethyl-6-methyl (R.T 3.57), Pyrazine, 2-ethyl-3, 5 dimethyl (R. T 4.91), 2-Cyclohexylpiperidine (R.T 17.99), 2, 5-Piperazinedione, 3-methyl-6-(1-methylethyl) (R.T 25.10), Uric acid (R.T 27.50), 3, 6-Diisopropylpiperazin-2, 5-dione R.T 31.65), 2, 5-Piperazinedione, 3, 6-bis(2-methylpropyl) (R. T 34.04), Pyrrolo[1,2-a]pyrazine-1, 4-dione, hexahydro-3-(2-methylpropyl) (R.T 34.43), 2, 5-Piperazinedione, 3-methyl-6-(phenylmethyl) (R.T 40.27), 2, 5-Piperazinedione, 3-(phenylmethyl) (R. T 42.54), 2, 5-Piperazinedione, 3-benzyl-6-isopropyl (R.T 42.79), Cyclo-(l-leucyl-l-phenylalanyl) (R.T 45.50), Ergotaman-3',6',18-trione, 9,10-dihydro-12'-hydroxy-2'-methyl-5'-(phenylmethyl)-, (5'a,10a) (R. T 45.62).

Amides can be formed through the self-condensation of amino acids. Amides observed in the bio-oil were Mefluidide (R. T 3.55), Glycine, N-(N-glycyl-L-leucyl) (R. T 27.76), dl-Alanyl-l-leucine (R. T 28.54), cis-9, 10-Epoxyoctadecanamide (R. T 29.00), Na-Acetyl-l-arginine (31.00), Deoxyspergualin (R. T 41.36), Pseudosolasodine diacetate (R. T 44.23). Amino acid characterized in the bio-oil was 4-Amino-1, 5-pentandioic acid (R. T 4.62). N & S containing compound appeared was Tenovin-6 (R. T 17.79).

Unsaturated fatty acids such as 8,11,14-Eicosatrienoic acid, (Z, Z, Z)- ($C_{20:3}$) (R. T 34.60), 9,12,15-Octadecatrienoic acid, (Z, Z, Z)- ($C_{18:3}$) (R.T 34.64), 9-Hexadecenoic acid-($C_{16:1}$) (R.T 35.35), cis-5,8,11,14,17-Eicosapentaenoic acid- ($C_{20:5}$) (R.T 45.07) were identified in the bio-oil. Long chain fatty acids are produced in the bio-oil from the hydrolysis of lipids [36]. Hydrocarbons characterized in the bio-oil were Tetradecane, 2, 6, 10-trimethyl (R.T 25.72), Nonadecane (R.T 25.73), Neophytadiene (R.T 30.45). Hydrocarbons in the bio-oil are produced from the decarboxylation of fatty acids due to the hydrolysis of lipids in the microalgae [37]. Neophytadiene characterized in the bio-oil produced from the dehydration of phytol [38, 39].

Phytol (3, 7, 11, 15-Tetramethyl-2-hexadecen-1-ol) (R.T 31.86) was identified in the bio-oil produced from Chlorophyll during the HTL of algae. Phytol rearranges to form Isophytol (R. T 34.04). Phytol chain linked to the chlorin ring of chlorophyll which upon hydrolysis to release

phytol molecule [40]. Other alcohols such as 13-Heptadecyn-1-ol (R.T 31.92), 12-Methyl-E, E-2, 13-octadecadien-1-ol (R.T 38.34) in the bio-oil are produced from the reduction of amino acids after deamination [34].

Esters are formed through esterification reaction. Long chain fatty acids obtained from hydrolysis of lipids can react with alcohols from the reduction of amino acids after deamination to produce esters. Significant esters obtain in the bio-oil are Isophytol, acetate (R. T 31.32), 7, 10, 13-hexadecatrienoic acid, methyl ester (R. T 34.53), 5,8,11,14-Eicosatetraenoic acid, methyl ester, (all-Z) (R. T 34.54), Methyl 8,11,14-heptadecatrienoate (R. T 34.59), 9, 12-octadecadienal dimethyl acetate (R. T 34.60), Ethyl 9-hexadecenoate (R.T 34.82), Hexadecanoic acid, ethyl ester (R.T 35.50), Hexanoic acid, tridec-2-ynyl ester (R. T 39.30), Linoleic acid ethyl ester (R.T 40.44), Ethyl 9,12,15-octadecatrienoate (R.T 40.61), N,N'-Bis(Carbobenzyloxy)-lysine methyl(ester) (R. T 42.81), 4-Hexyl-1-(7-methoxycarbonylheptyl)bicyclo[4.4.0]deca-2,5,7-triene (R. T 49.12). O-heterocycles characterized in the bio-oil are 2(4H)-Benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-, (R) (R.T 19.67), 7-Hydroxy-6,9a-dimethyl-3-methylene-decahydro-azuleno[4,5-b]furan-2,9-dione (R.T 45.57). Ketones identified in the bio-oil are 1,2-Cyclopentanedione, 3-methyl (R.T 4.13), 2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-1-methoxy (R.T 16.62), 7-Ethyl-4,6-pentadecandione (R.T 30.98), Androst-4-en-3-one, 17-methoxy-, 3-methoxime, (17ß) (R.T 46.78). Aldehyde, 12-Octadecenal (R.T 31.98) observed only in hydrogen plasma zeolite Y HTL of algae. O-heterocycle, aldehyde and ketone are likely produced from the degradation of carbohydrates through hydrolysis, dehydration, and cyclization [41].

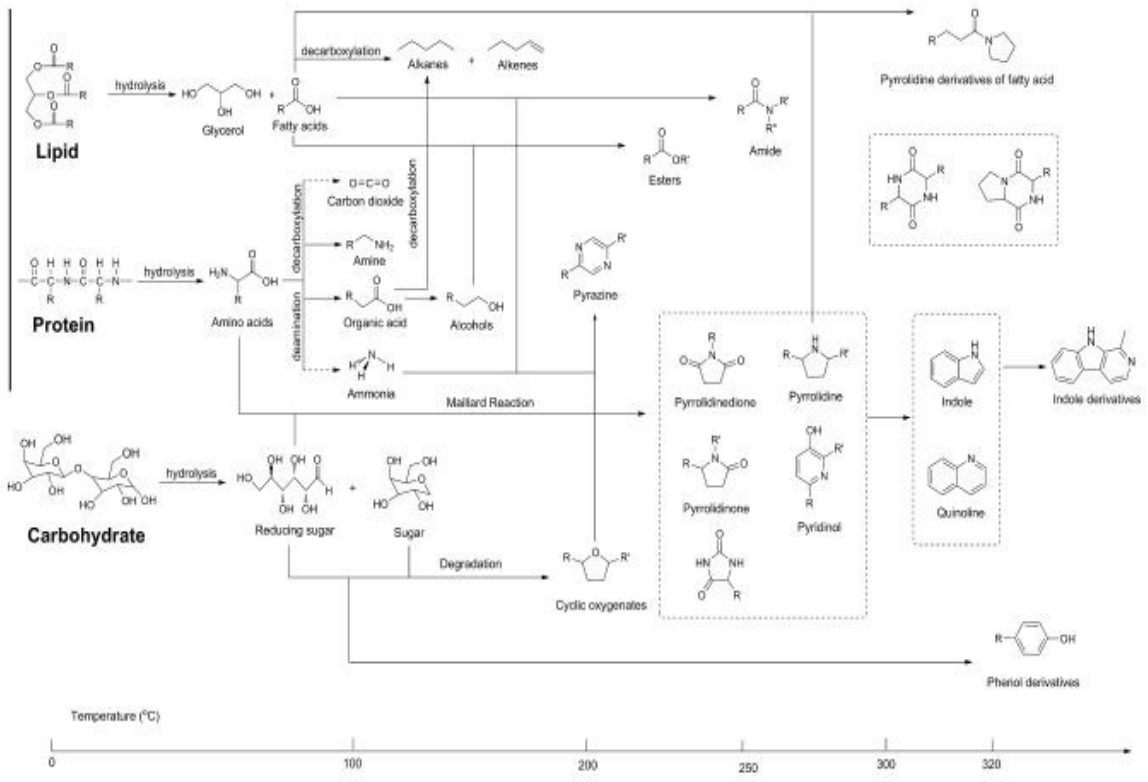


Figure 4: General reaction network of HTL of microalgae summarized by Zhang *et al* [33].

5.0 CONCLUSIONS

Hydrothermal liquefaction (HTL) is a fast and rapid method for the conversion of biomass to bio-oils. Plasma had a significant effect on zeolite Y for bio-oil yields. Argon and H_2 plasmas modified zeolite Y enhanced the bio-oil yield about 17-20% in comparison to with zeolite Y only.

The elemental compositions of bio-oil were influenced by reaction time and temperature also. With the increase of C content and decrease of 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 °C to 250 °C. Similar results were reported in the literature, high heating value (HHV) increased with increasing reaction time and temperature. Similarly, energy recovery increased with the increase of reaction time and temperature as well.

Plasma modified zeolite Y also increased the 110-300 °C fraction of bio-oils from HTL of *Chlorella* in H_2 at 250 °C for 0- and 15-min. Argon plasma treated zeolite Y in H_2 increased the110-300 °C fraction by 15%, from 31.94 % to 36.63 % at 250 ºC for 0 min. H_2 plasma modified zeolite Y increased the110-300 °C fraction of bio-oil by ~18% at 250 °C for 15 min.

In addition, plasma modified zeolite Y decreased (with some exceptions) the N-containing compounds in the bio-oil. Argon plasma modified zeolite Y decreased the N-containing compounds by ~90 %, from 29.42 % to 2.94 % at 240 °C for 0 min. H_2 plasma modified zeolite Y decreased the N-containing compounds by ~19 % at 240 °C for 0 min. Argon plasma modified zeolite Y also increased the portion of hydrocarbons, alcohols, and esters in bio-oils by ~43 % at 240 ºC for 0 min in H_2, while reducing the portion of O-containing compounds by ~66 %.

Overall, the introduction of plasma modified zeolite Y in the HTL of *Chlorella* increased the bio-oil yield, reduced the N-containing compounds and O-containing compounds, enhanced the content of hydrocarbons, alcohols, and esters, and increased the 110-300 °C fraction of bio-oils. The detailed promotion effects should be studied further. Especially, the plasma treatments on the surface properties of zeolite Y should be investigated to optimize the yield and quality of bio-oils.

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ASSOCIATED CONTEN

Supporting Information

Table of boiling point distribution of bio-oils, table of components of bio-oils and type of compounds present in the bio-oils, figures of variation of bio-oils compounds with catalysts at different temperatures.

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