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Full Length Article

Catalytic pyrolysis of raw and hydrothermally carbonized *Chlamydomonas debaryana* microalgae for denitrogenation and production of aromatic hydrocarbons

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ABSTRACT

Pyrolysis of raw and hydrothermally carbonized (HTC) *Chlamydomonas debaryana* with and without activated carbon (AC) or β-zeolite as the catalyst were studied. Monoaromatic hydrocarbon yields from the pyrolysis of raw and HTC treated algae without a catalyst were relatively low at optimum yields of 11.2% and 12.0% obtained at 600 °C, respectively. The maximum yields of monoaromatic hydrocarbons from the AC catalyzed pyrolysis of raw and HTC treated algae were 43.8% obtained at 600 °C and 43.5% obtained at 800 °C, respectively, compared to 32.3% and 32.7% for the maximum yields from the β-zeolite catalyzed pyrolysis at 500 °C and 600 °C, respectively. However, β-zeolite catalyzed pyrolysis produced higher yields of total hydrocarbons (aromatic + aliphatic) for raw and HTC algae compared to AC catalyzed pyrolysis. This means while β-zeolite was more effective in producing total hydrocarbon content, AC was more effective in aromatization of oxygenates. The combination of HTC pretreatment and catalytic pyrolysis were effective in reducing nitrogen content in bio-oil. The yields of nitriles and nitrogenous compounds were negligible for the AC catalyzed pyrolysis of HTC treated algae at 600 °C, compared to 8.3% using the β-zeolite at the same temperature. The AC catalyst had a lower tendency towards coking.

1. Introduction

A wide variety of biomass resources such as grass, wood, agricultural crops and residues, animal waste, municipal solid waste and aquatic plants have been studied for the production of liquid biofuels [4,5]; Hawash et al. [22,27,34,44]. Microalgae that are one of the most important aquatic organisms have been considered as a potential biomass source for mass production of liquid biofuels due to their high growth rate, ability to be cultivated on wastewater without the use of arable land, and high lipid content [17]. Furthermore, as microalgae have a high biological CO_2 fixation rate, they can be used to effectively reduce the industrial CO_2 emission [9]. Therefore, the cultivation of microalgae and utilization of microalgae as an energy source would be of great economic and environment benefits [26].

Various technologies have been developed to convert algal biomass into liquid fuels [8,13,38]. Pyrolysis and hydrothermal treatment are two widely studied thermochemical processes to convert algal biomass into liquid fuels commonly known as bio-oil [8,12,14,43]. Pyrolysis decomposes dry algal biomass into condensable vapors under an inert atmosphere at 450–600 °C [14]. Hydrothermal treatment (HTT) involves the application of heat to wet algae in a closed system to produce an organic hydrophobic phase of oil, water soluble substances, non-condensable gases and a solid residue [10,39]. HTT removes nitrogen which can improve the bio-oil quality and quantity towards downstream processes for diesel-like biofuels [12]. Hydrothermal liquefaction (HTL) and hydrothermal carbonization (HTC) are two major HTT methods. HTL is considered as a promising technology to liquefy solid biomass into bio-oil as a main product at various solid concentrations, a temperature of 300–375 °C and residence time of 5–15 min [12,14,30,40,36]. HTC occurs at a lower temperature (e.g., 200 °C) and longer residence time (e.g., several hours) to produce biochar as a main product from waste sludge [23] and wet microalgae [24]. It was reported that the higher heating value (HHV) of hydrochar produced by HTC of microalgae under 200 °C and 20 bar for 1 h was 30 MJ/kg [36].

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Heilmann et al. [25] found that most of the fatty acids in microalgae were retained in the hydrochar, about 55% of carbon stayed in the char and the remaining 45% was transferred into the aqueous phase during HTC [36]. As 80% N in algae was reported to be released into the aqueous phase during HTC, HTC provides an effective approach to recycle the N in the algal biomass into an aqueous phase for algal cultivation [24,25].

Catalytic pyrolysis using catalysts such as zeolites is one of the promising technologies for improving the yield and quality of liquid biofuel from microalgae [2,7,19,42,43]. The catalytic pyrolysis can produce a mixture of hydrocarbons, mostly aromatic hydrocarbons via the reactions of deoxygenation, decabonylation and decarboxylation. Zeolites have different acidities and pore sizes, which can facilitate the production of aromatic hydrocarbons and promote deoxygenation of bio-oil. Zeolites have been widely studied in the catalytic pyrolysis of lignocellulosic biomass [31,33,35] and algae [7,15]. As activated carbon usually has imperfect aromatic sheets of carbon atoms, incompletely saturated valences and unpaired electrons on its surface, it has high adsorption capacity for polar or polarizable molecules [45]. The surface functional groups of activated carbon are formed as a result of thermal or chemical treatments, which influence the acid–base properties of carbon surface and could be considered as potential active sites for catalysis [45].

Our previous research showed that *Chlamydomonas debaryana (C. debaryana)* is a promising algal species for both swine waste treatment and biofuel production [48,50,51]. The objective of this study was to evaluate and compare the yields of aromatic compounds, the potential of de-nitrogenation and the composition of the bio-oil during catalytic pyrolysis of raw and HTC treated *C. debaryana* algae over β- zeolite and activated carbon catalysts at different temperatures.

2. Materials and methods

2.1. Microalgae characterization

C. debaryana AT24 was isolated from a local swine wastewater lagoon located at the farm of North Carolina Agricultural and Technical State University [48]. The *C. debaryana* was cultured with swine wastewater [50]. The detailed experimental procedure of HTC was described elsewhere [51]. Briefly, *C. debaryana* slurry with a 5.7 wt% solid concentration was hydrothermally carbonized in a 75-ml Parr high-pressure reactor (Parr Instrument, Moline, IL, USA). The temperature of the reactor was increased to 200 °C at a heating rate of about 10 °C/min, and was held at 200 °C for 6 h. The hydrochar was separated from the aqueous fraction by filtration, then dried and milled to a size less than 150 μm. The hydrochar was kept in an air-tight container for this study. The yields of hydrochar, aqueous fractions and non-condensable gases from the HTC of *C. debaryana* were 28.3%, 68.6% and 3.1%, respectively.

The proximate analysis was conducted to determine the moisture, volatile matter, fixed carbon and ash content of raw and HTC treated microalgae according to the ASTM D1762-84. Crude protein analysis was determined by the Dumas method [28]. Crude fat content was determined gravimetrically via extraction with 2: 1 chloroform-methanol (v/v) co-solvent [48]. The carbohydrate content was estimated by subtracting lipid, protein, ash and moisture contents. Ultimate analysis was carried out to determine the element contents of C, H, N and S contents using an elemental analyzer (Model 2400, PerkinElmer). The oxygen content was calculated by subtracting C, H, N, ash and moisture contents. High heating values (HHV) were calculated according to the following equation [18]:

$$HHV\left(\frac{MJ}{kg}\right) = 3.55 \times C^2 - 232 \times C - 2230 \times H + 51.2 \times C \times H + 131 \times N + 20600 \times 10^{-3} \quad (1)$$

2.2. TGA analysis of the pyrolytic characteristics of raw and HTC treated microalgae

The pyrolysis experiments of raw and HTC treated microalgae were carried out in a TGA (SDT-Q600, TA Instruments) under a nitrogen atmosphere (99.99% N_2) at a flow rate of 60 mL min^{-1}. Approximately 10 mg of sample was heated from 25 to 800 °C at heating rates of 10, 20, 30 °C min^{-1}.

2.3. Catalytic pyrolysis of raw and HTC treated microalgae

Fast pyrolysis of raw and teated microalgal samples with and without a catalyst was conducted in a multi shot pyrolyzer system (EGA/PY-3030D, Frontier Laboratories Ltd, Japan) connected with a gas chromatography-mass spectrometry (GC/MS) (Model: 7890A GC and 5978MSD, Agilent Technologies, CA USA). Approximately 3 mm of quartz wool was first placed at the bottom of a stainless steel sample cup (Eco-cup LF) with 8 mm length and 4 mm diameter to hold powder sample and catalyst. Approximately 0.3 mg of microalgae and 3 mg catalyst were then placed into the sample cup in series. Another 3 mm of quartz wool was placed at the top of the catalyst layer. The sample cup was dropped into the preheated furnace using the double-shot sampler connected to the top of the multi shot pyrolyzer. The sample temperature was instantly increased to a given final pyrolysis temperature at a heating rate of approximately 1000 °C/s.

The temperatue of the valve connected between the pyrolyzer and the GC, and the temperature of the GC front inlet were maintained at 300 °C to prevent the condensation of product volitales. The temperature of the GC oven was initially set at 40 °C and held at 40 °C for 2 min, then ramped to 220 °C at a rate of 5 °C/min and held at 220 °C for 15 min. Helium at a flow rate of 1 mL/min was used as a carrier gas with a split ratio of 50:1. MS detection was carried out under electronimpact (EI) ionization conditions in full scan from m/z 30–400 with a threshold at 300. This enabled the detection of the major products of primary and secondary pyrolysis reactions. The yields of compounds were semi-quantified as the area determined by the MS profile per unit mass of the sample (area/μg of microalgae).

Non-catalytic flash pyrolysis of raw and HTC treated *C. debaryana* was performed at a heating rate of approximately 1000 °C/s, temperatures of 300, 400, 500, 600, 700 and 800 °C and at a residence time of 20 s.

Two different catalysts of β-zeolite in anhydrous powder (Zeolyst International) and activated carbon (Sigma Aldrich) were employed for catalytic pyrolysis. The β-zeolite has a Si/Al ratio of 38 and surface area of 710 m^2/g and activated carbon has a 100 mesh particle size and surface area of 600 m^2/g. The zeolite catalyst was initially activated to its protonated form in a furnace at 400 °C in air for 5 h. It was reported that there was a significant increase in aromatic hydrocarbon yield when a zeolite catalyst to biomass ratio was increased from 1:1 to 10:1 [7] Therefore, a catalyst to biomass ratio of 10:1 was used in this study. The samples were catalytically pyrolyzed at four different temperatures of 500 °C, 600 °C, 700 °C and 800 °C with a heating rate of 1000 °C/s and held at the final temperature for 30 s. All experiments were done in duplicate.

2.4. Analysis of the bio-oil compositions

A semi-quantitative procedure was used to determine the yields of individual bio-oil compounds [43]. The concentration (wt%) of each identified bio-oil compound was calculated as:

$$\%w_i = (w_i/W) \times 100 \quad (2)$$

where w_i is the estimate weight of a single identified bio-oil compound calculated by integrating the mass chromatogram of the selection ion (SIM) peak area at the characteristic mass-to-charge ratio (m/z) as:

$$W_i = A_{i,SIM} \quad (3)$$

where $A_{i,SIM}$ is the peak area of an identified bio-oil compound. W is the total amount of bio-oil calculated by integrating all the detected MS peaks in a total ion current as

$$W = A_{tot} \quad (4)$$

where A_{tot} is the summed area of all compounds in TIC mode. Overall yield of pyrolysis products Y was calculated as

$$Y = W/w_{sample} \quad (5)$$

where w_{sample} is the initial weight of a sample.

2.5. Estimating total hydrocarbon yield, carbon yield and higher heating value of pyrolysate from catalytic pyrolysis

The pyrolysates from the catalytic pyrolysis of untreated and HTC treated *C. debaryana* were assumed to form the fuel. The elemental composition (C, H, O and N) of the fuel was determined by the chemical formula of each compound identified in the GC-MS peaks. The total hydrocarbon content was estimated as the sum of aromatic and aliphatic hydrocarbon while the carbon yield was calculated from the carbon composition of the simulated fuel yield from catalytic pyrolysis of untreated and HTC treated *C. debaryana*. Higher Heating Value (HHV) was estimated from elemental composition of simulated fuel using Eq. (1) shown in Section 2.1

3. Results and discussion

3.1. Chemical and elemental compositions of raw and HTC treated microalgae

C. debaryana is composed of mainly protein, carbohydrates, lipids and ash. As given in Table 1, *C. debaryana* used in this study has a protein content of 59.4 wt% and a carbohydrate content of 10.1 wt%. The nitrogen content in *C. debaryana* was 9.5 wt%, which is much higher than that of most lignocellulosic biomass such as 0.5% in sugar cane bagasse, 0.3% in corn cob, 0.6% in corn stover and 0.62% in Eucalyptus grandis [7]. HTC of *C. debaryana* at 200 °C increased the carbon content from 50.8 wt% in raw *C. debaryana* to 72.7 wt% and decreased the nitrogen content from 9.5 wt% in raw *C. debaryana* to 5.2 wt%. The increase in carbon of HTC treated *C. debaryana* algae is a consequence of carbonization resulting from the removal of oxygen by dehydration and decarboxylation which also resulted in increased HHV [14]. The decrease in the nitrogen content can be explained by the hydrolysis of proteins and nucleic acids while the nitrogen remaining in the pretreated algae could be from hydrophobic peptides, amino acids or Maillard reaction products, as the pretreated algae had a rich dark brown color. The ash content of HTC treated *C. debaryana* was 13.5 wt % compared to 7.9 wt% for raw C. *debaryana*. Biomass with a high ash content can generally lower decomposition temperatures of polysaccharides in the biomass but may cause corrosion and slag formation [29].

Table 1
Chemical and elemental compositions of raw and HTC treated C. debaryana algae.

	Raw *C. debaryana* algae	HTC *C. debaryana* algae
Carbon (wt%)	51.2	72.7
Hydrogen (wt%)	7.2	9.7
Nitrogen (wt%)	9.5	5.2
Sulfur (wt%)	1.1	0.2
Oxygen (wt%)	31	12.2
HHV	21.9	35.3
Moisture (wt%)	2.7	–
Carbohydrates (wt%)	10.1	–
Protein (wt%)	59.4	–
Lipids (wt%)	19.9	–
Ash	7.9	13.5

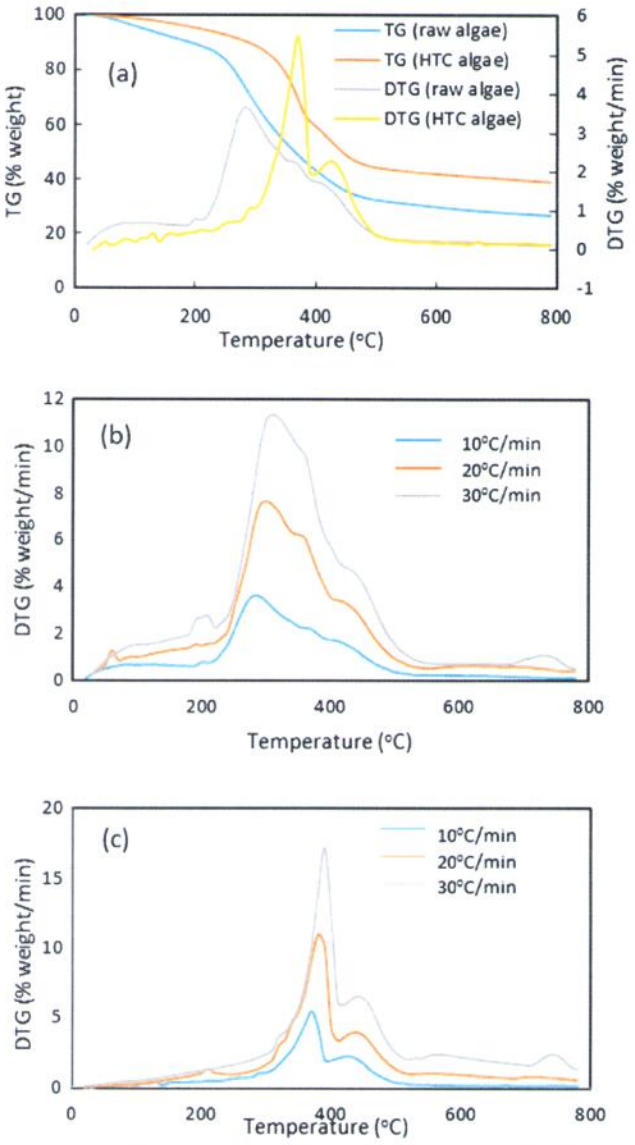

Fig. 1. (a) TG and DTG of raw and HTC algae at heating rate 10 °C (b) DTG of raw algae at different heating rates (c) DTG curves for HTC treated algae at different heating rates for non-catalytic pyrolysis of *C. debaryana* microalgae.

3.2. Thermogravimetric characteristics of raw and HTC teated C. debaryana during pyrolysis

Fig. 1(a) shows the TG and DTG pyrolysis curves of raw and HTC treated *C. debaryana*. As seen in Fig. 1(a), the pyrolysis process occurs mainly in three stages of dehydration, volatilization and decomposition, which have also been reported in literature [6,37]. The first stage starts from an ambient temperature to a temperature around 110 °C to mainly vaporize bound moisture and small fraction of lipids in the microalgae which ends at a temperature of 190 °C. The second stage from 110 to 550 °C volatilizes carbohydrates and protein into different condensable and non-condensable gases. In the third stage from 550 to 800 °C, remaining lipids and non-volatile matter vaporize into CO and CO_2. The third stage shows a gradual mass loss by the slow decomposition of lipids which finally leads to char formation [32]. There was significant difference in the TGA curves between the raw and HTC treated *C. debaryana*. The active decomposition of raw algae started at a

Table 2
Maximum mass loss rates and corresponding temperatures during non-catalytic pyrolysis of raw and HTC treated *C. debaryana* algae.

Heating rate (°C/min)	Zone 1 Temperature (°C)	DTG (max.) (%/min)	Zone 2 Temperature (°C)	DTG (max.) (%/min)	Zone 3 Temperature (°C)	DTG (max.) (%/min)
Raw algae						
10	280	3.62	410	1.69	680	0.17
20	300	7.67	420	3.35	690	0.57
30	330	10.8	420	4.88	730	1.09
HTC treated algae						
10	370	5.47	430	2.25	750	0.17
20	380	11.02	440	3.95	710	0.82
30	390	17.16	440	6.55	740	2.39

much lower temperature at 220 °C (Fig. 1a) than the decomposition of HTC treated algae at 300 °C (Fig. 1a). Additionally, the decomposition of the HTC treated algae showed two distinct peaks representing the decomposition of carbohydrates and proteins as a main peak and the decomposition of lipids as a shoulder peak while the decomposition of raw algae only generated single broad peak showing slight distinction between carbohydrates, proteins and lipids as shown in Fig. 1a. The DTG profiles of the pyrolysis of raw and HTC treated *C. debaryana* at different heating rates are shown in Fig. 1(b) and (c), respectively. The pattern of the curves was not affected by the increase of heating rate during pyrolysis. However, the peaks obviously were shifted to higher temperatures for both raw and HTC treated *C. debaryana* algae when the heating rate was increased. The maximum mass loss rate (% weight loss/min) increased with the heating rate for raw and HTC treated *C. debaryana*. It can also be seen that the maximum mass loss rate and its corresponding temperature of the HTC treated algae were slightly higher than those of the raw algae as given in Table 2.

3.3. Effects of pyrolytic conditions on the compositions of bio-oil produced from raw and HTC treated C. debaryana algae

Effects of pyrolytic temperatures of 300, 400, 500, 600, 700 and 800 °C and HTC treatment on the yield and composition of bio-oil produced from *C. debaryana* were analyzed. The volatiles that were detected by the GC-MS include various organic compounds and CO_2, but not including any other non-condensable gases such as H_2 and CO. The yields of the volatiles were quantified as their MS peak areas per unit mass of microalgae as shown in Fig. 2(a) and (c). For the simplicity, we assumed all detected volatile compounds excluding CO_2 to be the hypothetical bio-oil. The yields of detectable volatiles increased when the temperature increased from 300 °C to 500 °C during the pyrolysis of raw *C. debaryana* and from 300 °C to 600 °C during the pyrolysis of HTC treated *C. debaryana*. However, when the temperature was further increased to 800 °C, the yields of detected volatiles started to decrease for the pyrolysis of both raw and HTC treated algae, which might be caused by the decrease of detectable volatile compounds and the increase of no-detectable gases such as H_2 and CO at a very high temperature,

Fig. 2(b) and (d) show the distribution of the major pyrolysates produced at different pyrolysis temperatures. Aliphatic hydrocarbons (C_5–C_{30}), carboxylic acids, nitriles and nitrogenous compounds were identified as the major components produced during the pyrolysis of raw and HTC treated algae. In the range of the pyrolysis temperature from 300 °C to 800 °C, aliphatic hydrocarbons were from 11.8% to 22.2% of the overall volatiles for the raw algae and from 13.6% to 32.9% for the HTC treated algae. The carboxylic acids were dominant compounds in the volatiles obtained from the pyrolysis of both raw and HTC treated algae at 300 °C, which were 61.0%. When the pyrolysis temperature increased to 800 °C, the carboxylic acid content was decreased to 18.1% and 0.3% in the bio-oil produced from the pyrolysis of raw and HTC treated algae, respectively.

Microalgae grown in wastewater usually have a high content of proteins, which generate undesirable nitriles and nitrogenous compounds in the bio-oil during pyrolysis. The pyrolysis of algae with an HTC treatment might significantly reduce the formation of nitriles and nitrogenous compounds. The contents of the nitriles and nitrogenous compounds were reduced to from 0.2% to 11.6% for the pyrolysis of HTC treated algae at a temperature from 300 °C to 800 °C, compared with 10.7% to 32.4% in the bio-oil for the raw algae pyrolysis. When comparing at the same pyrolysis temperature of 500 °C, the contents of the nitriles and nitrogenous compounds in the bio-oil from the pyrolysis of the HTC treated algae and the raw algae were 10.2% and 21.5%, respectively. The content of the nitriles and nitrogenous compounds could be further reduced to 0.2% for the HTC treated algae when the temperature was further increased to 800 °C. A similar trend for nitrogenous compounds during the pyrolysis of *Spirulina* had been reported in the literature [7].

The content of the monoaromatics and cyclic organic compounds increased with temperature for the pyrolysis of both raw and HTC treated algae. The contents of the monoaromatics in the bio-oil from the pyrolysis of raw and HTC treated algae at 800 °C were 10.8% and 10.0%, respectively, compared to traceable amount for both raw and HTC treated algae at 300 °C.

The content of polyaromatic hydrocarbons (PAHs) were negligible for the pyrolysis of both raw and HTC treated algae at the temperature from 300 °C to 800 °C. The HTC treatment increased the content of sugars and anhydrosugars with a maximum content of 4.6% obtained at 500 °C, compared to a traceable amount in bio-oil from the pyrolysis of the raw algae.

3.4. Catalytic pyrolysis of raw and HTC treated C. debaryana algae

The HTC treatment prior to pyrolysis significantly could reduce the content of nitrogenous compounds in the bio-oil produced from algae. On the other hand, the content of aromatic hydrocarbons from the non-catalytic pyrolysis of algae, which are very important high-value chemicals, was very low as discussed in Section 3.3. A catalytic pyrolysis process using β-zeolite and activated carbon as catalysts was thus studied to improve the quality of the bio-oil by further reducing the nitrogen content and increasing the aromatic hydrocarbon content in the bio-oil produced from raw and HTC treated *C. debaryana* algae.

3.4.1. Influence of catalysts and pyrolysis temperature on bio-oil yields

Fig. 3. Shows the semi-quantified yields (represented by the MS peak areas) of total volatiles, bio-oil and CO_2 from non-catalytic, and β zeolite and activated carbon catalyzed pyrolysis of raw and HTC treated *C. debaryana* algae at different temperatures. As shown in Fig. 3(a), the overal yields of the volatiles from the pyrolysis of raw *C. debaryana* algae over both β-zeolite and activated carbon increased when the temperature increased from 500 to 800 °C.

As shown in Fig. 3(b), the catalytic pyrolysis of HTC treated *C. debaryana* over the activated carbon also increased the yields of volatiles as temperature increased. However, the maximum yield of volatiles during the catalytic pyrolysis of HTC treated *C. debaryana* over β-zeolite was obtained at 600 °C and the yield of the volatiles then declined as the temperature further increased higher than 600 °C. As shown in Fig. 3(c) and (d), for both raw and HTC treated algae, the hypothetical

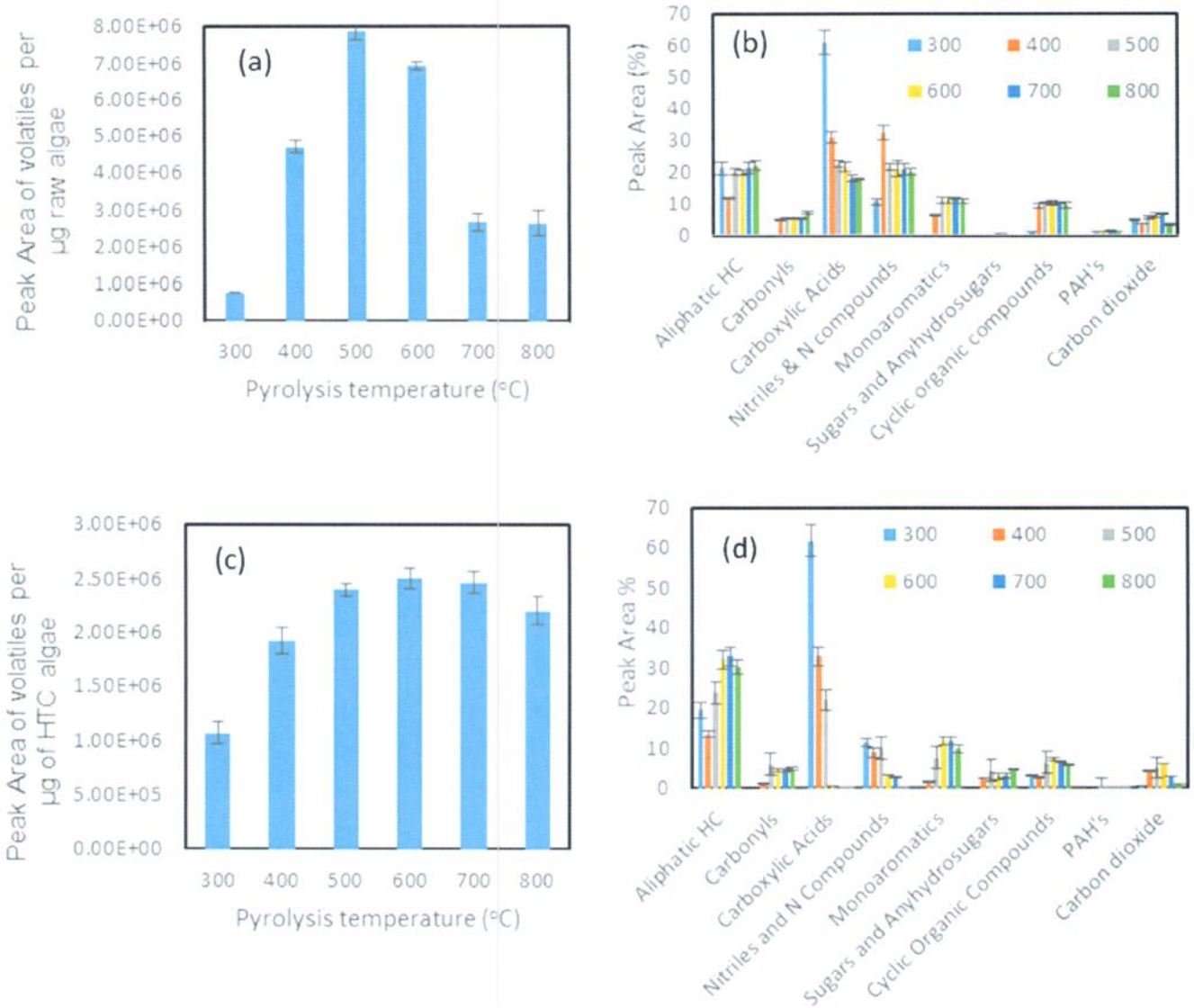

Fig. 2. Semi-quantified yields (MS peak area) of total volatiles and contents of selected volatile compounds from the non-catalytic pyrolysis of raw and HTC treated *C. debaryana* algae at different temperatures (°C). (a) Yield of volatiles for raw algae (b) Contents of selected volatile compounds for raw algae (c) Yield of volatiles for HTC treated algae (d) Contents of selected volatile compounds for HTC treated algae.

bio-oil fraction in the volatiles from the pyrolysis over β-zeolite was comparable to that of the non-catalytic pyrolysis but about 5% to 20% higher than that over activated carbon depending on the temperature.

As shown in Fig. 3(e) and (f), the the activated carbon catalyzed pyrolysis of both raw and HTC treated algae significantly increased the fraction of CO_2, compared to the non-catalytic pyrolysis. The β-zeolite catalyzed pyrolysis of raw algae significantly increased the fraction of CO_2, compared to the non-catalytic pyrolysis. However, the β-zeolite catalyzed pyrolysis of the HTC treated algae significantly decreased the fraction of CO_2 at a temperature below 700 °C, compared to the non-catalytic pyrolysis

3.4.2. Influence of HTC treatment on major hydrocarbons and nitrogenous compounds from catalytic pyrolysis

3.4.2.1. Aliphatic hydrocarbons. Aliphatic hydrocarbons in this study consisted of the total contributions of all C_5 to C_{30} straight and branched chain alkanes, alkenes and alkynes. As shown in Fig. 4(a) and (b), the non-catalytic pyrolysis of raw and HTC treated *C. debaryana* at 500 °C produced 20.2% and 23.8% of aliphatic hydrocarbons in the volatiles, respectively. At 500 °C, the β-zeolite catalytic pyrolysis slightly increased the contents of aliphatic hydrocarbons to 24.5% for the raw algae and 24.1% for the HTC treated algae. At 500 °C, the activated carbon catalyzed pyrolysis significantly decreased the content of aliphatic hydrocarbons to 0.5% for the raw algae and 1.9% for the HTC treated algae. The maximum contents of aliphatic hydrocarbons were 13.2% for the catalytic pyrolysis of raw *C. debaryana* algae over activated carbon obtained at 600 °C, and 20.4% for HTC treated *C. debaryana* obtained at 700 °C. If the temperature increased further, the contents of aliphatic hydrocarbons decreased in both β-zeolite and activated carbon catalyzed pyrolysis. A similar trend of temperature effect on aliphatic hydrocarbons has been reported for catalytic pyrolysis of biomass over a zeolite [46] and activated carbon [11].

3.4.2.2. Monoaromatic hydrocarbons. As shown in Fig. 4(c) and (d), the monoaromatic hydrocarbon contents from the non-catalytic pyrolysis of raw and HTC treated *C. debaryana* were very low. Their maximum contents were 11.2% for the raw algae and 12.0% for the HTC algae obtained at 600 °C. The catalytic pyrolysis increased the monoaromatic hydrocarbon content. It was also observed that the aromatization in activated carbon catalyzed pyrolysis was higher than that of the β-zeolite catalyzed pyrolysis for both raw and HTC treated algae. For the

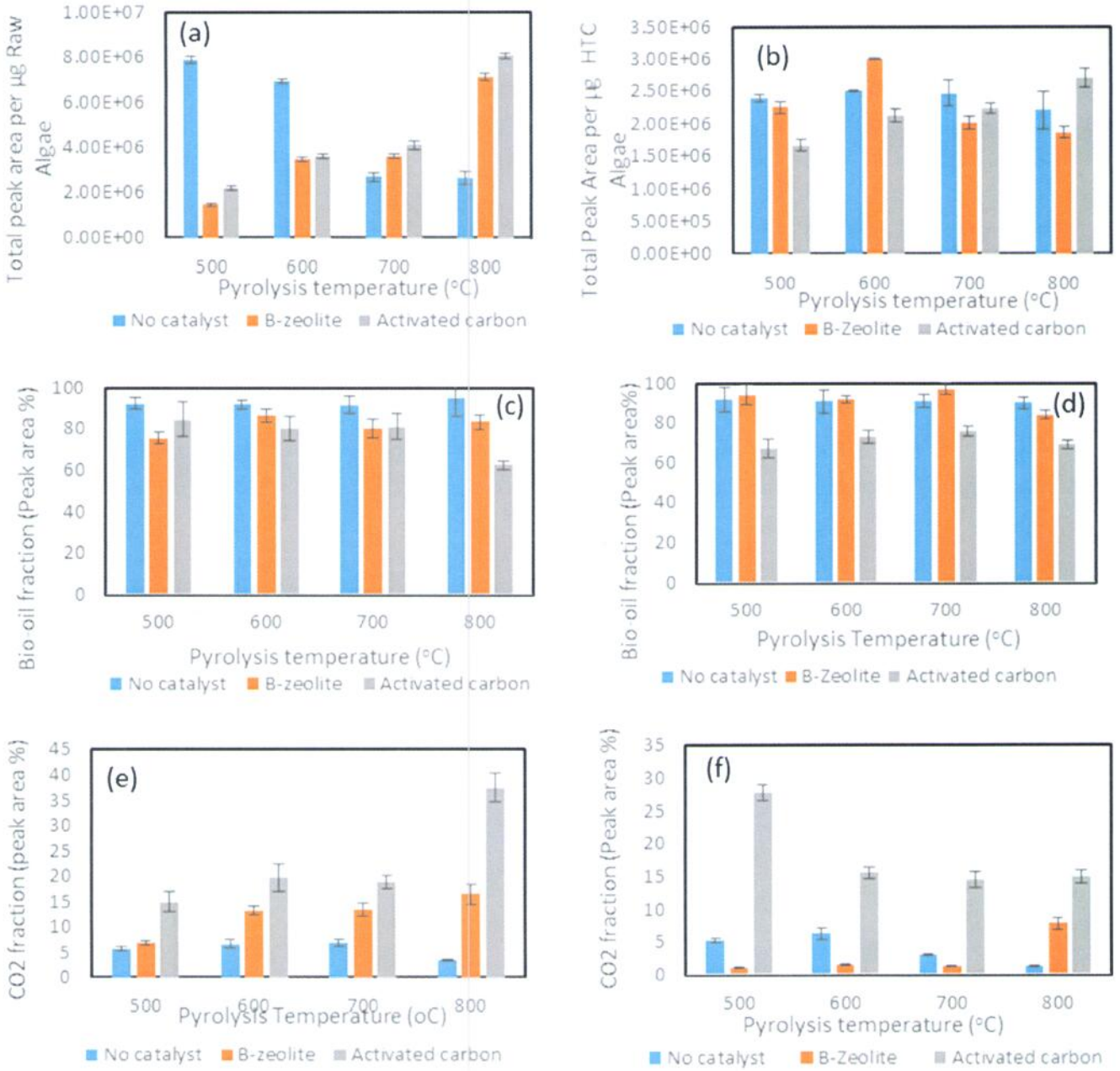

Fig. 3. Semi-quantified yields (MS peak areas) of total volatiles, and contents of bio-oil compunds and CO_2 in the volatiles from the pyrolysis of raw and HTC treated C. debaryana algae at different temperatures. (a) Yield of total volatiles from raw algae (b) Yield of total volatiles from HTC treated algae (c) Content of bio-oil compounds in the volatiles from raw algae (d) Content of bio-oil compounds in the volatiles from HTC treated algae (e) Content of CO_2 in the volatiles from raw algae (f) Content of CO_2 in the volatiles from HTC treated algae.

catalytic pyrolysis of raw algae over the activated carbon, the maximum content was 43.8% that was obtained at 600 °C. If the temperature increased to 800 °C, the content decreased to 31.6%. The β-zeolite catalytic pyrolysis of the raw algae produced a maximum content of monoaromatic hydrocarbon of 32.3% that was obtained at 500 °C and the content decreased to 21.2% if the temperature increased to 800 °C. A similar trend has been reported in the literature [41,49]. The HTC pretreatment had no significant effect on monoaromatic hydrocarbon content.

3.4.2.3. Nitriles and nitrogenous compounds. As shown in the appendix, several nitrogen-containing compounds were found in bio-oil including amides, nitriles, and aromatic amines. HTC treatment of *C. debaryana* algae significantly reduced nitriles and nitrogenous compounds in the bio-oil during the subsequent pyrolysis. This suggests that many nitriles and nitrogenous compounds were released in the aquous fraction during HTC treatment.

During catalytic pyrolysis of raw and HTC treated *C. debaryana* algae, the contents of nitriles and nitrogenous compounds generally decreased in both β-zeolite and activated carbon catalyzed pyrolysis at a high temperature as seen from Fig. 4(e) and (f). However, as shown in Fig. 4(f), we saw an increasing content of nitriles and nitrogenous compounds for activated carbon catalyzed pyrolysis of HTC treated algae as the temperature increased, and the maximum content of nitriles and nitrogenous compounds was 5.2% that was obtained at 800 °C. The β-zeolite was more effective in reducing the nitriles and nitrogenous compounds during the catalytic pyrolysis of raw *C. debaryana* algae than activated carbon as seen in Fig. 4(e). For the HTC

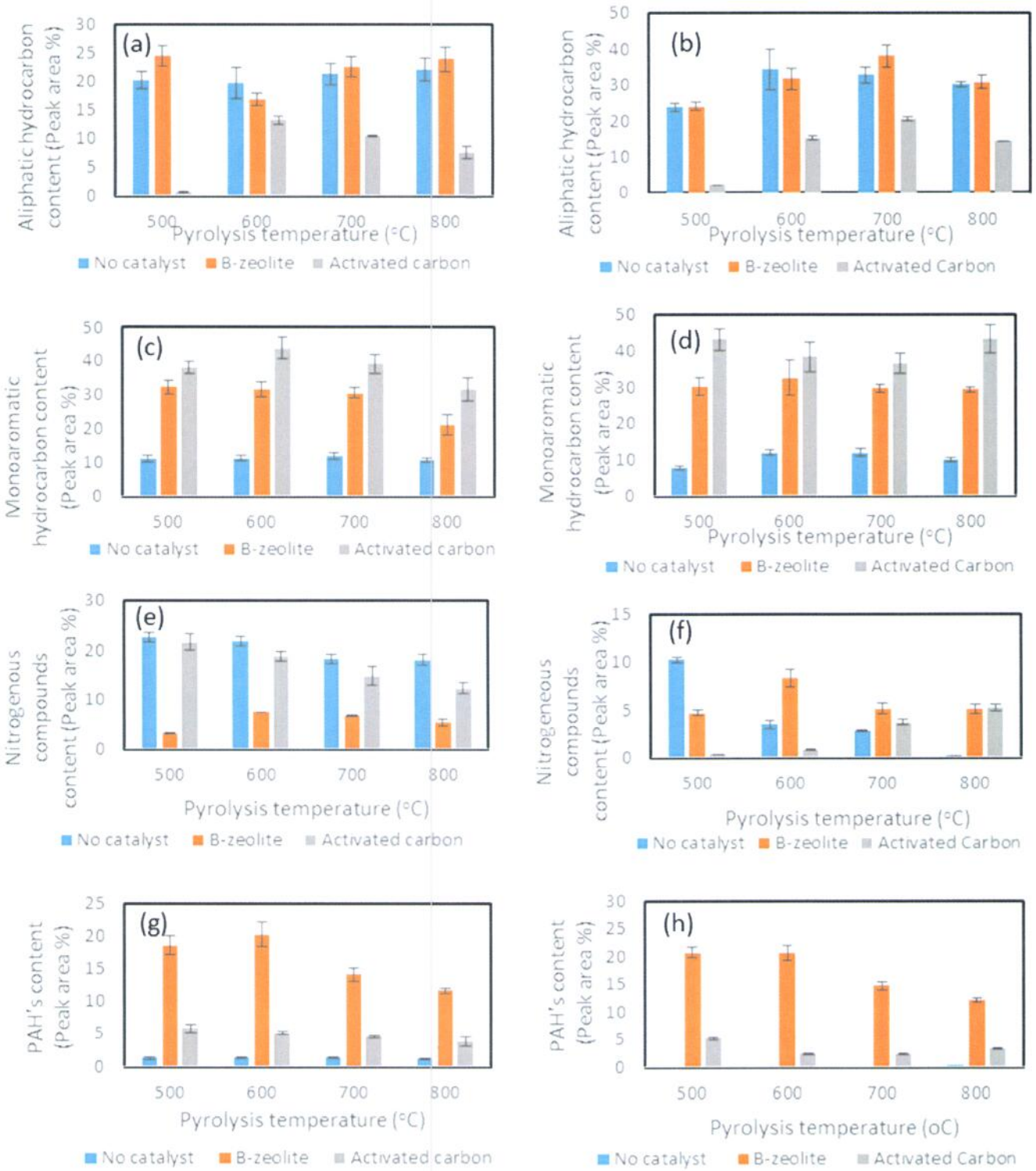

Fig. 4. Semi-quantified contents (peak area%) of selected compounds in the bio-oil obtained from the pyrolysis of raw and HTC treated C. debaryana algae at different temperatures. (a) Aliphatic hydrocarbons for raw algae (b) Aliphatic hydrocarbons for HTC treated algae (c) Monoaromatic hydrocarbons for raw algae (d) Monoaromatic hydrocarbons for HTC treated algae (e) N compounds for raw algae (f) N compounds for HTC treated algae (g) PAH's for raw algae (h) PAH's for HTC treated algae.

treated *C. debaryana* algae, activated carbon was better than β-zeolite in reducing nitriles and nitrogenous compounds at rather lower temperatures of 500 °C and 600 °C as shown in Fig. 4(f).

3.4.2.4. Polyaromatic hydrocarbons (PAH's). PAHs are compounds with large molecular weights formed during catalytic pyrolysis. As shown in the appendix, some examples of PAH compounds are the napthalenes, alkyl naphthalenes, indenes, alkyl indenes, flourenes, anthracene, phenanthrenes. Polyaromatics are commonly viewed as indicators of coke formation that may lead to catalyst deactivation during catalytic fast pyrolysis [47]. As seen from Fig. 4(g) and (h), the activated carbon catalyst showed lower selectivity towards polyaromatic hydrocarbons

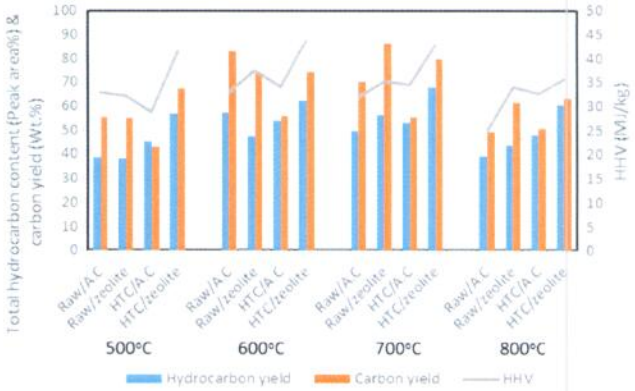

Fig. 5. Total hydrocarbon content, carbon yields and heating value of bio-oil from catalytic pyrolysis of raw and HTC treated C. debaryana algae.

than the β-zeolite catalyst, i.e., the activated carbon catalysts had a lower tendency towards coking. The lower catalytic reactivity of activated carbon than β-zeolite could be attributed to its lower acidity. HTC treatment did not significantly affect the generation of PAHs during the catalytic pyrolysis of algae. However, if the temperature increased, the content of PAHs decreased in both β-zeolite and activated carbon catalyzed pyrolysis, which means that more large molecules such as PAHs were cracked at high temperatures.

3.5. Comparison of hydrocarbon yield and heating value of raw and HTC algae during catalytic pyrolysis

The maximum total hydrocarbon (aromatic and aliphatic) content and carbon yield were obtained by the catalytic pyrolysis of raw and HTC treated algae at 600 °C and 700 °C, respectively, and then decreased at 800 °C (Fig. 5). Higher temperatures generally tend to decrease the total hydrocarbon yields [3]. It probably occurred due to the fact that high temperatures are more suitable for the formation of non-condensable gases such as CO and CO_2 via the deoxygenation process. Also, it can be seen that total hydrocarbon content and carbon yield for the pyrolysis of *C. debaryana* algae over β zeolite were generally higher than the pyrolysis of *C. debaryana* over activated carbon. This means that the β zeolite catalyst was more effective in producing total hydrocarbons (aromatic and aliphatic) than the activated carbon catalyst. In terms of energy content, greater values of HHV for bio-oil occurred at the optimum yields of total hydrocarbons (Fig. 5). It can be seen from Fig. 5 that β zeolite produced bio-oil with greater HHV than the AC for the pyrolysis of HTC algae. Similar trend of greater HHV for β zeolite compared to AC was observed for raw algae at temperatures from 600 to 800 °C while at 500 °C, the AC pyrolysis of raw algae produced greater HHV compared to β zeolite pyrolysis.

3.6. Reaction mechanism during catalytic pyrolysis of C. debaryana algae

Due to the complex structure of the microalgae, a wide range of complex organics were produced at various temperatures. To properly evaluate the pyrolytic products, the organic products were classified into functional groups based on chemical structure and chemical property. During catalytic pyrolysis of *C. debaryana* microalgae, light organics, including alcohols, acids and carbonyls from carbohydrates fraction of the algae are cracked and deoxygenated into C2-C6 olefins. These olefins undergo aromatization at the acive sites of the catalyst to produce benzene followed by alkylation and isomerization to produce other aromatics [1,20,21]). Similarly, the catalytic pyrolysis of lipids produce heavy oxygenated hydrocarbons, such as long chain fatty acids, ketones, esters, etc., which are then converted to heavy hydrocarbons by deoxygenation, cracked to olefins, which subsequently undergo a series of oligomerization, cyclization and aromatization to form aromatics [1,20,21]. Catalytic pyrolysis of some amines from protein fraction of microalgae produces olefins through deamination reactions which can subsequently undergo aromatization. Indole derivatives are relatively stable and they are not considered as the major source of aromatics [16].

4. Conclusions

The active pyrolysis of HTC treated algae started at 300 °C which was much higher than 220 °C for that of the raw algae. The maximum mass loss rate and its corresponding temperature for the pyrolysis of HTC treated algae were slightly higher than those for raw algae. The yields of volatiles from the pyrolysis of both raw and HTC treated *C. debaryana* increased with temperature and reached optimum at 500 °C and 600 °C respectively. The carboxylic acids were maximum at 61.0% in the bio-oil obtained from the pyrolysis of both raw and HTC treated algae at 300 °C, and decreased to 0.3% and 18.1% respectively as temperature increased to 800 °C. The monoaromatic hydrocarbon contents from the non-catalytic pyrolysis of raw and HTC treated *C. debaryana* were very low and its maximum content were 11.2% and 12.0% obtained at 600 °C, respectively. The catalytic pyrolysis could significantly increase the content of total hydrocarbon (aliphatic and aromatic). The activated carbon could achieve higher aromatization than the β-zeolite for the pyrolysis of both raw and HTC treated algae while β-zeolite catalyzed pyrolysis produced higher yields of total hydrocarbons (aliphatic + aromatic) than the AC catalyzed pyrolysis. The combination of hydrothermal carbonization and catalytic pyrolysis were effective in reducing nitrogen content in the bio-oil. The activated carbon was better than the β-zeolite in reducing nitriles and nitrogenous compounds during the catalytic pyrolysis of the HTC treated algae at low temperatures of 500 °C and 600 °C. As the activated carbon catalyst showed lower selectivity towards polyaromatic hydrocarbons than the β-zeolite catalyst, the activated carbon catalyst had a lower tendency towards coking.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2018.04.163.

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