

Catalytic hydrothermal carbonization of invasive macrophyte Hornwort (*Ceratophyllum demersum*) for production of hydrochar: a potential biofuel

M. A. Rather¹  · N. S. Khan¹ · R. Gupta²

Received: 14 April 2016 / Revised: 27 September 2016 / Accepted: 21 December 2016 / Published online: 31 December 2016
© Islamic Azad University (IAU) 2016

Abstract Biofuels are environment friendly and economical. First-generation biofuels are made from sugar, starch and vegetable oils, and have an impact on food security, while second generation biofuels are generated from plant or algal material and are greener and sustainable. The present work focused on lab-scale application of *hydrothermal carbonization* to convert aquatic weed *Ceratophyllum demersum* into a second-generation biofuel—hydrochar. *Hydrothermal carbonization* has been carried out with and without catalysts in a high-pressure reactor under subcritical temperatures 240–320 °C, residence times 10–40 min and biomass to water dilution ratios varying from 1:4 to 1:12. Under noncatalytic conditions higher heating value and energy density were highest, 24.11 MJ/kg and 1.64 respectively at temperature of 300 °C and residence time of 30 min. The calorific value of noncatalytic hydrochar was enhanced further, respectively, to 29.0, 27.5 and 26.48 MJ/kg by catalysts KOH, Na₂CO₃ and acetic acid. Catalytic hydrochar had H/C and O/C atomic ratios of same order as that of high-rank bituminous coal. Van Krevelen diagram indicated KOH to be better catalyst followed by Na₂CO₃ and acetic acid. Hydrochar yield of 38% obtained in noncatalytic *hydrothermal carbonization* decreased with catalysts in following order; acetic acid > Na₂CO₃ > KOH, however, energy density was enhanced in order KOH > Na₂CO₃ > acetic acid. The

research can prove a way forward in the direction of meeting part of global energy demand. At the same time, the problem of secondary pollution caused by piling up and decay of aquatic weeds will also be addressed to.

Keywords Aquatic weed · Catalyst · Energy · Higher heating value · Fuel

Introduction

Majority of present-day energy requirements in world are met by fossil fuels which exist mainly in form of petroleum and coal based products. Development of alternate fuels is the need of hour as fossil fuels are fast declining and cause environmental pollution. Among many other resources explored for alternate energy biofuels and fuel cells have received lot of attention in recent decades (Gupta et al. 2014; Yola et al. 2016; Atar et al. 2015a, b; Akyildirim et al. 2016). Biodiesel and bioethanol have successfully been produced from variety of food crops, but most people think this to be a compromise with food security (To and Grafton 2015). Bio-fuel generation from non-food crops like aquatic weeds (microalgae, macroalgae and macrophytes) has great potential to meet part of our future energy demand without compromising with food security. The menace of water weeds has become alarming now in many parts of the world, especially in tropical water bodies where they have led to serious ecological and economic losses (Aloo et al. 2013). World famous lake *Dal Lake* located in Srinagar India is one of such water bodies facing pollution and weed proliferation challenging its very existence (Amin et al. 2014). The lake exists at an altitude of about 1584 m above mean sea level located between 34°6' to 34°10'N latitude and 74°50' to 74°54' E longitude, covering an area of about 11.50 km² (Jeelani and Shah 2006). Every year

Editorial responsibility: Necip Atar.

✉ M. A. Rather
marather@nitsri.net

¹ Chemical Engineering Department, National Institute of Technology (NIT), Hazratbal, Srinagar 190006, India

² National Institute of Technology (NIT), Hazratbal, Srinagar 190006, India

more than 100,000 cubic meters of weed are removed manually or by using machines, from the lake and thrown away as waste. *Ceratophyllum demersum* commonly known as hornwort or coontail is a submerged free floating aquatic plant, widely growing in all the basins of *Dal Lake*. This weed is unwanted organism under biosecurity act of New Zealand government (New Zealand government website 2016). Hydrothermal carbonization (HTC) conversion is utilized in this research to transform the weed into solid biofuel.

HTC was used in production of fuels from biomass for the first time by Bergius in early twentieth century (Bergius 1932). The process obviates the need for drying of the feedstocks and is highly suitable for aquatic biomass like *C. demersum*. HTC converts wet biomass into a coal-like material commonly called ‘hydrochar’ along with aqueous products and gases (Funke and Ziegler 2010). HTC process takes place at subcritical water conditions (below the water critical point temperature of 374 °C and pressure of 22 MPa). It mimics the conversion of biomass into fossil fuels, thought to have occurred naturally in early ages under high pressure and temperature conditions (Savage et al. 2010). Various forms of nonaquatic biomass as HTC feedstocks used till date are micro- and macroalgae (Anastasakis and Ross 2011; Garcia Alba et al. 2012; Brown et al. 2010; Zhou et al. 2010; Eboibi et al. 2014), wheat straw (Suwelack et al. 2015), sewage sludge (Danso-Boatenga et al. 2015), olive mill waste, canned artichoke and orange wastes (Benavente et al. 2015) and wheat straw, poplar wood and olive residues (Wiedner et al. 2013). Aquatic macrophytes too lead to formation of substantial amounts of hydrochar in HTC. Some of the examples of aquatic weeds used as HTC feedstocks along their corresponding hydrochar yields (wt%) are duck weed (33.6–40.6%) (Duan et al. 2013), water hyacinth (16–32%) (Singh et al. 2015), *Laminaria saccharina* (10.7–30.5%) (Anastasakis and Ross 2011), *Tetraselmis* sp (13 to 19%) (Eboibi et al. 2014) and *Enteromorpha prolifera* (16.9–20.2%) (Zhou et al. 2010). As is clear from above fairly high yields of hydrochar in the range of 11–40.6 wt% are obtained from aquatic weeds. Till date, however, lesser attention has been paid toward hydrochar as potential fuel in comparison with biocrude.

In this study, HTC of *C. demersum* was carried out with an aim of producing a solid biofuel with its energy characteristics matching to coal. Macrophyte is posing a challenge to health of many water bodies and becomes a source of secondary pollution due to its decay upon storage. The effects of process temperature, reaction time, dilution ratio and catalysts (KOH, Na₂CO₃ and acetic acid) upon yield and higher heating value (HHV) etc. are investigated. The research having focused primarily upon macrophyte *C. demersum* can pave a way in the direction of meeting part of global energy demand by

utilization of aquatic biomass. In present research, feedstock was collected from *Dal lake* in the month of November 2014 and processed in Energy Engineering laboratory of Chemical Engineering Department at NIT Srinagar India.

Materials and methods

Processing and characterization of feedstock and hydrochar product

Feedstock for hydrothermal carbonization process, viz., *C. demersum* or Hornwort was collected from *Dal lake* in the month of November 2014. All adhering matter to weeds was removed first by washing with ordinary tap water and then in a solution of 1% ethylenediaminetetraacetic acid (EDTA), lime scale remover. Weeds were sundried for 3–4 days and then ground to size ranging from 0.25 to 4 mm (particles passed standard screen ASTM 5 but retained on ASTM 60). Fine powdered material was packed in airtight PVC containers and stored in desiccators for further use during HTC process.

Proximate analysis of feedstock and hydrochar for parameters moisture, ash and volatile matter was carried out by automatic proximate analyzer (Modal APA-2 of Advance Research Instruments India) as per standard ASTM procedures for particulate wood. Moisture content is found by standard procedure ASTM E871–82 (2013a) at temperature of 103 ± 10 °C for 2 h or till constant weight is obtained. Ash is found by test method ASTM D1102–84 (2013b) at temperature of 580 °C for 30 min. For volatile matter ASTM E872–82 (2013c) is followed using temperature of 950 °C for 7 min. Fixed carbon is a calculated value and is resultant of the summation of the percentages of moisture, ash and volatile matter subtracted from 100. All percentages are on same moisture reference basis. Elemental analysis of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) is carried out using CHNS elemental analyzer (Euro EA3000 of Eurovector Italy) according to ASTM D5373-08 (2008). All tests were conducted in triplicate.

Calorific value is calculated by Eq. 1 (Channiwalaa and Parikh 2002)

$$\text{HHV} \left(\frac{\text{Mj}}{\text{kg}} \right) = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{A} \quad (1)$$

where C, H, O, N, S and A represent, respectively, the elemental carbon, hydrogen, oxygen, nitrogen, sulfur and ash contents of material, expressed in mass percentages on dry basis (db).

Experimental

HTC was carried out in a cylindrical autoclave reactor of 700 ml capacity, made of alloy steel (SS 316L). Controlled heating by PID temperature controller was carried out by means of an external ceramic band heater of 2000 W power rating (Fig. 1). All experiments were carried out below sub-critical temperature and pressure. Before experimentation, reactor was thoroughly cleaned by washing and rinsing with double-distilled water. In a typical run, 30 g of feed (stored in desiccator and priorly dried at 60 °C for 1 h) was taken from container for processing. To this demineralized water of specified quantity was added and fed to reactor to make a homogeneous mixture. Reactor was properly sealed and head tightened by traditional wrenches for leak proof operation. Heating was started and autogenic pressure buildup allowed under inert atmosphere. Carbonization was carried out in the absence and then in the presence of chemicals acetic acid (1 ml of 1 molar solution), KOH (3 wt% of initial feed wt.) and Na_2CO_3 (0.5 wt% of initial feed wt.). All chemicals were analytical reagent grade (AR grade) purchased from Merck India. When the desired temperature in reactor was attained, carbonization reaction was further continued for holding or residence time varying from 10 to 40 min. At this stage, heating was stopped, reactor was cooled to room temperature and gas phase was vented. The carbonized solids were separated from the liquid phase by vacuum filtration using 0.45- μm nylon filters. During filtration about 50 ml of organic solvent dichloromethane (DCM) was added to dissolve any bio-oil sorbates to char. The solid product recovered is referred as hydrochar and was dried in an oven at 50 °C for 24 h to remove any residual moisture. Dried hydrochar was then weighed. All experiments were conducted in triplicate and

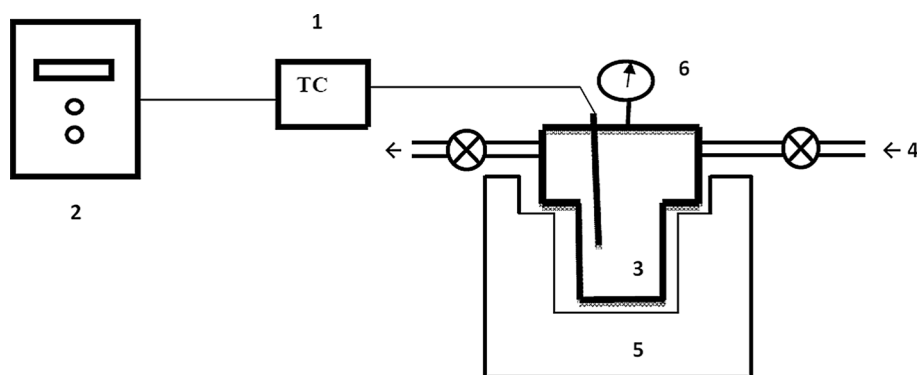
yield and other energy characteristics studied as function of temperature, dilution (biomass to water ratio) and residence time. Dried hydrochar was further analyzed for residual moisture, ash, volatile matter and elements carbon (C), hydrogen (H), nitrogen (N) and sulfur(S) contents.

As per past experience and literature evidences hydrochar yield was influenced by parameters; reaction temperature, time and feed to water dilution ratio. Role of these factors and chemicals KOH, Na_2CO_3 , acetic acid as catalysts on energy characteristics of hydrochar were evaluated. Previous study on HTC of *Laminaria saccharina* (Anastasakis and Ross 2011) suggested that temperature was most influential parameter for the HHV of hydrochar. Therefore, temperature was selected as first parameter in investigation. The process was carried out with biomass/water ratio of 1:8 for holding time of 30 min while varying temperature from 240 to 320 °C. Dilution ratio of 1:8 was used in view that weed practically contained about 90% of moisture (as received) and after sundrying retains about 8% of it, so using dilution ratio of 1:8 ratio will approximately correspond to moisture of wet weed (as received). Subsequent studies focused upon role of time and dilution ratio. Influence of catalysts acetic acid, KOH and Na_2CO_3 was investigated at most favorable temperature, holding time and dilution ratio conditions of noncatalytic HTC.

Hydrochar analysis

In addition to proximate analysis, ultimate analysis and HHV other important parameters like hydrochar yield (Y), energy densification (E_d), % energy yield (E_y) and carbon recovery (C_{rec}) were determined as per following relationships;

Fig. 1 Hydrothermal reactor assembly



- | | |
|---|------------------------|
| 1 | Thermocouple |
| 2 | Temperature Controller |
| 3 | Reactor |
| 4 | Inert Gas Supply |
| 5 | Band Heater |
| 6 | Pressure Gauge |



Table 1 Effect of temperature, time, dilution ratio and catalysts on different properties of hydrochar

Parameter	Yield (wt%)	CHNS/O Analysis					H/C	O/C	HHV (MJ/kg)	E_d	E_y (%)	C_{rec} (%)
		C	H	N	S	O ^a						
Feed	–	35.58	5.89	3.26	0.21	13.92	41.13	1.98	0.867	14.74 ± 0.0	–	–
<i>Temperature °C (residence time 30 min, dilution ratio 1:8)</i>												
240	46 ± 2.45	54.05	6.08	3.65	0.43	6.99	28.8	1.35	0.40	22.81 ± 0.22	1.55 ± 0.12	71.15 ± 2.12
260	42 ± 1.23	56.52	5.43	3.53	0.36	7.00	27.13	1.15	0.36	23.10 ± 0.11	1.57 ± 0.02	65.76 ± 1.23
280	40 ± 1.12	57.2	5.40	3.20	0.30	8.73	25.17	1.13	0.33	23.50 ± 0.02	1.60 ± 0.03	63.66 ± 0.43
300	38 ± 1.20	60.00	5.10	3.10	0.30	5.9	25.6	1.02	0.32	24.11 ± 0.10	1.64 ± 0.10	62.13 ± 0.23
320	38 ± 1.26	62.10	4.30	3.00	0.30	5.46	24.84	0.83	0.30	23.98 ± 0.05	1.62 ± 0.01	61.82 ± 0.21
<i>Time (min) (temperature 300 °C, dilution ratio 1:8)</i>												
10	43 ± 1.78	52	6.21	3.7	0.37	9.23	28.49	1.43	0.41	22.24 ± 0.12	1.51 ± 0.04	65.08 ± 0.23
20	40 ± 1.23	56	6.04	3.5	0.35	7.33	26.78	1.29	0.36	23.65 ± 0.23	1.60 ± 0.02	64.38 ± 0.34
30	38 ± 1.23	60	5.1	3.1	0.3	5.9	25.6	1.02	0.32	24.11 ± 0.31	1.64 ± 0.04	62.30 ± 0.78
40	37.4 ± 0.0	60.4	5.03	3.1	0.3	5.8	25.37	0.99	0.31	24.20 ± 0.11	1.64 ± 0.03	61.53 ± 0.12
<i>Dilution ratio (temperature 300 °C, residence time 30 min)</i>												
1:4	42 ± 1.22	48.2	4.2	3.88	0.2	6.48	37.04	1.04	0.57	17.73 ± 0.45	1.20 ± 0.20	50.63 ± 1.23
1:6	39 ± 0.45	58	5.4	3.21	0.2	4.88	28.31	1.12	0.36	23.51 ± 0.24	1.60 ± 0.02	62.31 ± 0.12
1:8	38 ± 0.33	60	5.1	3.1	0.3	5.9	25.6	1.02	0.32	24.10 ± 0.13	1.64 ± 0.30	62.31 ± 0.45
1:12	38 ± 0.0	60	5.2	3	0.24	6.22	25.34	1.04	0.32	24.25 ± 0.11	1.64 ± 0.23	62.64 ± 0.12
<i>Catalyst (temperature 300 °C, residence time 30 min, dilution ratio 1:8)</i>												
Acetic Acid	36 ± 1.22	64.2	5.53	4	–	4	22.27	1.03	0.26	26.48 ± 1.23	1.80 ± 0.06	64.67 ± 0.48
KOH	31.40 ± 1.24	71.1	5.1	3.2	–	4.3	16.3	0.86	0.17	29.00 ± 0.43	1.97 ± 0.03	61.79 ± 0.34
Na ₂ CO ₃	34 ± 0.12	68	5	4.4	–	4.1	18.5	0.88	0.20	27.56 ± 0.25	1.87 ± 0.02	63.58 ± 0.32

db dry basis

^a Calculated as difference between 100 and total of C/H/N/S

$$Y(\%) = \frac{\text{mass of dry hydrochar}}{\text{mass of dry feedstock}} \times 100 \quad (2)$$

$$E_d = \frac{\text{HHV}_{\text{char}}}{\text{HHV}_{\text{feedstock}}} \times 100 \quad (3)$$

$$E_y = E_d \times Y \quad (4)$$

$$C_{\text{rec}} = \frac{\frac{\% C_{\text{char}}}{100} \times \text{char mass}}{\frac{\% C_{\text{feedstock}}}{100} \times \text{mass of dry feedstock}} \times 100 \quad (5)$$

Results and discussion

Fresh weeds (as received) had moisture content of 90%, which was determined from the weight loss after drying at temperature of 105 °C for 1.5 h (ASTM E871–82 2013a). By same procedure after sundrying for 3–4 days weeds contained 8% of remaining moisture. Volatile matter and ash (on db) were, respectively, as 76 and 13.92%. Elemental percentages of C, H, N, S and O were 35.58, 5.89, 3.26, 0.21 and 41.13%, respectively, where % O was determined by subtraction of total of C, H, N and S from 100. HHV of dry feedstock (from Eq. 1) was found to be 14.74 MJ/kg.

Effect of temperature, time and dilution ratio on yield, HHV and ash content of hydrochar

Table 1 given at below depicts the effect of temperature, time and dilution ratio on yield (%), HHV and ash content, etc., of hydrochar.

Effect of temperature

Effect of temperature was studied at residence time of 30 min and biomass/water ratio of 1:8. Yield (%) and HHV of hydrochar corresponding to temperatures of 240, 260, 280, 300 and 320 °C are presented in Table 1. HHV upon which main focus is laid down increased from a value of 22.81 MJ/Kg at temperature of 240 °C to 24.11 MJ/kg when temperature was 300 °C. Increase in HHV shows that the feed was only partially carbonized at lower temperatures during the process. Increasing temperature further to 320 °C led to decrease in the HHV probably due to loss in more hydrogen.

Yield decreased from 46% at temperature of 240 °C to 38% at temperatures of 300 and 320 °C. The decrease was closely connected with deoxygenating reactions (e.g., dehydration, decarboxylation) and volatile matter conversion, as the oxygen and hydrogen contents become lower at higher temperatures. The yields obtained in this study are in same range as reported by previous study of Duan et al. (2013) with duck weed. Yields were, however, higher than study on water hyacinth by Singh et al. (2015). In his case, yields at different temperatures were 32% at 250 °C, 16% at 280 °C and 16% at 300 °C.

Ash content decreased from 6.99% at 240 °C to 5.46% at 320 °C. The observation was almost in same range as in cases of olive mill waste (3.35–1.95, 7.35–6.96%), orange waste (4.45–4.01%) (Benavente et al. 2015), wheat straw (10.9–5.8%) (Wiedner et al. 2013) and sunflower stem (4.3–2.7%) (Roman et al. 2012). Ash content was much lower when compared to sewage sludge (where it is in range 39.1–22.89%) (Danso-Boatenga et al. 2015) and *Laminaria saccharina* (58.5–29.9%) (Anastasakis and Ross 2011). In HTC, high values for both yield and HHV of hydrochar simultaneously might be plausible goals. But practical observation was that yield decreased with temperature (probably because of increased carbonization), while HHV increased. Higher HHV out balances the lower yield, same is evident from higher value of E_d . Table 1 shows the effect of temperature upon yield (%) and HHV of hydrochar.

Effect of time

Studies on variation of yield (%) and HHV were carried out at temperature of 300 °C and biomass/water dilution ratio of 1:8 while varying residence time as 10, 20, 30 and 40 min. Residence time or holding time is time after instant when feed temperature of 300 °C is reached in HTC. With increasing time from 10 to 40 min yield decreased from 43 to 37.4%. The reduced yields may be due to enough time available for decarboxylation and dehydration reactions to transfer components into liquid phase. Almost similar results were obtained for duck weed by Duan et al. (2013).

With increasing time from 10 to 40 min, HHV increased from 22.24 to 24.20 MJ/kg. In case of *Laminaria saccharina* also, HHV showed increasing trend from 10.8 to 11.4 MJ/kg, although with different times (15–120 min) (Anastasakis and Ross 2011). The increasing trend in HHV with time suggests that more complete carbonization of the product was achieved at longer residence times. Corresponding decrease in yield of hydrochar means higher transformation of mass to carbon.

Ash content (db) decreased from 9.23 to 5.8% with increasing time from 10 to 40 min. Decreasing trend in ash content with increasing time was also observed by Anastasakis and Ross (2011) for *Laminaria saccharina*, but variation was high in this case from 56.7 to 51%. Above results may be different for *Laminaria saccharina* as it is a macroalgae and time varied is different from 2 to 8 h at 225 °C. In case of olive mill waste, ash content decreased from 2.26 to 2.07% (Benavente et al. 2015). Table 1 depicts the affect of time upon yield (%) and HHV of hydrochar.

Effect of dilution ratio

Biomass/water ratios (gm biomass per ml of water) of 1:4, 1:6, 1:8 and 1:12 were used at temperature of

300 °C and residence time of 30 min. Yield decreased from 42% at dilution ratio of 1:4 to a constant value of 38% at ratios of 1:8 and 1:12. Above observation was indicative of incomplete hydrolysis taking place at low dilution ratios. Anastasakis and Ross (2011) studied effect of water ratio upon macroalgae *Laminaria Saccharina* and also obtained a decreasing trend for yields varying from 52.6% at 1:5 ratio to 31.7% at 1:20 ratio. Singh et al. (2015) studied dilution ratios of 1:3–1:6 in case of water hyacinth and observed a decreasing trend in yields from 47 to 13%.

Heating value increased from 17.73 to 24.25 MJ/kg while varying dilution ratio from 1:4 to 1:12. As per our information no observations of HHV as function of dilution ratios are available in the literature except for macroalgae *Laminaria Saccharina* (Anastasakis and Ross 2011) where HHV was 28.8 MJ/Kg at 1:5 ratio and 12.6 MJ/Kg at 1:20 ratio. Table 1 summarizes the effect of dilution ratio on yield (%) and HHV of hydrochar. The dilution ratio studies at above demonstrated fully that fresh feed (containing moisture content of about 90%) can directly be processed as HTC feed to produce hydrochar having fairly high HHV, no alteration in its water content by means of further dilution, etc., is required.

HTC with catalysts KOH, Na₂CO₃ and acetic acid

For further enhancement in HHV of hydrochar catalysts, KOH, Na₂CO₃ and acetic acid were employed under conditions of temperature, residence time and dilution ratio in noncatalytic HTC where otherwise maximum HHV was obtained. A.R grades of acetic acid (1 ml-1 M), KOH (3 wt% of initial feed wt.) and Na₂CO₃ (0.5 wt% of initial feed wt.) were used with 30 gm of feed. Yields of hydrochar decreased from 38% without a catalyst to 36% in case of acetic acid, 34% in case of Na₂CO₃ and 31.40% in case of KOH. Calorific value was enhanced by utilization of each of above catalysts from a value of 24.11 MJ/kg without catalyst to 26.48 MJ/kg by acetic acid, 27.56 MJ/kg by Na₂CO₃ and 29.00 MJ/kg by KOH. So all above chemicals acted as catalysts leading to enhancement in the HHV. Role of KOH, Na₂CO₃ and acetic acid as catalysts was not reported earlier, although there are examples when such chemicals have been used primarily for enhancement of biocrude yield in hydrothermal processes (Shi et al. 2012). The value of HHV of hydrochar with help of above catalysts was in the same range as that of high-rank bituminous coal with value of 27.9 MJ/kg (Demirel 2012). Effect of catalysts KOH, Na₂CO₃ and acetic acid on the yield (%) and HHV of hydrochar are summarized in Table 1. HHV might have been enhanced by Na₂CO₃ and KOH due to providing of better reducing environment for improved conversion of carbohydrates in comparison with noncatalytic HTC. Acetic acid on the other hand might itself have been consumed in decarboxylation and dehydration reactions.

Study of energy densification, energy yield and carbon recovery of hydrochar

In hydrothermal process, solid mass decreased as a result of dehydration and decarboxylation reactions, same is indicated by increase in carbon contents and decrease in oxygen and hydrogen contents of hydrochar. When temperature was increased from 240 to 320 °C, energy densification ratio increased from 1.55 to 1.64 up to temperature of 300 °C thereafter at temperature of 320 °C it decreased again to 1.62. When time was increased from 10 to 40 min energy densification ratio increased from 1.51 to 1.62 up to time of 30 min, and thereafter, it remained at constant value of 1.62 for time of 40 min. When biomass/water ratio was increased from 1:4 to 1:12 energy densification ratio increased from 1.20 to 1.65.

Temperature, time and biomass/water ratio all significantly affected the energy density. E_d was highest at temperature of 300 °C, time of 30 min and dilution ratio of 1:8 (same value at dilution ratio of 1:12 as well). Acetic acid, Na₂CO₃ and KOH enhanced the energy density of hydrochar (from a value of 1.64 without any additive), respectively, to 1.8, 1.87 and 1.97. As is clear all the above catalysts have significantly enhanced the energy density value thus. Catalysts had decreased the yield of hydrochar, but simultaneously, energy density was highly enhanced.

Liquid fraction pH was measured using portable pH meter. Noncatalytic liquid fraction showed pH in acidic range (5.0 ± 0.30). With catalysts it decreased further to 4.0 ± 0.20 (acetic acid), 4.3 ± 0.1 (Na₂CO₃) and 4.4 ± 0.20 (KOH). This is thought to be due to formation of organic acids like acetic acid, benzene acetic acid, butanoic acid, pentanoic acid, levulinic acid and propanoic acid (Reza et al. 2013).

Energy yield is defined as energy densification ratio times the mass yield of hydrochar. It is means of providing energy remaining with hydrochars to that of original biomass feedstock. This is significantly influenced by temperature, time and dilution ratio (Benavente et al. 2015). E_y decreased as reaction temperature was increased from 240 to 320 °C and time increased from 10 to 40 min. Energy yield was lowest (50.31%) for biomass/water ratio of 1:4. Increasing ratio to 1:6, 1:8 and 1:12, it increased and remained almost at constant value (62.31–62.64%). Relative proportion of carbon as evidenced by elemental analysis of hydrochars was higher than that of feedstock following carbonization. It increased with increase in temperature, residence time and dilution ratio. All catalysts enhanced it with order acetic acid < Na₂CO₃ < KOH. Carbon recovery (C_{rec}) within hydrochars as percentage based on that of carbon initially present in the feedstock decreased significantly as temperature increased. Rest of other factors also exerted their effect (Table 1) although to lesser extent. Table 1 lists the energy densification, energy

yield and carbon recovery values of hydrochar as function of temperature, time, dilution ratio and catalysts KOH, Na_2CO_3 and acetic acid.

Van Krevelen diagram gives an indication of carbonization process and thus an idea of hydrochar properties. As expected the feedstock has higher H/C and O/C ratios compared to hydrochars. The Van Krevelen diagram suggests an improvement in the fuel properties. The H/C and O/C ratios of all carbonized feedstocks decreased with increasing production temperature indicating a loss of oxygen and hydrogen during progressing carbonization. With increasing temperature from 240 to 320 °C, H/C and O/C ratios showed a decreasing trend with respective final values of 0.83 and 0.30 at 320 °C. With increasing time from 10 to 40 min, H/C and O/C ratios again showed a decreasing trend with respective values of 0.99 and 0.31 at holding time of 40 min. Varying of biomass/water dilution ratio from 1:4 to 1:8, H/C and O/C ratios, respectively, decreased to 1.02 and 0.32. However, corresponding to dilution ratio of 1:12, H/C value again increased to 1.04 while as O/C value remained constant at 0.32. The catalysts had thus exerted a profound effect upon the H/C and O/C ratios of hydrochar. H/C values changed from a value of 1.02 without catalyst at temperature of 320 °C to 0.86, 0.88 and 1.03 using, respectively, the catalysts KOH, Na_2CO_3 and acetic acid. O/C values decreased from a value of 0.32 without using a catalyst to 0.17, 0.20 and 0.26 using, respectively, the catalysts KOH, Na_2CO_3 and acetic acid. A decreasing H/C ratio indicates demethylation (loss of CH_3), and a decreasing O/C ratio indicates decarboxylation (loss of CO_2) which forms products more rich in carbon (Van Krevelen 1961). Figure 2 shows the Van Krevelen diagram.

Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis

Figure 3 shows the FT-IR spectra of unprocessed feed and derived hydrochars. Feed has undergone visible transformations during HTC. The region in between 3200 and 3400 cm^{-1} shows a broadband in unprocessed feed and hydrochar produced with chemical additive KOH and acetic acid indicating the presence of OH functional group of alcohols and phenols. This band around 3400 cm^{-1} is associated with O–H stretching vibrations in hydroxyl or carboxyl group which becomes less intense in case of thermal, i.e., noncatalytic hydrochar. The band around 2900 cm^{-1} is present in all hydrochars, and raw feed is related to stretching vibrations of aliphatic C–H. This band is most intense in case of hydrochar produced in acetic acid HTC. Band around 1600–1700 cm^{-1} is present in all hydrochars, and feed is attributed to C=C vibrations in aromatic ring structure. After hydrochar due to acetic acid this band is most intense in case of hydrochar produced by KOH catalysis. Intense band around 900 cm^{-1} in

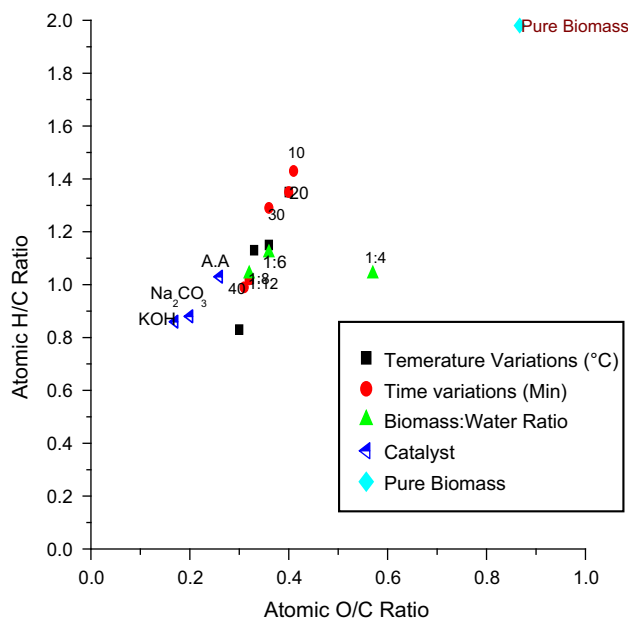


Fig. 2 Van Krevelen diagram

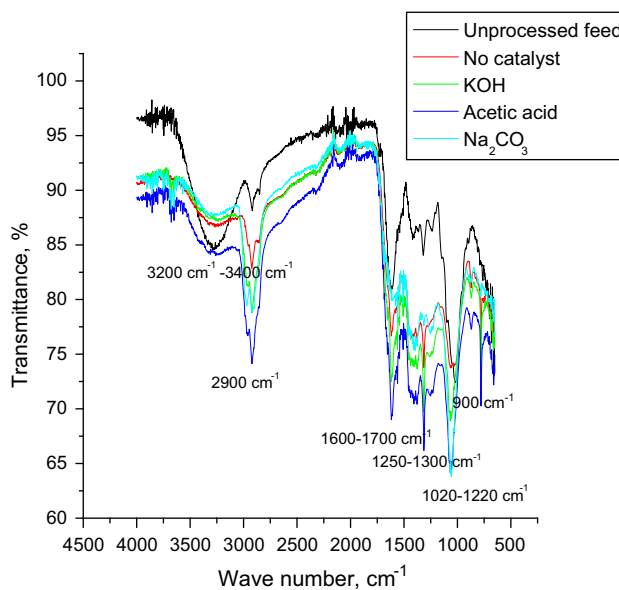


Fig. 3 FT-IR spectra of unprocessed feed and derived hydrochars

case of raw feed is due to presence of C–H bond. A band in wave number range 1250–1300 cm^{-1} exists in all hydrochars but not in feed is attributed to presence of C–O. The band in wave number range 1020–1220 cm^{-1} is observed in all cases except noncatalytic hydrochar is associated with the presence of aliphatic amines.

Morphology and surface composition were probed by SEM (Hitachi Japan model 3600) coupled with EDS. Small quantities of the samples were sprinkled onto double-sided carbon tape mounted on a SEM stub. Samples were initially dried so as to be free from

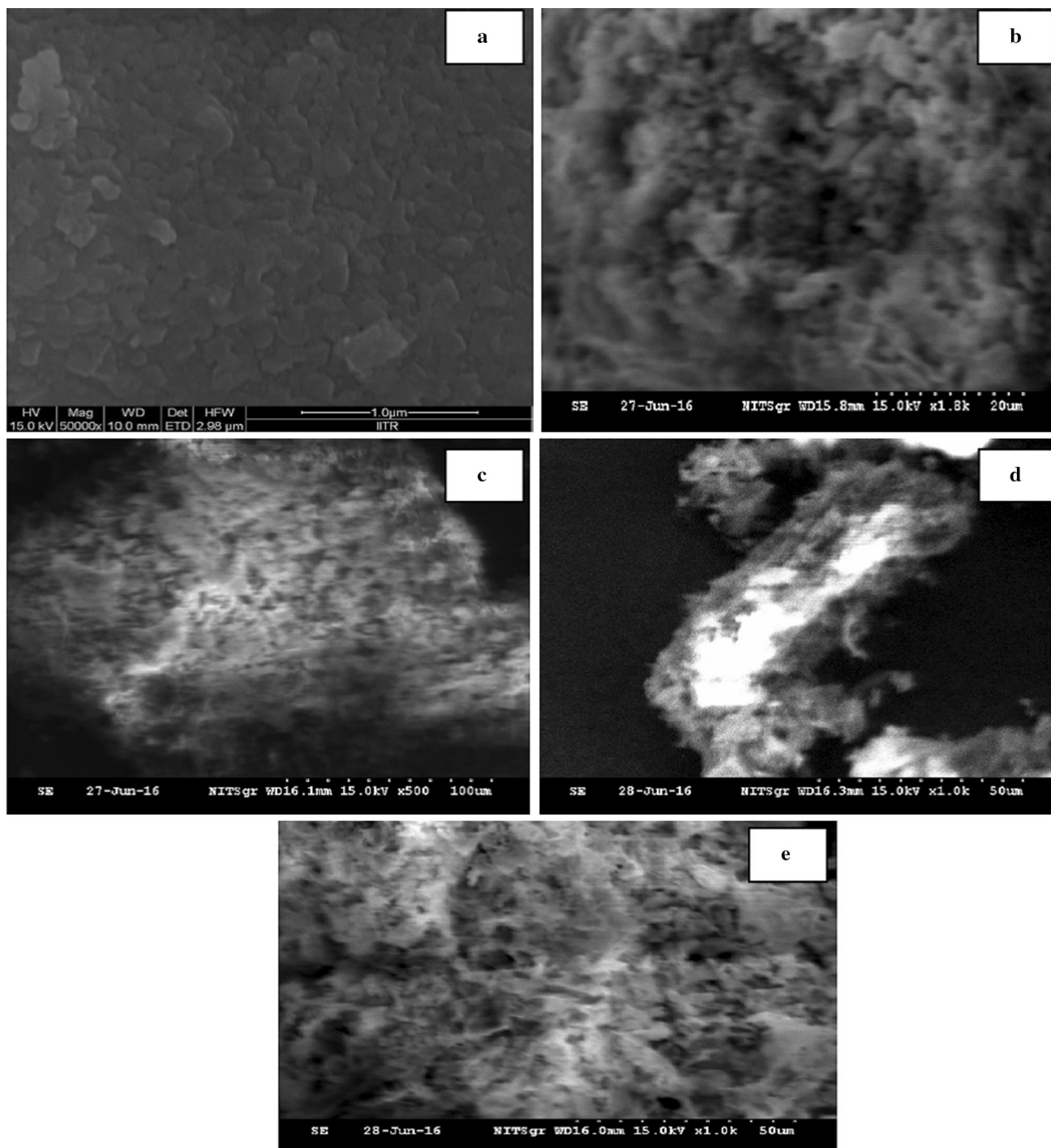


Fig. 4 SEM pictures of unprocessed feed (a), hydrochar with no catalyst (b), and with catalysts Na₂CO₃ (c), KOH (d) and acetic acid (e)

moisture. SEM/EDX analysis provided insight into the particle morphology, external surface structure and external elemental distribution. A comparison of SEM pictures of raw feed and HTC product (Fig. 4) obtained by noncatalytic and by employing catalysts Na₂CO₃, acetic acid and KOH indicate breakdown of biomacromolecules which might have occurred to produce fuel or fuel precursors.

EDX is an analytical technique used for the elemental analysis or chemical characterization of a sample. The mean surface composition of the hydrochars detected by EDS is given in Fig. 5 and Table 2. The EDS analysis indicates that the surface of the hydrochar particles is constituted majorly of compounds of carbon and oxygen. Besides Mg, Mo, P, Al, Cr and Fe are also observed as expected in view that feed is derived from lake.



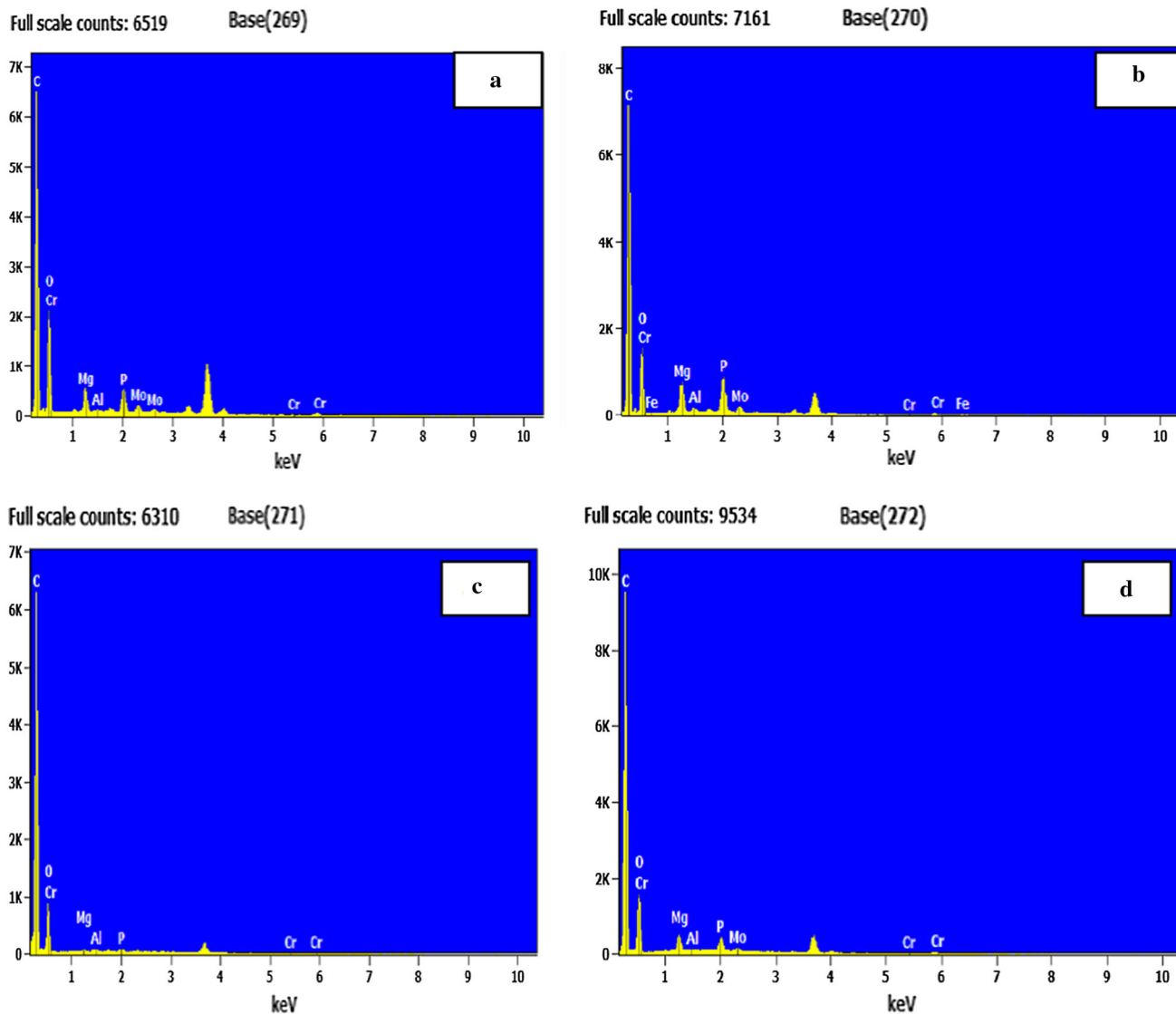


Fig. 5 EDS spectra of hydrochars; without catalyst (a), with catalysts Na_2CO_3 (b), KOH (c) and acetic acid (d)

Table 2 Major and minor elemental surface composition of different hydrochars (in wt%)

Element	Hydrochars			
	No catalyst	KOH	Acetic acid	Na_2CO_3
C	44	58.05	57.41	55.06
O	42	39.48	31.97	23.27
Mg	3.92	0.49	3.5	5.6
Al	0.3	0.65	0.5	0.46
P	4.89	0.99	3.79	8.59
Cr	0.24	0.34	–	–
Fe	–	–	–	2.81
Mo	4.41	–	2.82	4.21

Conclusion

World famous lake *Dal lake* in Srinagar India is among the largest fresh water lakes existing in Asia. The lake has undergone serious ecological changes including invasion by macrophytes with *C. demersum* being a prominent one. Excessive weed growth is posing threat to esthetics of lake with tons of such macrophytes being harvested annually. Weeds have potential for exploitation in fuel production by HTC, a process highly suitable for upgrading of aquatic biomass. In present study, *C. demersum* collected from *Dal lake* is subjected to HTC to produce solid fuel in form of hydrochar. Effect of process parameters temperature, time and dilution ratio in catalytic and noncatalytic HTC were studied. Increasing reaction time, residence time and dilution ratio improved carbon content, heating value, energy density. H/C and O/C ratios also changed

favorably on Van Krevelen diagram with values matching to coal. KOH, Na₂CO₃ and acetic acid were successful as catalysts in enhancing the calorific value and energy density in comparison with noncatalytic process. Under noncatalytic conditions HHV and energy density were highest at temperature of 300 °C and residence time of 30 min with respective values of 24.11 MJ/kg and 1.64. HHV of hydrochar is further enhanced to 29.0, 27.5 and 26.48 MJ/kg, respectively, by using catalysts KOH, Na₂CO₃ and acetic acid. HHV of hydrochar in catalytic HTC was found to be as good as that of high-rank bituminous coal following order KOH > Na₂CO₃ > acetic acid. The research on the one hand is environmentally important in paving a way in exploitation of obnoxious aquatic weeds, but at same time is helpful in the generation of biofuels.

Acknowledgements Authors express their gratitude toward the authorities of NIT Srinagar for providing necessary facilities for the research in Energy Engineering laboratory of Chemical Engineering Department. Further authors thank Professor I. M. Mishra of Chemical Engineering Department at Indian Institute of technology (IIT) Roorkee, India, for providing the useful inputs regarding the research.

References

- Akyildirim O, Kotan G, Yola ML, Eren T, Atar N (2016) Fabrication of bimetallic Pt/Pd nanoparticles on 2-thiolbenzimidazole functionalized reduced graphene oxide for methanol oxidation. *Ionics* 22:593–600
- Aloo P, Ojwang W, Omondi R, Njiru JM, Oyugi D (2013) A review of the impacts of invasive aquatic weeds on the biodiversity of some tropical water bodies with special reference to Lake Victoria (Kenya). *Biodivers J* 4:471–482
- Amin A, Fazal S, Muftaba A, Singh SK (2014) Effects of land transformation on water quality of Dal Lake, Srinagar, India. *J Indian Soc Remote Sens* 42(1):119–128
- Anastasakis K, Ross AB (2011) Hydrothermal liquefaction of the brown macro-alga *Laminaria Saccharina*: effect of reaction conditions on product distribution and composition. *Bioresour Technol* 102(7):4876–4883
- ASTM (2008) Standard test methods for instrumental determination of carbon, hydrogen and nitrogen in laboratory samples of coal, ASTM D5373-08. ASTM International, Pennsylvania
- ASTM (2013a) Standard Test Method for moisture analysis of particulate wood fuels, ASTM E871–82(2013). ASTM International, Pennsylvania
- ASTM (2013b) Standard test method for ash in wood, ASTM D1102–84. ASTM International, Pennsylvania
- ASTM (2013c) Standard test method for volatile matter in the analysis of particulate wood fuels, ASTM E872–82. ASTM International, Pennsylvania
- Atar N, Eren T, Yola ML, Karimi-Maleh H, Ogena BD (2015a) Magnetic iron oxide and iron oxide@goldnanoparticle anchored nitrogen and sulfur functionalized reduced graphene oxide electrocatalyst for methanol oxidation. *RSC Adv* 5:26402–26409
- Atar N, Eren T, Demirdogen B, Yola ML, Caglayan MO (2015b) Silver, gold, and silver@gold nanoparticle-anchored L-cysteine-functionalized reduced graphene oxide as electrocatalyst for methanol oxidation. *Ionics* 21:2285–2293
- Benavente V, Calabuig E, Fullana A (2015) Upgrading of moist agro-industrial wastes by hydrothermal carbonization. *J Anal Appl Pyrol* 113:89–98
- Bergius F (1932) Chemical reactions under high pressure. Nobel Lect
- Brown TM, Duan P, Savage PE (2010) Hydrothermal liquefaction and gasification of *Nannochloropsis* sp. *Energy Fuels* 24(6):3639–3646
- Channiwala SA, Parikh PP (2002) A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 81(8):1051–1063
- Danso-Boatenga E, Shamaa G, Wheatleyb AD, Martinc SJ, Holdicha RG (2015) Hydrothermal carbonization of sewage sludge: effect of process conditions on product characteristics and methane production. *J Bioresour Technol* 177:318–327
- Demirel Y (2012) *Energy, green energy and technology*. Springer, London
- Duan P, Chang Z, Xu Y, Bai X, Wang F, Zhang L (2013) Hydrothermal processing of duckweed: effect of reaction conditions on product distribution and composition. *J Bioresour Technol* 135:710–719
- Eboibi BE, Lewis DM, Ashman PJ, Chinnasamy S (2014) Effect of operating conditions on yield and quality of biocrude during hydrothermal liquefaction of halophytic microalga *Tetraselmis* sp. *J Bioresour Technol* 170(2014):20–29
- Funke A, Ziegler F (2010) Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. *J Biofuels Bioprod Biorefin* 4(2):160–177
- Garcia Alba L, Torri C, Samorì C et al (2012) Hydrothermal treatment (HTT) of microalgae: evaluation of the process as conversion method in an algae biorefinery concept. *Energy Fuels* 26(1):642–657
- Gupta VK, Yola ML, Atar N, Ustundag Z, Solak AO (2014) Electrochemical studies on graphene oxide-supported metallic and bimetallic nanoparticles for fuel cell applications. *J Mol Liq* 191:172–176
- Jeelani G, Shah AQ (2006) Geochemical characteristics of water and sediment from the Dal Lake, Kashmir Himalaya: constraints on weathering and anthropogenic activity. *Environ Geol* 50:12–23
- Ministry for primary industries New Zealand government website <http://www.biosecurity.govt.nz/pests/hornwort>. Accessed 9 Feb 2016
- Reza MT, Yan W, Uddin MH, Lynam JG, Hoekman SK, Coronella CJ, Vasquez VR (2013) Reaction kinetics of hydrothermal carbonization of loblolly pine. *J Bioresour Technol* 139:161–169
- Roman S, Nabais JMV, Laginhas C, Ledesma B, Gonzalez JF (2012) Hydrothermal carbonization as an effective way of densifying the energy content of biomass. *Fuel Process Technol* 103:78–83
- Savage PE, Levine RB, Huelsman CM (2010) Hydrothermal processing of biomass (Chapter 8). In: Crocker M (ed) *Thermochemical conversion of biomass to liquid fuels and chemicals*. Royal Society of Chemistry Publishing, London, pp 190–219
- Shi F, Wang P, Duan Y, Morreale B (2012) Recent developments in the production of liquid fuels via catalytic conversion of microalgae: experiments and simulations. *RSC Adv* 2:9727–9747
- Singh R, Balagurumurthy B, Prakash A, Bhaskar T (2015) Catalytic hydrothermal liquefaction of water hyacinth. *J Bioresour Technol* 178:157–165
- Suwelack K, Wust D, Zeller M, Kruse A, Krumpel J (2015) Hydrothermal carbonization of wheat straw—prediction of product mass yields and degree of carbonization by severity parameter. *Biomass Convers Biorefin* 6:347–354
- To H, Grafton RQ (2015) Oil prices, biofuels production and food security: past trends and future challenges. *Food Secur* 2:323–336
- Van Krevelen DW (1961) *Coal: typology, chemistry, physics, constitution*. Elsevier, Amsterdam
- Wiedner K, Naisse C, Rumpel C, Pozzi A et al (2013) Chemical modification of biomass residues during hydrothermal carbonization—what makes the difference, temperature or feedstock. *Org Geochem* 54:91–100
- Yola ML, Eren T, Atar N, Saral H, Ermis I (2016) Direct-methanol fuel cell based on functionalized graphene oxide with mono-metallic and bimetallic nanoparticles: electrochemical performances of nanomaterials for methanol oxidation. *Electroanalysis* 28:570–579
- Zhou D et al (2010) Hydrothermal liquefaction of macroalgae *Enteromorpha prolifera* to bio-oil. *Energy Fuels* 24(7):4054–4061