



Impact of time on yield and properties of biocrude during downstream processing of product mixture derived from hydrothermal liquefaction of microalga

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Abstract

This paper is a study on effects of separation procedures on yield and characteristics of biocrude derived from hydrothermal liquefaction (HTL) of *Tetraselmis* sp. microalgae. The algae was grown and cultivated in outdoor open raceway ponds. The HTL experiments were performed using 1 l custom built high pressure–temperature reactor with inbuilt magnetic stirrer. HTL experimental studies were conducted at reaction temperature of 350 °C and 15 min holding time using alga solids loading of 16 w/v%. HTL product mixture diluted with dichloromethane (ratio 1:1) was allowed to stand for 1 h, 3 h, 6 h, 7 h, 8 h, 9 h, 10 h, 11 h, 12 h and 15 h at room temperature. The result showed that varying stand times for product mixture separation influenced yields in biocrude, solid residue and dissolved aqueous solids. Biocrude yields were in the range of 30 wt% to 56 wt% characterised with higher heating value of ~ 35 to 37 MJ/kg and hydrogen to carbon atomic ratios of 1.56 to 1.95. Maximum yield of biocrude was obtained after 9 h stand time for product mixture and dichloromethane (PM–DCM) mixture. Although, varying PM–DCM mixture stand times showed variation in product yields, there was no clear trend in distribution of elemental contents. Majority of alkali metals distributed in aqueous phase and solid residue, which could be used as nutrients, an alternative to conventional fertiliser.

Keywords Hydrothermal liquefaction · Microalgae biomass · Renewable energy · Separation processes

1 Introduction

Biomass availability and accessibility across the World is considered as one of the main feedstocks for producing renewable energy and value-added chemicals [1, 2]. Due to microalgae faster growth rate, higher oil content, higher biomass productivity and its renewability, microalgae have been considered as promising feedstocks for biofuel production when compared to terrestrial biomass [3]. Hydrothermal liquefaction (HTL), also referred to as direct conversion, is one of the promising technologies for conversion of biomass to biofuels.

HTL decomposes large organic molecular-weight compounds to small molecules [4]. Specifically, HTL is performed

at moderate temperature (200 to 370 °C) and high pressure (2 MPa to 25 MPa) with or without catalyst [5] using 5 to 20 wt% algae biomass solids loading. HTL main product is an organic liquid referred to as biocrude having an energy content in the range of 30 to 40 MJ/kg. Biocrude is produced through different reaction pathways such as depolymerisation, decomposition and reformation [6, 7]. The resultant biocrude is characterised with undesired high heteroatoms such as oxygen and nitrogen; hence, upgrading is necessary in order to meet standard fuel specifications [8]. Solid residue, aqueous and gas phases are other products derived from HTL.

A review of scientific literatures showed that several research studies have been investigated on HTL of algae, ranging from effects of reaction conditions, kinetic modelling, solvent types, algal strains, upgrading and review papers [7, 9–16]. These studies mainly aimed at optimising yield and properties of biocrude. These studies have demonstrated the feasibility of future commercialization of HTL algal biorefinery. Despite these numerous investigations, the separation methods for effective

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recovery of HTL products are still unclear [17]. Recovering of biocrude from HTL–product mixture (HTL–PM) could be categorised into two separation methods [17, 18]. One method is to allow the PM to separate spontaneously into biocrude, residue and aqueous phases as a result of their immiscibility and differences in density [10, 18, 19]. The second method is the addition of an organic solvent to the cooled PM, which dissolves the biocrude and enhances its separation from solid and aqueous phases [12, 14, 20]. Higher molecular weight organic compounds are extracted in biocrude using latter method [9], leading to an increase in total biocrude yields [10, 16, 19]. Hence, almost all HTL experimental studies in the literature applied this approach to recover biocrude from HTL–PM [2, 11–13]. Moreover, dichloromethane (DCM) is the most frequently used organic solvent [4, 14, 17, 18, 21], which could be due to its moderate dielectric constants and capability to dissolve both polar and non-polar chemical compounds [22]. Vlaskin et al. [9] and Yang et al. [23] reported that DCM led to highest yields in biocrude and of better quality compared to other solvents such as acetone, hexane, chloroform and tetrahydrofuran.

Typically, after the HTL reaction step, a product mixture is produced, where an organic solvent (such as dichloromethane (DCM)) is mixed with the product mixture. Thereafter, the mixture of product mixture and DCM (now referred to as PM–DCM) is allowed to stand for phase separation. However, almost all HTL studies have not reported on the allowed stand time for PM–DCM mixture. Although, Bi et al. [5] reported 4 h PM–DCM stand time when investigating catalytic effects on biocrude yields from treatment of partially defatted *Cryptococcus curvatus* at 300 °C and 350 °C. Eboibi et al. [11] reported 8 h PM–DCM stand time for thermal upgrading of biocrude produced from HTL of *Spirulina* sp. and *Tetraselmis* sp. These studies reported influence of catalysts and upgrading on biocrude yields, but no report on effects of PM–DCM stand time on biocrude yield and properties.

The reason for differences in allowed stand time for PM–DCM mixture in previous reports is not clear; hence, further investigations may be required. It is believed there is transfer of molecules between layers towards formation of biocrude phase, residue and aqueous phases. Therefore, the allowed stand time for PM–DCM mixture to equilibrate prior to separation of layers may influence yields and properties of products, particularly biocrude. To the best of my knowledge, there is no published report on this aspect of study. If biocrude yield and properties are affected by product mixture and solvent stand time, then reported data in literature may be a concern. To a very large extent, biocrude yields are important data used to evaluate performance of HTL algal biorefinery [23, 24].

Thus, it is essential to examine impact of stand time of PM–DCM on biocrude recovery from HTL product mixture. This could provide more information and potentially discover hidden effects for more economical and efficient separation methods for HTL algal biorefinery.

Moreover, after liquefaction reaction, Boens et al. [12] added distilled water and DCM into the reactor containing product mixture and then stirred for 1 h 30 min. The stirred solution was transferred to a separating funnel for phase separation. This procedure enhanced biocrude yield; however, allowed stand time was not reported. Biller and Ross [13] added 50 ml each of DCM and water to the product mixture, of which two layers were obtained. Although yields in biocrude, solid residue and aqueous phase were reported, there was no data on stand time. Also, centrifugation technique has been used in previous HTL product and separation procedures to extract biocrude from solid and aqueous phase mixture [4, 14]. However, such practices may not be applicable at large scale. Even after using a centrifuge, time is normally given for contents in a vial to equilibrate before using pipette to withdraw product fractions. Hence, knowing a suitable time may be necessary during separation of products from PM–DCM mixture.

Sheng et al. [14] and Wang et al. [25] after mixing DCM with product mixture immediately filtered (using microporous membranes 0.45 µm) the PM–DCM mixture to remove solids. Then, the filtrate was transferred to a separating funnel where it was allowed to stand for certain period; however, time allowed was not reported. In related studies, Huang et al. [26], Jindal and Jha [27] and Yang et al. [28] initially filtered solid residue from product mixture before mixing DCM to the filtrate (containing water and organic phase). The filtered solid residue has been reported to contain residual organics [16, 29]; hence, such procedure may reduce total amount of biocrude and increase in yield of solid residue.

Based on reviewed scientific literature, it could be agreed that different separation procedures have been used to obtain yields after liquefaction. Also, extraction of biocrude from product mixture has been carried out arbitrary, in terms of product mixture and solvent stand time. Moreover, mixing solvent with product mixture and allowed to stand for certain period enhances dissolution, thereby improving recovery of hydrocarbons and reduction in solid residue and aqueous phase by-products. Hence, knowledge of PM–DCM stand time is necessary as it would help to formulate specific recommends for HTL separation procedure. Also, it would help for recovery of optimum yield in biocrude of better quality during downstream processing of HTL products. Therefore, the main aim of this reported study was to investigate the effects of stand time for the mixture of PM–DCM on yields and properties of biocrude after hydrothermal liquefaction.

2 Materials and methods

2.1 Materials

Tetraselmis sp. microalga biomass was used in the present study. The alga was grown and cultivated in outdoor open raceway ponds at Pilot Plant, Biotechnology Division, Aban Infrastructure Pvt. Limited, Chennai, India. Details of the alga biomass culturing, harvesting and characterisation have been reported elsewhere [30]. Harvested biomass slurry having ~ 16 w/v% alga solids was stored ($-8\text{ }^{\circ}\text{C}$) in refrigerator prior to liquefaction experiments. Dichloromethane (DCM) of 99% purity was used as the organic solvent.

2.2 Hydrothermal liquefaction: product mixture production

Production of product mixture was achieved by HTL of the harvested alga using a custom built Inconel batch reactor of 1 l capacity. The reactor has a designed capacity of 500 °C and 350 bar as operating temperature and pressure, respectively, with an inbuilt magnetic stirrer. HTL experiment was conducted at reaction temperature of 350 °C at 15 min holding time. Typically, in each run, 500 g alga slurry was loaded in the reactor. Then, the reactor was sealed and heated to 350 °C ($\pm 4\text{ }^{\circ}\text{C}$) using an inbuilt electrical heating jacket. Holding time started when reaction temperature reached 350 °C and then maintained for 15 min. After complete holding time, the reactor was switched off and cooled to room temperature.

2.3 Product separation and quantification procedure

The gas phase was released via the gas valve after cooling to room temperature. Then, the reactor content now referred to as product mixture was transferred to a beaker. About 200 ml (50 ml of water and 150 ml DCM) was used to rinse products stuck to the reactor wall and internal parts (magnetic stirrer) and then transferred to the beaker containing the rest product mixture. The water helps to wash/remove nonoil solution while DCM for oily substance. Thereafter, DCM was mixed with the product mixture in ratio 1:1 and then stirred at 300 rpm for 5 min. The mixed product mixture and DCM is defined as PM–DCM. Then, equal volumes (100 ml) of PM–DCM were transferred to separating funnels SF_1 , SF_3 , SF_6 , SF_7 , SF_8 , SF_9 , SF_{10} , SF_{11} , SF_{12} and SF_{15} and sealed with rubber cork. Separating funnel SF_1 , SF_3 , SF_6 , SF_7 , SF_8 , SF_9 , SF_{10} , SF_{11} , SF_{12} and SF_{15} were allowed to stand for 1 h, 3 h, 6 h, 7 h, 8 h, 9 h, 10 h, 11 h, 12 h and 15 h, respectively, for phase separation.

After each predefined stand time, the PM–DCM was separated into three layers, a bottom layer (residue), middle layer (biocrude phase) and a top layer (aqueous phase or also known as wastewater). Then, each layer was decanted into

separate beaker and labelled accordingly. The residue and aqueous phases were rinsed with DCM three times, in order to enhance extraction of hydrocarbons stuck to pores. The washed fractions were allowed to stand for 3 h after decanting and added to respective beakers containing biocrude, residue and aqueous phases. The biocrude phase was vacuum evaporated at $\sim 40\text{ }^{\circ}\text{C}$ in order to remove DCM and residual water, and the remnant was defined as biocrude [2, 17]. The residue was dried at $\sim 100\text{ }^{\circ}\text{C}$, the dried fraction referred to as solid residue [11, 29]. Similarly, the aqueous phase was dried at $\sim 100\text{ }^{\circ}\text{C}$, and dried fraction was defined as dissolved aqueous solids [16, 24]. The experimental runs and separation procedures were conducted in triplicate and average yields reported. A schematic diagram of production and separation procedure is shown in Fig. 1.

2.4 Analysis

The gravimetric yields in biocrude (ash free dry weight), solid residue and aqueous phase were determined by relating the mass of product to mass of algal slurry loaded into the reactor, whereas yields in gas phase + loss were determined by difference using the calculated yield of remaining fractions. Samples of biocrude, solid residue and dissolved aqueous solids were analysed with regard to elemental content of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) using an elemental analyser (VariOEL III elemental analyser system

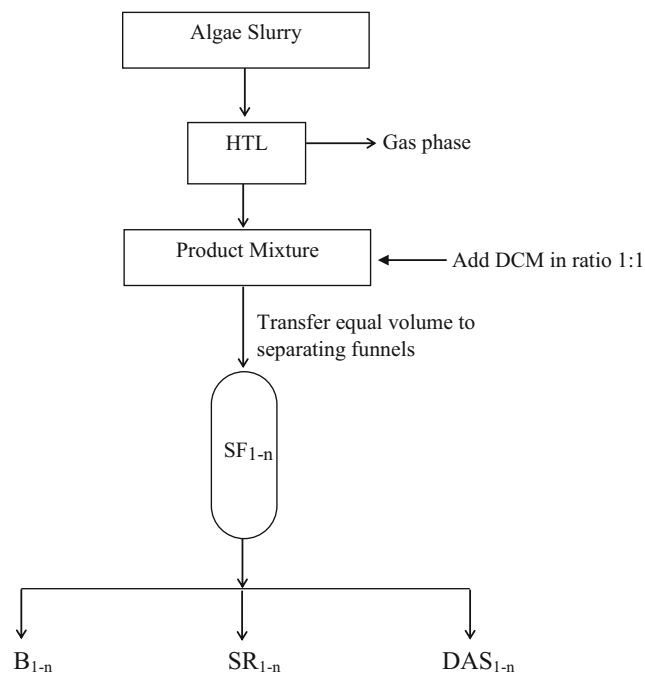


Fig. 1 HTL production and separation procedures with respect to stand time. SF_{1-n} : separating funnels at time intervals. DCM: dichloromethane. B_{1-n} : biocrude obtained from separating funnels with respect to time. SR_{1-n} : solid residue obtained from separating funnels with respect to time. DAS_{1-n} : dissolved aqueous solids obtained from separating funnels with respect to time

GmbH) in accordance with ASTM D5291. The elemental content of oxygen (O) was determined by difference. Based on CHNSO data, the higher heating value was estimated using a unified correlation (Eq. (1)) proposed by Chinnawala and Parikh [31]. Equation (1) has been used previously to estimate HHV of biocrudes from HTL of algae [2, 11, 16, 24].

$$\text{HHV} \left(\frac{\text{MJ}}{\text{kg}} \right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.211A \quad (1)$$

where C, H, S, O, N and A represent elemental carbon, hydrogen, sulphur, oxygen, nitrogen and ash. The amount of energy recovered (ER) in biocrudes from SF_{1-n} was estimated using Eq. (2) [29, 32].

$$\text{ER} = \frac{\text{HHV of product} \left(\frac{\text{MJ}}{\text{kg}} \right) \times \text{Mass of product (kg)}}{\text{HHV of algal slurry loaded} \left(\frac{\text{MJ}}{\text{kg}} \right) \times \text{Mass of algal slurry loaded (kg)}} \times 100\% \quad (2)$$

In Eq. (2), 19.2 MJ/kg was used as the HHV of algal slurry [11, 24]. The H/C, N/C and O/C atomic ratios were estimated according to the methods explained in previous report [14].

To know the compositional changes in resultant biocrudes, sample of biocrudes (diluted with acetone to 2.5 v/v%) obtained from SF_{1-n} were analysed for chemical compounds using Gas Chromatography-Mass Spectroscopy (GC-MS) (Agilent HP-5 column of $50m \times 200\mu m \times 0.33\mu m$) according to method reported previously [24]. In addition, the ash fractions of

biocrudes derived from SF_{1-n} were analysed for their metallic composition using Inductively Couple Plasma Mass Spectroscopy (ICP-MS) (Agilent 7500 Series). Ash fractions were determined in accordance with the method explained in previous report [11].

3 Results and discussion

3.1 HTL product yields

The obtained mass yields in biocrude, solid residue, dissolved aqueous solids and gas + loss are presented in Fig. 2. The data obtained showed substantial variation in fractional yields, suggesting stand time could have influenced PM–DCM mixture during phase separation. The yields in biocrude yield increased from 30 to 56 wt% when stand time increased from 1 to 9 h. However, biocrude yields decreased from 56 to 42 wt% with further increased in stand time. Although there could be several reasons behind variation in yields, one of the reasons could be that mixture having different molecular weights and densities needs suitable time to equilibrate. Suitable time is important to allow molecules of similar density in a mixture to equilibrate.

The solid residue decreased from 20 to 14 wt% when stand time increased from 1 to 9 h. Although there were no substantial differences in solid residue with further increase in time, the numerical differences suggest side reactions could have occurred. Such side reactions seem to have favoured formation of solid residue.

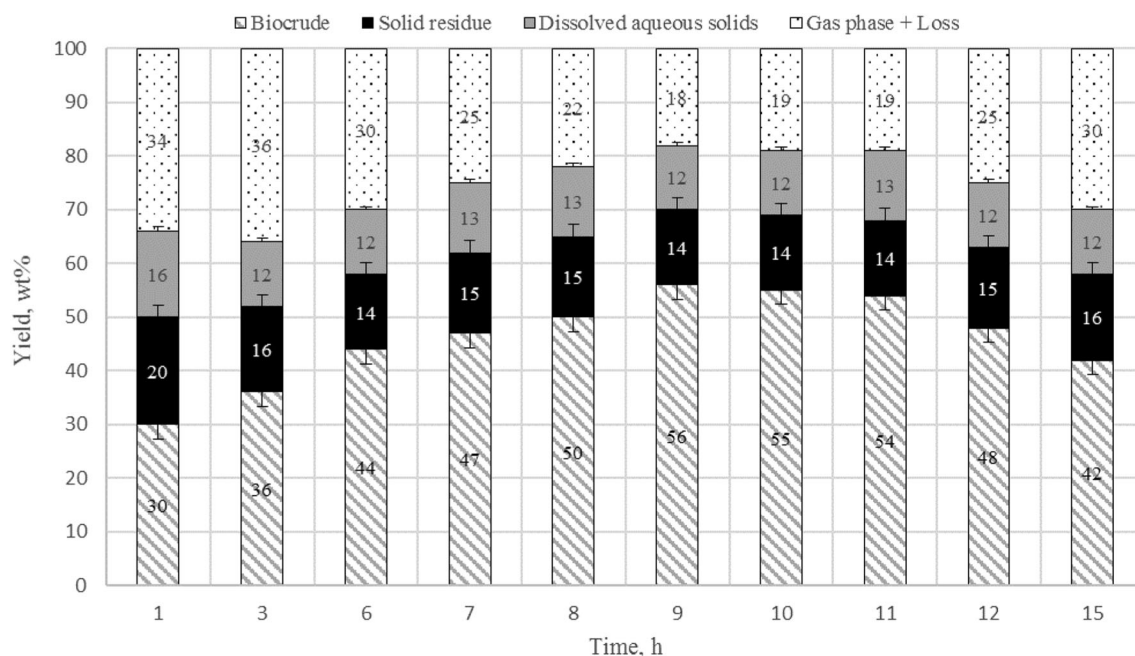


Fig. 2 HTL products obtained from HTL of algae with respect to PM–DCM stand time

Decomposition of cyclic oxygenates leads to formation of residue. In addition, Maillard and dehydration reactions favour intermolecular restructuring [33]. Also, it leads to an increase residue formation and reduction in biocrude yield. This finding suggests decomposition and repolymerizations occur if PM–DCM mixture is maintained for a certain period. Moreover, the dissolved aqueous solids decreased from 16 to 12 wt%, whereas the gas + loss was between 18 and 36 wt%.

3.2 Elemental composition

The elemental composition (CHNSO) of biocrudes obtained from SF_{1-n} is illustrated in Fig. 3a–e. As shown in Fig. 3, there were little variations in the elemental contents. The carbon contents were in the range of 72 to 75 w/w% (shown in Fig. 3a). As illustrated in Fig. 3b, hydrogen content varies between 9.80 and 10.2 w/w%, whereas nitrogen was in range of 2 to 2.4 w/w% (Fig. 3c). Elemental sulphur

distribution is presented in Fig. 3c. As shown in Fig. 3d, the sulphur content was between 0.6 and 0.7 w/w%, and oxygen was 12 to 15.6 w/w% (Fig. 3d). The data presented in Fig. 3 showed no clear trend in variation of elemental distributions, though there were some changes in compositions. In addition, impact of stand time on PM–DCM mixture for phase separation could not produce biocrude of better quality for direct use. Thus, hydrotreatment is necessary, in order to improve biocrude fuel properties. Moreover, despite variation in stand time, similar trends in elemental carbon and distribution in biocrudes were found when compared with previous reports [16, 20, 24, 25, 29]. Generally, carbon content has been reported to be in the range of 67 to 79 w/w%, 6.5 to 10.5 w/w% for hydrogen, 3.5 to 6.5 w/w% for nitrogen, <0.9 w/w% for sulphur and 10 to 16 w/w% for oxygen. Although the nitrogen content in present study is lower than 3.5 to 6 w/w%, it is still relatively high due to its environmental implications and potentially poisonous to catalyst used in refining process [13, 34].

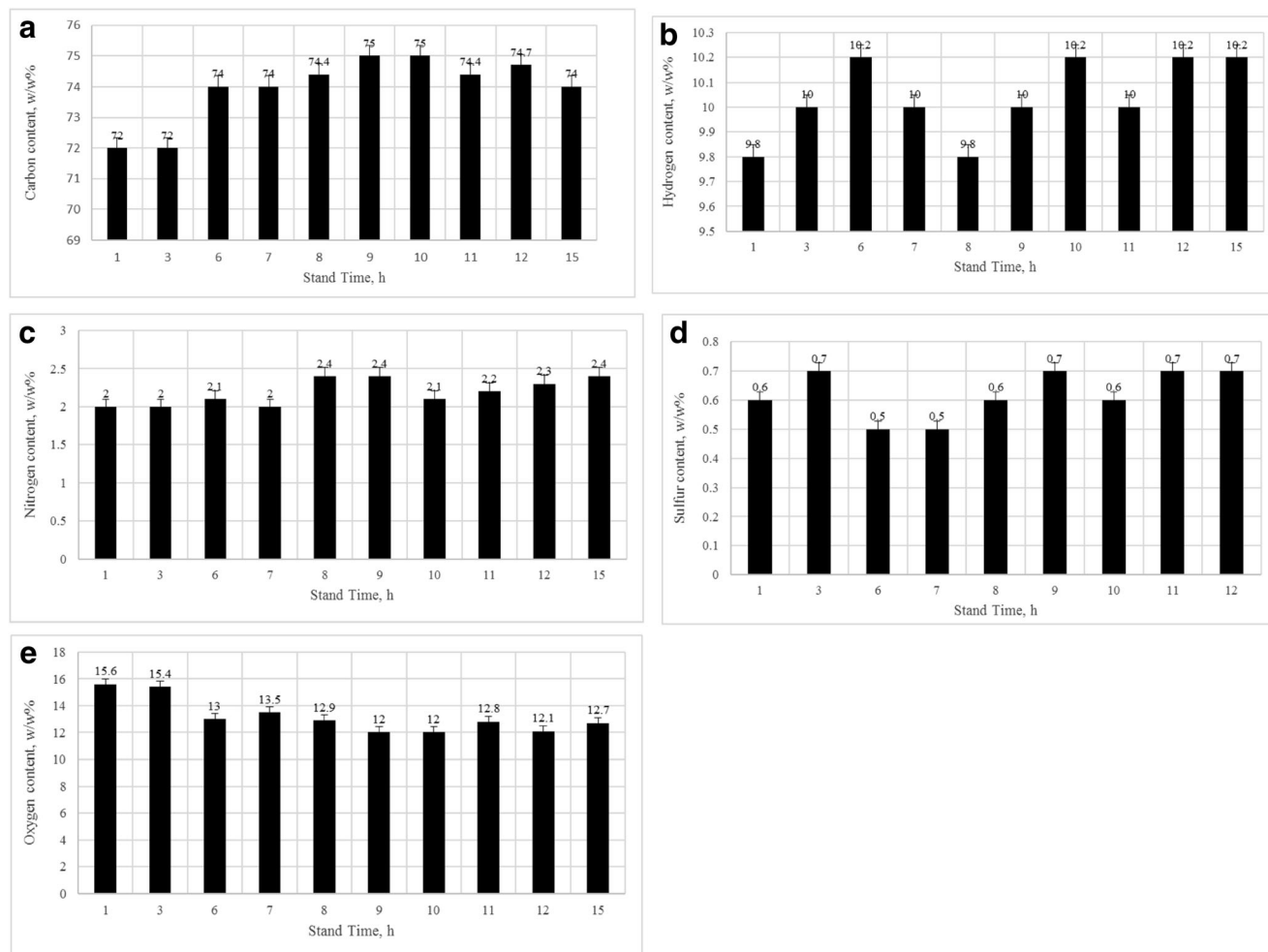


Fig. 3 a Carbon content of biocrude with respect to PM–DCM stand time. b Hydrogen content of biocrude with respect to PM–DCM stand time. c Nitrogen content of biocrude with respect to PM–DCM stand

time. d Sulphur content of biocrude with respect to PM–DCM stand time. e Oxygen content of biocrude with respect to PM–DCM stand time

Fig. 4 HHV and ER of biocrudes with respect to PM–DCM stand time

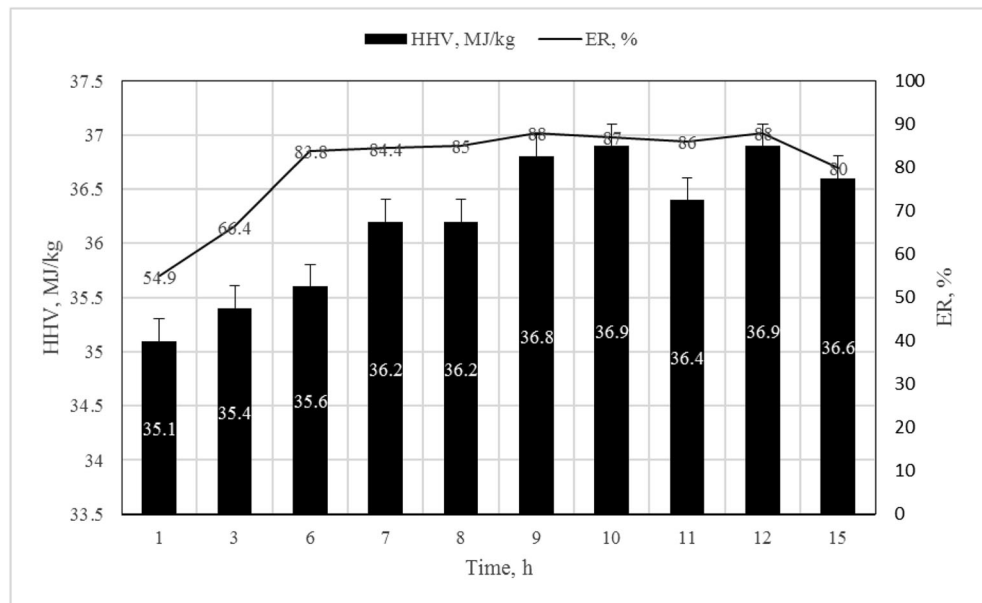


Table 1 Biocrude chemical composition with respect to PM–DCM stand time

S/ N	Identified chemical compounds	Chemical formula	Molecular weight ^a (g/mol)	RT (min)	Relative abundance (% area)									
					1 h	3 h	6 h	7 h	8 h	9 h	10 h	11 h	12 h	15 h
1	Eicosanoic acid	C ₂₀ H ₄₀ O ₂	312	23.2	2.6	2.4	2.1	2.0	2.1	2.1	2.1	2.0	2.0	2.0
2	Egtazic	C ₁₄ H ₂₄ N ₂	380	12.6	3.0	2.8	3.0	3.0	3.1	3.2	3.2	3.2	3.3	3.2
3	Heptadecene, 17-chloro	C ₁₇ H ₃₃ Cl	272	12.2	bdl	bdl	0.5	0.5	1.0	1.0	1.0	1.0	1.4	1.8
4	2-Heptacosanone	C ₂₇ H ₅₄ O	334	14.2	1.8	1.8	1.8	1.8	1.8	1.8	2.0	2.4	2.4	2.4
5	Hexadecane	C ₁₆ H ₃₀	226	16.2	1.6	1.6	1.6	1.6	1.6	1.6	1.4	1.4	1.4	1.4
6	Hexadecanedioic acid, 3-methyl, dimethyl ester	C ₁₇ H ₃₂ O	361	18.4	1.0	1.0	1.5	2.0	2.0	3.2	3.2	3.2	4	4
7	9-Hexadecenoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	270	16.2	bdl	bdl	1.5	1.5	1.5	1.5	1.7	1.5	1.7	2.0
8	Indole	C ₈ H ₇ N	117	14.2	2.6	2.4	2.5	2.4	2.4	2.1	2.0	2.0	2.4	2.4
9	Oleic acid	C ₁₈ H ₃₂ O ₃	296	19.1	3.2	3.1	3.8	3.8	3.8	4.0	4.0	4.0	4.0	4.0
10	Octadec-9-enoic acid	C ₁₈ H ₃₄ O ₂	282	19.8	1.0	1.3	1.6	1.6	1.6	1.6	1.4	1.4	1.4	1.4
11	Oxiraneoctanoic acid	C ₁₉ H ₃₆ O ₃	312	20.6	bdl	bdl	bdl	bdl	bdl	bdl	3.8	3.8	3.8	3.8
12	8-Octadecenal	C ₁₈ H ₃₄ O ₂	266	16.8	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.4
13	10-Octadecenoic acid methyl ester	C ₁₉ H ₃₆ O ₂	286	18.9	41.8	41.8	41.5	39.4	39	37.3	35.6	35	35	35
14	9-Octadecenoic acid, methyl ester	C ₁₉ H ₃₆ O ₃	296	18.9	34	34	32	32	31.7	32	30	30.1	28.6	26.6
15	8-Octadecenoic acid methyl ester Glycerol sterate	C ₁₉ H ₃₆ O ₃	296	19.2	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6
16	Pentadecanoic acid, 14-methyl	C ₁₅ H ₃₀ O ₂	242	17.1	2.0	2.0	2.0	2.0	1.7	1.7	1.7	1.7	1.7	1.7
17	Phenol, 2-cyclohexyl-4,6-dinitro	C ₁₂ H ₁₄ O ₅	234	16.1	2.0	2.4	2.8	2.8	3.0	3.0	3.0	3.0	3.0	3.0
18	Pyrrrole	C ₄ H ₅ N	137	10.2	1.7	1.7	1.8	1.6	1.6	1.8	1.8	1.8	1.8	1.8
19	Tetradecanoic acid, 2-hydroxy	C ₁₄ H ₂₈ O ₃	244	15.1	1.2	1.2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

RT retention time, *bdl* below detection level

^a Obtained using atomic mass of respective elements (C 12, H 1, N 14, Cl 35, O 16)

3.3 Energy analysis

The higher heating value and energy recovered in biocrude are presented in Fig. 4. Due to little variations in CHNSO contents, there were some changes in HHVs and ER in biocrudes. Biocrude HHVs were between ~35 and ~37 MJ/kg, whereas the energy recovered was in the range of 54.9% and 88%. In this study, the ER was found to be within range of previous reports investigating hydrothermal liquefaction of microalgae. For example, Shakya et al. [20] reported an ER of 83% from HTL of *Nannochloropsis* sp., 78% from *Scenedesmus* sp. and 47% from *Chlorella* sp. at reaction temperature of 220 to 320 °C at 30 min reaction time. An ER of 43 to 61% from liquefaction of *Nannochloropsis* sp. at 300 °C for 30 min was reported by Wang et al. [35], whereas Eboibi et al. [11] reported up to 87% ER. This suggests that similar amount of ER could still be recovered from PM–DCM considering stand time.

This study has shown that PM–DCM stand time may influence product yield and properties. Based on the data presented in Fig. 4, in addition to that in Fig. 2, the optimum PM–DCM stand time was found to be after 9 h. The hydrogen-to-carbon ratio of biocrudes was between 1.63 and 1.65, which was found to be similar to 1.56 to 1.95 from HTL of *Galdieria sulphuraria* and *Nannochloropsis salina* [34] and 1.4 to 2.0 for petroleum [36]. Similarly, the nitrogen-to-carbon ratio of 0.2 to 0.5 was found to be within the range of 0.05 of petroleum. The oxygen-to-carbon ratio of 0.13 to 0.16 was substantially lower than 0.67 of algae, however higher than 0.05 of conventional petroleum. Therefore, upgrading biocrude is

necessary, in order to improve its fuel properties, as mentioned previously.

3.4 Biocrude chemical composition: GC-MS analysis

GC-MS analysis shows that biocrude produced from HTL of algae is a complicated mixture consisting numerous compounds. The chemical compounds identified with GC-MS having relative abundance area greater than 1% are presented in Table 1. It should be noted that only light compounds unlike high boiling point compounds such as asphaltene that can vaporise through the GC column could only be identified with the GC-MS [17].

Based on the data presented in Table 1, there were variations in composition relative to time, suggesting possibility of reaction during extraction of biocrude from the product mixture. For example, heptadecene, 17-chloro, 9-hexadecenoic acid, methyl ester, oxiraneoctanoic acid and B8-octadecenal were not detected at 1 h stand time but were detected with increase in stand time. This finding suggests that PM–DCM mixture continuously undergoes side reactions during recovery of biocrude from solid residue and aqueous phases.

3.5 Metal composition in biocrude

One of the important factors in HTL algal biorefinery is the composition of metals in biocrude produced. Low metallic composition in biocrude is desirable in order to improve combustion and avoiding refining issues [29, 37]. Therefore, the fate of metals during liquefaction of alga, particularly marine

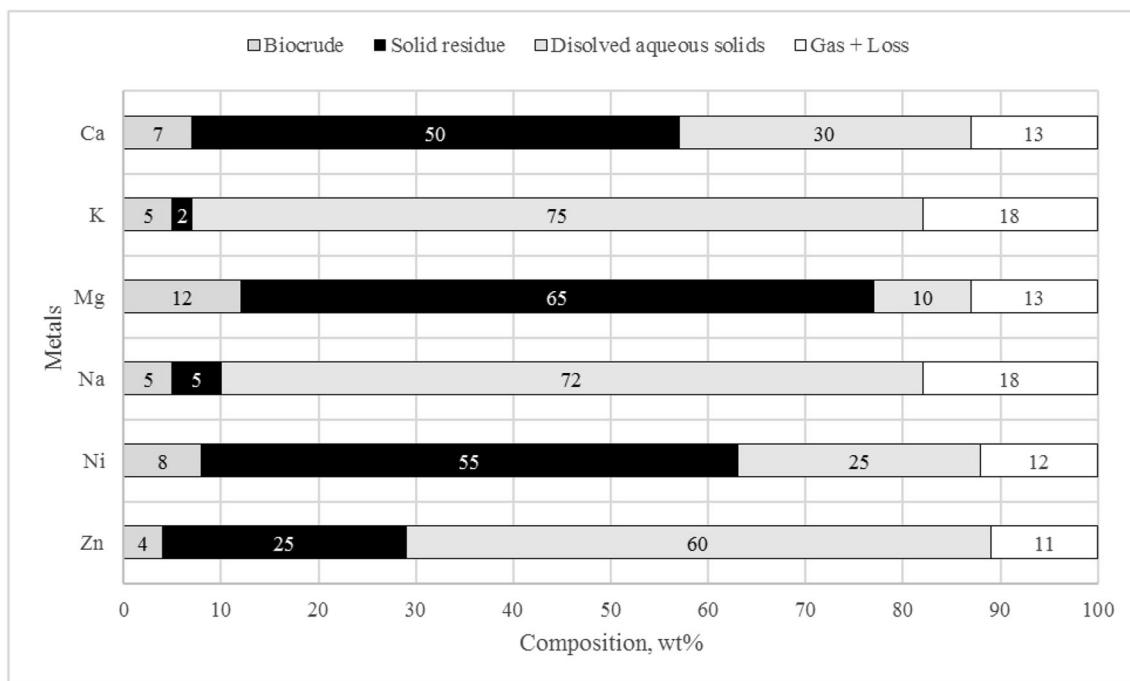


Fig. 5 Metal composition in biocrude, solid residue, dissolved aqueous solid and gas + loss derived from HTL of alga and at 9 h PM–DCM stand time

algae with high alkali metals, is a concern. The metals calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), nickel (Ni) and zinc (Zn) were assessed, and the metal balance is presented in Fig. 5.

Most of the metals were distributed to either the solid residue and dissolved aqueous solids. Approximately 50 wt% Ca, 65 wt% Mg and 55 wt% Ni were recovered in the solid residue. The aqueous fraction was high in Na (72 wt%), K (75 wt%) and Zn (60 wt%), which are essential nutrients for algae cultivation that can be recycled to algae pond to reduce cost of cultivation and energy production [38]. The resultant biocrude was found to contain 7 wt% Ca, 5 wt% K, 12 wt% Mg, 5 wt% Na, 8 wt% Ni and 4 wt% Zn. About 11 to 18 wt% of these metals fractionated in the gas phase. The low composition of these metals in biocrude suggests that biocrude could be refined avoiding issues associated with fouling and slagging [34, 37].

4 Conclusion

In this reported study, the effects of stand time for product mixture and solvent on yields and properties from hydrothermal liquefaction of *Tetraselmis* sp. algal were investigated. The first demonstration of stand time effects on PM–DCM mixture to form layers has been shown to have effects on yields of biocrude, solid residue and aqueous phase. PM–DCM stand time seems to have no substantial effects on quality of biocrude. This finding suggests HTL product mixture is unstable; hence, more attention is needful to develop effective downstream separation methods for recovery of HTL product fractions.

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