I&EC research
Industrial & Engineering Chemistry Research

pubs.acs.org/IECR

Article

Effects of Plasma Modification and Atmosphere on the Catalytic Hydrothermal Liquefaction of *Chlorella*

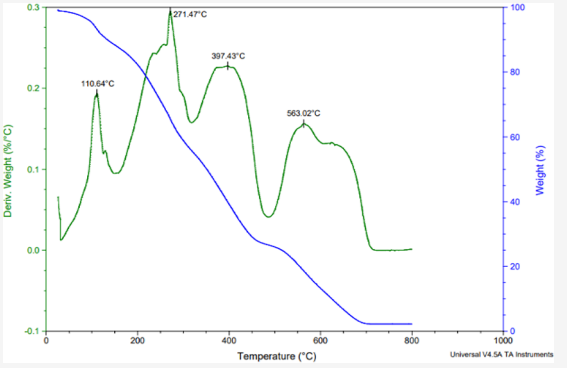
Tarek Md. Anamul Haque, Martin Perez, Michael Brdecka, Valeria Duran Salas, and Ben Jang*

Cite This: https://doi.org/10.1021/acs.iecr.2c02300

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The development of third-generation biofuels from microalgae has been extensively researched over the last few years. Hydrothermal liquefaction (HTL) is a promising route for producing bio-oils from wet algae. The major drawback in HTL is the high temperature and high pressure that result in the high capital cost of the process. To make HTL an economical process for bio-oil production, the temperature and pressure should be reduced, which 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 a hydrogen atmosphere versus air at different reaction times (0 and 15 min) and temperatures (240 and 250 °C). The mixture of solvents (50 vol % water and 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 the higher heating value (HHV). The introduction of DBD plasma to modify zeolite Y improved the bio-oil quality and yield from HTL processes. The H_2 plasma modified catalyst enhanced the bio-oil yield at 240 °C 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. The 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 °C.



1. INTRODUCTION

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

The conversion of biomass via hydrothermal liquefaction (HTL) is 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 temperatures and high pressures via hydrothermal liquefaction. The process is generally carried out at temperatures between 200 and 400 °C and pressures ranging between 10 and 25 MPa with or without a 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 that 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) determine the properties and product distribution of the bio-oils.[6]

Biofuels obtained from HTL contain a 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 and CH_3COOH) and alkali (Na_2CO_3 and KOH) are widely used as homogeneous catalysts in HTL.[7] The

Received: June 27, 2022
Revised: July 26, 2022
Accepted: July 28, 2022

homogeneous catalyst Na_2CO_3 can efficiently liquefy the algae that contain a high amount of carbohydrate but not so for algae containing a 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 remain stable in drastic conditions and (ii) the 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 and Ce/HZSM-5) on HTL of *Chlorella pyrenoidosa* in a N_2 atmosphere at 300 °C for 20 min. Active acidic sites, the large surface area, and the channel structure of zeolites enhance the cracking reaction of bio-oils.[10] Widayatno *et al.*[11] investigated four high-silica zeolites, namely, HSZ-385, 890, 960, and 990, in HTL processes and found that all zeolites enhanced the bio-oil deoxygenation and that HSZ-960 (beta) exhibited a unique selectivity for hydrocarbons. Duan *et al.*[12] studied the effect of nine types of zeolites in a 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 the 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 the HZSM-5 catalyst at 400−500 °C in H_2 for 0.5−4 h. HZSM-5 greatly reduced the content of N, S, and 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 the dielectric barrier discharge (DBD) plasma modified zeolite catalyst (zeolite Y) on the production of bio-oils and improve the bio-oils' quality from microalgae (*Chlorella*) through hydrothermal liquefaction. Meanwhile, no research work has been performed on the application of DBD plasma modified zeolite Y in the HTL process. DBD plasma works at atmospheric pressure and produces 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 in the modification of material surfaces.[15,16] A lot of details have been summarized in the review by Liu *et al.*[17] Liu *et al.*[18] studied CeO_2 enhanced CO_2 decomposition via frosted dielectric barrier discharge plasma.

2. EXPERIMENTAL SECTION

2.1. Materials. *Chlorella* was used as a biomass purchased from Stakich Inc. The zeolite Y purchased from Alfa Aesar has surface area of 780 m^2/g and 30:1 mole ratio of SiO_2/Al_2O_3. For ethanol reactions, 200 proof absolute purity ethanol was purchased from VWR U.S. and dichloromethane was 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-2000K 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.[19] The discharge is generated between two plane electrodes that are covered by 3 mm 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 30 mL/min was used in the plasma. The DBD plasma was run for 30 min to modify the catalyst.

2.3. Hydrothermal Liquefaction. The hydrothermal liquefaction was carried out in a 100 mL batch reactor equipped with an automated stirrer, an electric heater, a temperature controller, and a sample tube. Dried algae (4.5 g) were introduced into the sample tube of the reactor followed by adding 22.5 g of deionized water and 17.75 g of ethanol. In experimental runs including the catalyst, 0.225 g of the catalyst (5 wt %) was also loaded into the sample tube. Hydrothermal liquefaction (HTL) of *Chlorella* was run under an air atmosphere and hydrogen atmosphere. During the HTL in the hydrogen atmosphere, hydrogen gas was purged into the reactor at a pressure of 150 psi. Hydrogen gas was purged five times to expel the air from the reactor. The reactor was heated from the ambient temperature to the desired temperature, 240 or 250 °C, with a temperature ramp of 6 °C/min. The automated stirrer was used at a constant stirring rate to keep the temperature uniform inside the sample tube. After reaching the 240 or 250 °C temperature, the holding time of the sample was 0 and 15 min. The HTL reaction condition is denoted as 240-0-air for the reaction at 240 °C in air atmosphere for 0 min reaction time and 250-15-H_2-ZY-HP for the reaction at 250 °C in H_2 atmosphere for 15 min reaction time, and H_2 plasma modified zeolite Y acted as a catalyst. Once the holding time was completed, the temperature was set to the ambient temperature to cool down the reactor using a 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) was mixed with the final product. The aim of adding DCM is the extraction of organic components from both liquid and solid products. The mixture was then filtered by a Buchner funnel connected to a vacuum pump, and the filter paper used in the filtration was a medium mesh size. Two immiscible liquid phases (organic solvent soluble, water soluble) were kept in a separation funnel overnight. After the extraction of first phase bio-oil, the same method followed by adding 25 mL of dichloromethane (DCM) with the residue left (aqueous phase) in the separation funnel. This is called the second 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 components has a dark color and high viscosity. During the evaporation of DCM, some light components of the bio-oil are lost, which are reported to be less than 3% of the total mass of the bio-oil.[20] The percentage of yield of bio-oil was calculated by the following formula:

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

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

https://doi.org/10.1021/acs.iecr.2c02300
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

Table 1. The Percentages of Yield of Bio-oil from HTL of *Chlorella* at Different HTL Conditions[a]

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

[a]ZY, zeolite Y; AP, argon plasma; HP, hydrogen plasma; air, air atmosphere; and H_2, hydrogen atmosphere.

Table 2. Elemental Analysis and HHV of the First and Second Extraction Bio-oil Obtained from HTL of *Chlorella*

		elemental analysis (%)							HHV (MJ/g)	energy recovery (%)
HTL condition	1st extraction bio-oil yield (%)	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**
		elemental analysis (%)							HHV (kJ/g)	energy recovery (%)
HTL condition	2nd extraction 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**

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

()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:

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

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

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

https://doi.org/10.1021/acs.iecr.2c02300
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

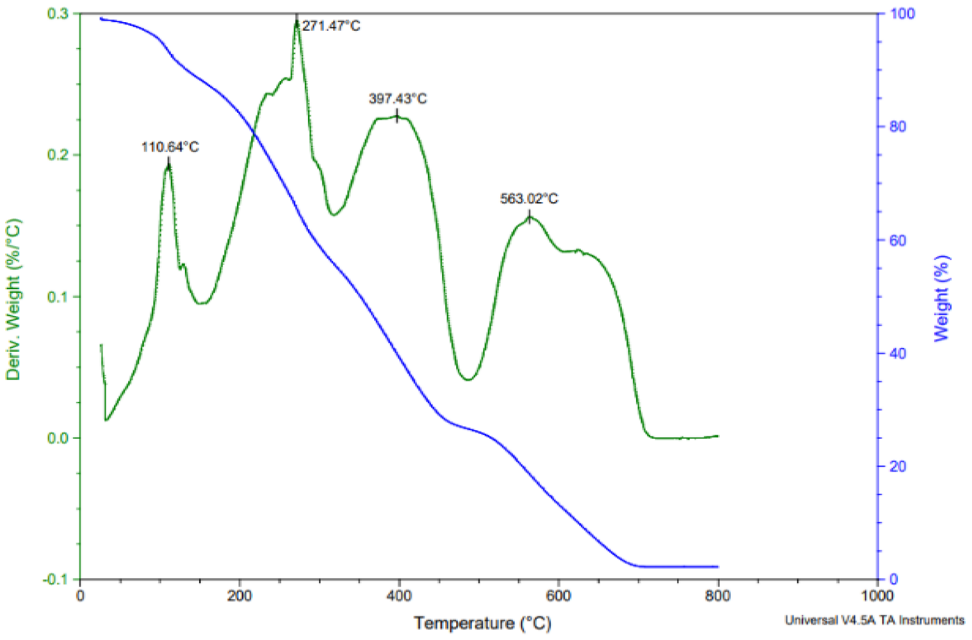


Figure 1. TGA graph of bio-oil from H_2 plasma modified zeolite Y in a H_2 atmosphere at 240 °C for 15 min.

2.4.1. 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 was carried out (TGA-Q500, TA Instrument) from the ambient temperature to 800 °C under a 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 and at 800 °C for 5 min.

3. RESULTS

3.1. Bio-oil Yield. The hydrothermal liquefaction (HTL) of *Chlorella* was run under different conditions (temperature, time, atmosphere, and catalyst) to investigate the influence of these factors on the bio-oil yield. We classified the reactions as catalytic HTL and plasma modified catalytic HTL. We emphasized the first extraction of the bio-oil yield because this is mainly coming from the organic layer and more than 80% of the total yield of bio-oil is from the organic layer. Table 1 shows the percentages of the yield of bio-oil at different HTL conditions of *Chlorella*. The HTL condition was presented including four 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 plasmas 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 noncatalytic HTL.[24]

In this study, plasma increased the bio-oil yield from 36.37% with zeolite Y to 43.76% with H_2 plasma treated zeolite Y at 240 °C for 0 min. At 240 °C for 0 min, H_2 plasma zeolite Y was more effective than argon plasma zeolite Y. H_2 plasma treatment leads to a higher degree of surface functionalization (partial dealumination of the zeolite Y and thereby an increase in 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 at 240 °C for 15 min 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 zeolite Y was more effective than H_2 plasma modified zeolite Y.

3.3. Elemental Analysis of Bio-oil. CHNOS analysis results of the bio-oils are presented in Table 2. We consider the average percentage of (bolded rows in Table 2) the elements at different HTL conditions to explain the variation of CHNOS and its high heating value (HHV) with the reaction time and temperature. Eighteen samples of the first extraction of bio-oil were placed at the top of Table 2, and six samples of the second extraction of bio-oil were 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 to much higher HHVs of the biomass (Table 2). The elemental analysis shows that the C content of the bio-oils increases with temperature for 0 and 15 min reaction times. The C content in the first extraction (61.83% at 240 °C, 15 min) bio-oil is higher than that of the second extraction (60.71% at 240 °C, 15 min). The N content of the first extraction bio-oil increases with temperature as well for 0 and 15 min reaction times. Nitrogen compounds are polar and tend to be more easily found in the second extraction bio-oil (from the aqueous phase). Therefore, the N content of the second extraction (10.84% at 240 °C for 15 min) is higher than that in the first extraction (7.76% at 240 °C 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 that can influence the oxygen

https://doi.org/10.1021/acs.iecr.2c02300
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

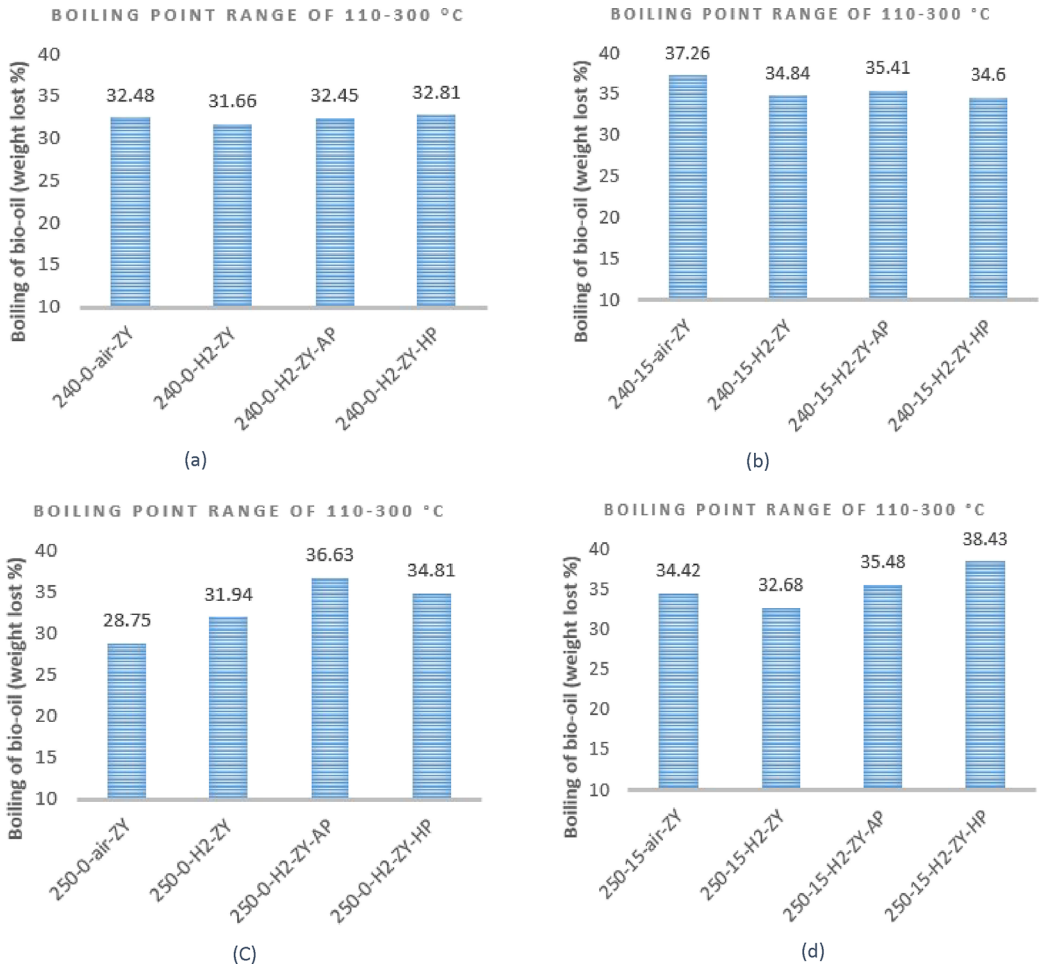


Figure 2. Effect of plasma modified zeolite Y on bio-oil in the boiling point range of 110−300 °C from HTL of *Chlorella* (a) at 240 °C for 0 min reaction time, (b) at 240 °C for 15 min, (c) at 250 °C for 0 min, and (d) 250 °C for 15 min.

removal of bio-oil, especially in the presence of zeolite catalysts.[27] In general, the O content of first extraction bio-oils is slightly higher that of the the second extraction, for example, 21.52 vs 20.24% at 240 °C for 15 min.

As shown in Table 2, the contents of C and H in the first extraction increase with the increase of reaction time (0 to 15 min), and N and O contents decrease with the reaction time (0 to 15 min). The reduction of N and O content in the bio-oils during HTL reactions is typically via dehydration, decarboxylation, and deamination.[28,29] Longer reaction times and higher temperatures 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 first extraction bio-oils decrease with increasing temperature from 240 to 250 °C. On the other hand, under the same HTL condition, such as 240 °C for 15 min, the O/C and H/C ratios in the second extraction are lower than those in the first extraction, but the N/C ratio is higher in the second extraction.

The high heating value (HHV) in the first extraction bio-oils increases with increasing reaction time and temperature. The HHV of the second extraction bio-oil at 240 °C for 15 min (28.94 kJ/g) is lower than that of the first extraction under the same HTL condition (30.02 kJ/g for 15 min at 240 °C). 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 °C for 15 min. Energy recovery increases with increasing reaction time from 0 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 °C 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]

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 a N_2 atmosphere from 25 to 800 °C resulted in a percentage of weight loss about >95%. Figure 1 shows TGA results the first extraction of bio-oil from catalytic HTL of *Chlorella* at 240 °C. It is revealed from the TGA graph, including the weight loss and derivative of weight loss versus temperature, that the highest four peaks are at 110.64, 271.47, 397.43, and 563.02 °C. The first peak at 110.64 °C can be corresponding to the boiling point ranges of both 25−110 °C 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

https://doi.org/10.1021/acs.iecr.2c02300
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

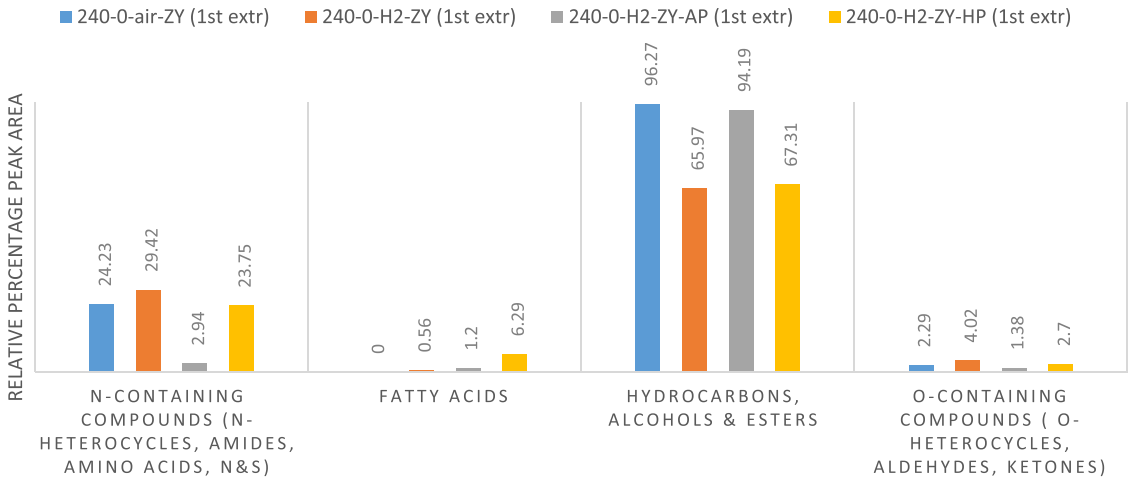


Figure 3. Variation of bio-oil components (first extraction) with zeolite Y and plasma modified zeolite Y at 240 °C for 0 min reaction time.

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. The boiling point distribution of bio-oils with catalysts in different atmospheres at 240 °C and 250 °C for 0 and 15 min is shown in Tables S1−S4 in the Supporting Information. The percentage of weight loss can be influenced by the reaction atmosphere and plasma treatments. Figure 2 presents the effect of the 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 and 15 min.

Plasma treated 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 °C 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 °C 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 a H_2 atmosphere at 250 °C for 15 min can produce the most fuels in bio-oils with the 110−300 °C boiling range.

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 can be characterized through GC−MS because (i) low-molecular-weight compounds might be lost during the solvent evaporation process for bio-oil recovery and (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 that could be present in the second 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 are shown in Tables S5−S12 in the Supporting Information. For the first 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 zeolite Y did not show a significant effect on the reduction of N-containing compounds in the second 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 zeolite Y. Plasma zeolite Y enhanced the content of hydrocarbons, alcohols, and esters at 240 °C for 15 min and at 250 °C for 0 min. Plasma zeolite Y performed better in the first extraction than the second extraction for enhancing contents of hydrocarbons, alcohols, and esters in the bio-oils. The content of O-containing compounds was effectively reduced with plasma zeolite Y in the first extraction bio-oils at 240 °C for 0 min (see Figures S1−S7 in the Supporting Information).

4. DISCUSSION

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

Based on our knowledge, there is no prior study using nonthermal plasma 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 a short treatment time and leading to a restructuring of the surface of the materials. It is 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[33]

https://doi.org/10.1021/acs.iecr.2c02300
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

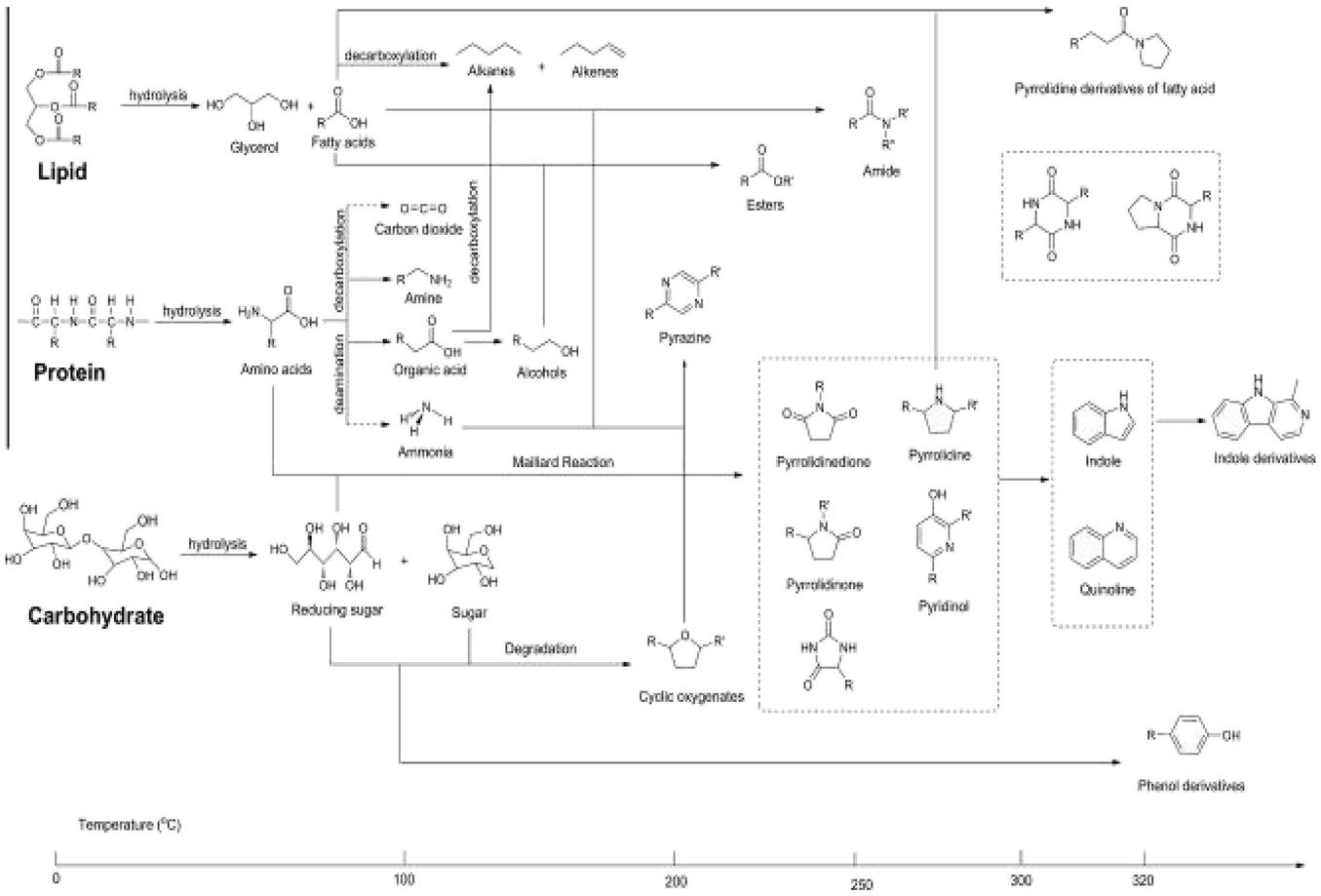


Figure 4. General reaction network of the HTL of microalgae summarized by Zhang *et al.*[35]

and to reduce metal ions to its neutral form, which could also happen to the zeolite Y used in this investigation. In this very first study, the results showed that plasmas had a very significant effect on zeolite Y for the 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 the 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 °C to 18.21% at 250 °C 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 the HZSM-5 catalyst at 400−500 °C in H_2 for 0.5−4 h. They reported that the content of C increased with increasing temperature and O reduced with increasing temperature. The O content of the bio-oil reduced to about one-third (from 8.35 to 2.81%) by treatment with HZSM-5 at 400 °C. 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 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 °C to 31.38 kJ/g at 250 °C for 15 min (Table 2). Reddy *et al.*[34] reported that the HHV of bio-oil increased with temperature due to the deoxygenation of bio-oil at high temperatures. The trend of HHV in our present study matched well with previous studies. As a result, the 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 °C due to the higher HHV of bio-oil from a longer reaction time (Table 2).

Based on TGA results, argon plasma mildly increased the 110−300 °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 °C for 15 min, i.e., ∼18% increase (Figure 2). This aspect indicates that plasma modified zeolite Y with acidic sites and a 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 show that plasma modified zeolite Y is effective to reduce the N-containing compounds in H_2 atmosphere. Argon plasma modified zeolite Y decreased the N-containing compounds from 29.42% (240-0-H_2-ZY) to 2.94% (240-0-H_2-ZY-AP) at

https://doi.org/10.1021/acs.iecr.2c02300
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

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, decreasing 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, i.e., ∼19% (Figure 3). Wu *et al.*[13] reported that 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 decreased them 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 the 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 °C for 0 min in H_2, 240-0-H_2-ZY vs 240-0-H_2-ZY-AP (Figure 3). Similar results were obtained by 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%.

4.1. General Reaction Network of Bio-oil Components from the HTL of Microalgae. Hydrothermal liquefaction involves the hydrolysis, depolymerization, and repolymerization of microalgae. Zhang *et al.*[35] summarized the general reaction network of the 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, which can be applied to *Chlorella* in this study.

The bio-oil contained an abundance of N-heterocycle compounds that 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.[4] N-Heterocycle compounds consist of a pyrazine ring, piperidine ring, piperazinedione ring, and 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); and 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); and pseudosolasodine diacetate (R.T 44.23). The amino acid characterized in the bio-oil was 4-amino-1,5-pentandioic acid (R.T 4.62). The N & S containing compound that 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); and *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.[32] Hydrocarbons characterized in the bio-oil were tetradecane, 2,6,10-trimethyl (R.T 25.72); nonadecane (R.T 25.73); and 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.[36] Neophytadiene was characterized in the bio-oil produced from the dehydration of phytol.[37,38]

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). The phytol chain linked to the chlorin ring of chlorophyll upon hydrolysis to release the phytol molecule.[39] Other alcohols such as 13-heptadecyn-1-ol (R.T 31.92) and 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.[35]

Esters are formed through the esterification reaction. Long-chain fatty acids obtained from the hydrolysis of lipids can react with alcohols from the reduction of amino acids after deamination to produce esters. Significant esters obtained 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); and *N*,*N*′-bis(carbobenzyloxy)-lysine methyl(ester) (R.T 42.81); and 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(4*H*)-benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-, (R) (R.T 19.67) and 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(3*H*)-naphthalenone, 4,4a,5,6,7,8-hexahydro-1-methoxy (R.T 16.62); 7-ethyl-4,6-pentadecandione (R.T 30.98); and androst-4-en-3-one, 17-methoxy-, 3-methoxime, (17β) (R.T 46.78). Aldehyde, 12-octadecenal (R.T 31.98) was observed only in the 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.[40]

5. 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 plasma modified zeolite Y enhanced the bio-oil yield by about 17−20% in comparison to zeolite Y only.

The elemental compositions of bio-oil were influenced by reaction time and temperature also. With the increase of C

https://doi.org/10.1021/acs.iecr.2c02300
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

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 to 250 °C. Similar results were reported in the literature; the 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 the 110−300 °C fraction by 15%, from 31.94 to 36.63% at 250 °C for 0 min. H_2 plasma modified zeolite Y increased the 110−300 °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 °C 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.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c02300.

Tables of boiling point distribution of bio-oils, tables of components of bio-oils and type of compounds present in the bio-oils, and figures of variation of bio-oil compounds with catalysts at different temperatures (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Ben Jang − *Chemistry Department, Texas A&M University−Commerce, Commerce, Texas 75429-3011, United States;* orcid.org/0000-0002-1464-235X; Email: Ben.jang@tamuc.edu

Authors

Tarek Md. Anamul Haque − *Chemistry Department, Texas A&M University−Commerce, Commerce, Texas 75429-3011, United States;* orcid.org/0000-0003-2457-5223

Martin Perez − *Chemistry Department, Texas A&M University−Commerce, Commerce, Texas 75429-3011, United States*

Michael Brdecka − *Chemistry Department, Texas A&M University−Commerce, Commerce, Texas 75429-3011, United States*

Valeria Duran Salas − *Chemistry Department, Texas A&M University−Commerce, Commerce, Texas 75429-3011, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.2c02300

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is partially supported by the Welch Foundation (#T-0014) and NSF REU and S-STEM grants (#1643567, #1659852, and #2050417). Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for partial support of this research, ACS PRF (#57596-UR5).

■ REFERENCES

(1) Schenk, P. M.; Thomas-Hall, S. R.; Stephens, E.; Marx, U. C.; Mussgnug, J. H.; Posten, C.; Kruse, O.; Hankamer, B. Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production. *BioEnergy Res* **2008**, *1*, 20−43.

(2) Wang, M.; Kuo-Dahab, W. C.; Dolan, S.; Park, C. Kinetics of nutrient removal and expression of extracellular polymeric substances of the microalgae, Chlorella sp. and Micractinium sp., in wastewater treatment. *Bioresour. Technol.* **2014**, *154*, 131−137.

(3) Rawat, I.; Kumar, R. R.; Mutanda, T.; Bux, F. Sustainable Downstream Processing of Microalgae for Industrial Application. *Appl. Energy* **2011**, *154*, 131−137.

(4) Toor, S. S.; Rosendahl, L.; Rudolf, A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* **2011**, *36*, 2328−2342.

(5) Biller, P.; Ross, A. B.; Skill, S. C.; Lea-Langton, A.; Balasundaram, B.; Hall, C.; Riley, R.; Llewellyn, C. A. Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process. *Algal Res.* **2012**, *1*, 70−76.

(6) Barreiro, D. L.; Zamalloa, C.; Boon, N.; Vyverman, W.; Ronsse, F.; Brilman, W.; Prins, W. Influence of strain-specific parameters on hydrothermal liquefaction of microalgae. *Bioresour. Technol.* **2013**, *146*, 463−471.

(7) Brand, S.; Susanti, R. F.; Kim, S. K.; Lee, H.; Kim, J.; Sang, B. I. Supercritical ethanol as an enhanced medium for lignocellulosic biomass liquefaction: Influence of physical process parameters. *Energy* **2013**, *59*, 173−182.

(8) Biller, P.; Riley, R.; Ross, A. B. Catalytic hydrothermal processing of microalgae: Decomposition and upgrading of lipids. *Bioresour. Technol.* **2011**, *102*, 4841−4848.

(9) Xu, Y.; Zheng, X.; Yu, H.; Hu, X. Hydrothermal liquefaction of Chlorella pyrenoidosa for bio-oil production over Ce/HZSM-5. *Bioresour.Technol.* **2014**, *156*, 1−5.

(10) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem. Rev.* **2006**, *106*, 4044−4098.

(11) Widayatno, W. B.; Guan, G.; Rizkiana, J.; Du, X.; Hao, X.; Zhang, Z.; Abudula, A. Selective catalytic conversion of bio-oil over high-silica zeolites. *Bioresour. Technol.* **2015**, *179*, 518−523.

(12) Duan, P.; Xu, Y.; Wang, F.; Wang, B.; Yan, W. Catalytic upgrading of pretreated algal bio-oil over zeolite catalysts in supercritical water. *Biochem. Eng. J.* **2015**, *116*, 105−112.

(13) Zhang, B.; Lin, Q.; Zhang, Q.; Wu, K.; Pu, W.; Yang, M.; Wu, Y. Catalytic hydrothermal liquefaction of *Euglena* sp. microalgae over zeolite catalysts for the production of bio-oil. *RSC Adv.* **2017**, *7*, 8944−8951.

(14) Li, Z.; Savage, P. E. Feedstocks for fuels and chemicals from algae: Treatment of crude bio-oil over HZSM-5. *Algal Res.* **2013**, *2*, 154−163.

(15) Yavuz, Ö.; Saka, C. Surface modification with cold plasma application on kaolin and its effects on the adsorption of methylene blue. *Appl. Clay Sci.* **2013**, *85*, 96−102.

(16) Naseh, M. V.; Khodadadi, A. A.; Mortazavi, Y.; Pourfayaz, F.; Alizadeh, O.; Maghrebi, M. Fast and clean functionalization of carbon nanotubes by dielectric barrier discharge plasma in air compared to acid treatment. *Carbon* **2010**, *48*, 1369−1379.
(17) Wang, Z.; Zhang, Y.; Neyts, E. C.; Cao, X.; Zhang, X.; Jang, B. W.-L.; Liu, C.-j. Catalyst Preparation with Plasmas: How Does It Work? *ACS Catal.* **2018**, *8*, 2093−2110.
(18) Xia, M.; Ding, W.; Shen, C.; Zhang, Z.; Liu, C.-j. CeO_2-enhanced CO_2 decomposition via frosted dielectric barrier discharge plasma. *Ind. Eng. Chem. Res.* **2022**, 10455.
(19) Rui, N.; Zhang, X.; Zhang, F.; Liu, Z.; Cao, X.; Xie, Z.; Zou, R.; Senanayake, S. D.; Yang, Y.; Rodriguez, J. A.; Liu, C.-J. Highly active Ni/CeO_2 catalyst for CO_2 methanation: Preparation and characterization. *Appl. Catal., B* **2021**, *282*, 119581.
(20) Valdez, P. J.; Nelson, M. C.; Wang, H. Y.; Lin, X. N.; Savage, P. E. Hydrothermal liquefaction of *Nannochloropsis* sp.: Systematic study of process variables and analysis of the product fractions. *Biomass Bioenergy* **2012**, *46*, 317−331.
(21) Guo, B.; Walter, V.; Hornung, U.; Dahmen, N. Hydrothermal liquefaction of *Chlorella vulgaris* and *Nannochloropsis gaditana* in a continuous stirred tank reactor and hydrotreating of biocrude by nickel catalysts. *Fuel Process. Technol.* **2019**, *191*, 168−180.
(22) Stodghill, S. P. Thermal Analysis − A Review of Techniques and Applications in the Pharmaceutical Sciences. *Am. Pharm. Rev.* **2004**, 1−9.
(23) Huang, Y.; Chen, Y.; Xie, J.; Liu, H.; Yin, X.; Wu, C. Bio-oil production from hydrothermal liquefaction of high-protein high-ash microalgae including wild *Cyanobacteria* sp. and cultivated *Bacillariophyta* sp. *Fuel* **2016**, *183*, 9−19.
(24) Jena, U.; Das, K. C.; Kastner, J. R. Comparison of the effects of Na_2CO_3, $Ca_3(PO_4)_2$, and NiO catalysts on the thermochemical liquefaction of microalga *Spirulina platensis*. *Appl. Energy* **2012**, *98*, 368−375.
(25) Gupta, V.; Madaan, N.; Jensen, D. S.; Kunzler, S. C.; Linford, M. R. Hydrogen Plasma Treatment of Silicon Dioxide for Improved Silane Deposition. *Langmuir* **2013**, *29*, 3604−3609.
(26) Shakya, R.; Whelen, J.; Adhikari, S.; Mahadevan, R.; Neupane, S. Effect of temperature and Na_2CO_3 catalyst on hydrothermal liquefaction of algae. *Algal Res.* **2015**, *12*, 80−90.
(27) Haider, M.; Castello, D.; Michalski, K.; Pedersen, T.; Rosendahl, L. Catalytic Hydrotreatment of Microalgae Biocrude from Continuous Hydrothermal Liquefaction: Heteroatom Removal and Their Distribution in Distillation Cuts. *Energies* **2018**, *11*, 3360.
(28) Biller, P.; Ross, A. B. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresour. Technol.* **2011**, *102*, 215−225.
(29) Eboibi, B. E.; Lewis, D. M.; Ashman, P. J.; Chinnasamy, S. Effect of operating conditions on yield and quality of biocrude during hydrothermal liquefaction of halophytic microalga. *Tetraselmis sp. Bioresour. Technol.* **2014**, *170*, 20−29.
(30) Osonio, A. P.; Vasquez, M. R., Jr. Plasma-assisted reduction of silver ions impregnated into a natural zeolite framework. *Appl. Surf. Sci.* **2018**, *432*, 156−162.
(31) Gai, C.; Zhang, Y.; Chen, W.-T.; Zhang, P.; Dong, Y. Energy and nutrient recovery efficiencies in biocrude oil produced *via* hydrothermal liquefaction of *Chlorella pyrenoidosa*. *RSC Adv.* **2014**, *4*, 16958−16967.
(32) Ross, A. B.; Biller, P.; Kubacki, M. L.; Li, H.; Lea-Langton, A.; Jones, J. M. Hydrothermal processing of microalgae using alkali and organic acids. *Fuel* **2010**, *89*, 2234−2243.
(33) Cagomoc, C. M. D.; Vasquez, M. R., Jr. Enhanced chromium adsorption capacity via plasma modification of natural zeolites. *J. Appl. Phys.* **2017**, *56*, 01AF02.
(34) Reddy, H. K.; Muppaneni, T.; Ponnusamy, S.; Sudasinghe, N.; Pegallapati, A.; Selvaratnam, T.; Seger, M.; Dungan, B.; Nirmalakhandan, N.; Schaub, T.; Holguin, F. O.; Lammers, P.; Voorhies, W.; Deng, S. Temperature effect on hydrothermal liquefaction of *Nannochloropsis gaditana* and *Chlorella* sp. *Appl. Energy* **2016**, *165*, 943−951.
(35) Gai, C.; Zhang, Y.; Chen, W. T.; Zhang, P.; Dong, Y. An investigation of reaction pathways of hydrothermal liquefaction using *Chlorella pyrenoidosa* and *Spirulina platensis*. *Energy Convers. Manage.* **2015**, *96*, 330−339.
(36) Guo, J.; Zhuang, Y.; Chen, L.; Liu, J.; Li, D.; Ye, N. Process optimization for microwave-assisted direct liquefaction of *Sargassum polycystum* C. Agardh using response surface methodology. *Bioresour. Technol.* **2012**, *120*, 19−25.
(37) Rontani, J.-F.; Combe, I.; Giral, P. J.-P. Abiotic degradation of free phytol in the water column: A new pathway for the production of acyclic isoprenoids in the marine environment. *Geochim. Cosmochim. Acta* **1990**, *54*, 1307−1313.
(38) Xu, X.; Antal, M. J.; Anderson, D. G. M. Mechanism and Temperature-Dependent Kinetics of the Dehydration of *tert*-Butyl Alcohol in Hot Compressed Liquid Water. *Ind. Eng. Chem. Res.* **1997**, *36*, 23−41.
(39) Changi, S.; Brown, T. M.; Savage, P. E. Reaction kinetics and pathways for phytol in high-temperature water. *Chem. Eng. J.* **2012**, *189*−*190*, 336−345.
(40) Yang, W.; Li, X.; Liu, S.; Feng, L. Direct hydrothermal liquefaction of undried macroalgae *Enteromorpha prolifera* using acid catalysts. *Energy Convers. Manage.* **2014**, *87*, 938−945.

https://doi.org/10.1021/acs.iecr.2c02300
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX