Elucidation of Sodium Hydroxide Catalyst and Solids Loading for Thermochemical Liquefaction of *Tetraselmis* sp. Microalga

B. E. Eboibi*

Department of Chemical and Petroleum Engineering, Delta State University, Oleh Campus, Nigeria.

ABSTRACT: The production of biocrude with and without sodium hydroxide catalyst (Na_2CO_3) through hydrothermal liquefaction of *Tetraselmis* sp. microalga at different organic solids loading was investigated. The HTL experimental study was conducted at reaction temperatures of 310°C, 330°C, 350°C and 370°C at 5 min fixed reaction time with organic solids loading of 10%w/w, 15%w/w, 20%w/w, 25%w/w, 30%w/w, and at 40%w/w. The results of the study showed that organic solids loading above 20%w/w had no substantial changes on biocrude yield. The catalyst had very little effect on the yield of biocrude but substantially enhanced its quality when compared with non-catalysed reactions. Although, Na_2CO_3 catalyst may be used for HTL of *Tetraselmi* sp. in laboratory-scale studies, it is highly unnecessary for commercial-scale. Thus potentially reducing the production cost in future commercialization of HTL-alga-biorefinery.

KEYWORDS: Biocrude, Na_2CO_3 catalyst, hydrothermal liquefaction, Microalga, organic solids loading

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I. INTRODUCTION

Hydrothermal liquefaction of wet biomass to biofuel is an emerging technique which has been highly considered for decarbonisation of liquid transportation fuels. This has led to an increase research on hydrothermal liquefaction (HTL) of microalgae biomass for biofuel production (Bauer et al., 2019; Li et al., 2019). Microalga has been identified as promising feedstock for biofuel production mostly due to their high photosynthetic efficiency, CO_2 fixation and energy content when compared to terrestrial plants (Petrus, and Noordermeer, 2016; Pienkos and Darzins, 2009).

HTL of microalgae to biofuels is considered as a "green" energy process. HTL is performed at subcritical water conditions, mostly within reaction temperature range of 250°C to 370°C, pressure 5 MPa to 21MPa and at reaction times of 5min to 60 min (Han et al., 2019; Jena et al., 2011). At these reaction conditions, there is breakdown of large macromolecules to simple organic molecules via hydrolysis and depolymerisation reactions (Prestigiacomo et al., 2019). HTL produces a primary oil generally referred to as biocrude. Also, it produces solid residue, aqueous and gas phase co-products. The applied HTL reaction conditions seems to "mimics" natures geological processes forming fossil crude and hydrocarbon gases. Apparently, these formations occurs over thousands of years but HTL reaction is performed in minutes. However, the primary product biocrude is still a concern, as it contains undesired hetereoatoms. Hence, the necessity to improve its yield and quality. Other concerns include suitable feedstock, solids loading, catalysts, optimum operating parameters and upgrading of biocrude to have similar properties to conventional petroleum.

Consequently, heterogeneous and homogeneous catalyst have been investigated to improve yield and quality of the biocrude oil (Jena et al., 2012; Liu et al., 2018; Shakya et al., 2015; Xu et al., 2019). Although, these reports have shown higher energy recovery, improved yield and quality biocrude, it is still not clear. In addition, these studies have reported contradictory data on catalytic effect on biocrude yield with use of catalyst (Kohansal et al., 2019; Prestigiacomo et al., 2019; Ren et al., 2018). Hence further scientific research investigation is necessary to explain its true catalytic effect and realistic scenario.

Review of the scientific literature showed limited data on hydrotreatment of *Tetraselmis* sp. microalga for biocrude production. The few studies that have investigated HTL of *Tetraselmis* sp. has been on effect of: operating conditions (Eboibi et al., 2014), alga pretreatment (Eboibi et al., 2015), separation methods (Eboibi, 2018) and harvesting methods (Das et al., 2019) on biocrude yield and quality from *Tetraselmis* sp. Although, these reports have demonstrated feasibility of producing biocrude from *Tetraselmis* sp., there is limited information on catalytic and solids loading during its liquefaction. In this present study, and for the first time, sodium hydroxide (Na_2CO_3) catalyst and organic solids loading influence for HTL of *Tetraselmis* sp. microalga is investigated. Therefore, the aim of this study is elucidation of Na_2CO_3 catalyst and solids loading for hydrothermal

*Corresponding author: blessingeboibi@gmail.com

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liquefaction of halophytic *Tetraselmis* sp. microalga, particularly on the biocrude fraction.

II. MATERIALS AND METHODS

A. Materials

A halophytic microalga *Tetraselmis* sp. was used as feedstock in present study. Details of its cultivation, harvesting and analysis has been reported previously (Fon Sing et al., 2014; Eboibi et al., 2015). The biochemical and elemental composition of *Tetraselmis* sp. alga is presented in Table 1.

A 1L custom built high-pressure Inconel batch reactor with an inbuilt magnetic stirrer was used for the HTL experimental studies at Biotechnology Division Pilot Plant of Aban Infrastructure Pvt. Limited, Chennai, India. The reactor was designed to operate at maximum reaction temperature of 500ºC and 350bar reaction pressure. Dichloromethane reagent grade solvent (of more than 99% purity) and sodium hydroxide catalyst were purchased from Sigma-Aldrich.

B. Hydrothermal Liquefaction

The HTL experimental studies were conducted using IL Inconel batch reactor, as mentioned previously. For catalytic studies: each HTL experimental run had the reactor loaded with 500 g of *Tetraselmis* sp. alga slurry containing 16w%w/w alga solids with or without 5wt% sodium hydroxide catalyst (of alga feed) at reaction temperature of 310ºC, 330ºC, 350ºC and 370ºC at 5 min fixed reaction time.

For studies involving solids loading, for each HTL experimental run, the reactor was loaded with 500 g of alga slurry containing 10%w/w, 15%w/w, 20%w/w, 25%w/w, 30%w/w and 40%w/w alga solids. The HTL experimental studies were conducted at reaction temperature of 350ºC and 5min reaction time.

Then, after each reactor loading, the reactor was sealed and heated to set reaction temperature using an electrical heating jacket (with a heating rate of ~ 20ºC/min). At attainment of set reaction temperature, the reactor was maintained (at ± 4ºC) for 5min reaction time. During heating and reaction times, the reactor was stirred continuously at 300 rpm with a magnetic drive impeller type agitation device in all experimental runs. This is in order to ensure proper mixing of reactants. After complete reaction time, the reactor was switched-off, and allowed to cool to room temperature.

Following cooling, the gas produced were vented via the gas valves, while the reactor content referred here as product mixture was transferred to a 1L separating funnel. Then the reactor wall and magnetic stirrer was washed with 150mL of dichloromethane and water mixture of ratio 1:1. The washed fractions were then added to the separating funnel containing the product mixture. Then, dichloromethane were added to the product mixture in ratio 1:1, and agitated for about 5min. Thereafter, the separating funnel was allowed to stand for 17hr under room temperature (~28ºC). Biocrude, solid residue and aqueous phases were gravimetrically obtained, while the gas phase was estimated by combined mass difference of other fractions.

C. Product Analysis

The gravimetric HTL product yield were estimated using Eq. (1) (Eboibi et al., 2019).

$$Yield = \frac{M_p}{M_f} x\ 100\% \qquad (1)$$

From Eq. (1), M is the mass (kilograms); f is the feedstock; and p represents biocrude, solid residue, gas or aqueous phase coproduct.

The composition of elemental carbon (C), hydrogen (H), nitrogen (N) sulfur (S) were determined using a varioEL III Elemental Analyser system, GmbH in accordance to ASTM D-5291 and D-3176 methods. The elemental analyser was calibrated using sulphanilamide as a standard. The oxygen (O) content was estimated by difference (O w/w%=100-(C+H+N+S)). The higher heating value (HHV) was estimated in accordance to the unified correlation equation (Eq. 2) proposed by Channiwala and Parikh (2002).

Table 1: Properties of a halophytic microalga *Tetraselmis* sp.

Microalgae	**Elemental content**						**Biochemical content**			**References**
	C	**H**	**N**	**S**	**[a]O**	**HHV (MJ/kg)**	**Carbohydrate**	**Protein**	**Lipids**	
[b]*Tetraselmis* sp.	42.0	6.8	8.0	3.0	40.2	19.2	22	58	14	Present study
Arthrospis sp.	45.7	6.9	10.1	1.0	36.3	[c]20.2	7.1	60.7	12.1	Vlaskin *et al*., (2018)
Chlorella sp.	49.5	6.9	10.4	1.6	31.4	[d]22.1	23.7	63.2	1.0	Yang *et al*., (2018)
Scenedesmus sp.	56.4	7.9	7.4	0.4	27.9	[e]26.0	5.6	46.3	48.1	Wadrzyk *et al*., (2018)

[a]: obtained by difference
[b]: Eboibi *et al*., (2014)
[c, d, e]: calculated using reported CHNSO data.
HHV: Higher heating value.
C, H, N, S, and O represents Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen, respectively.

$$HHV\left(\frac{MJ}{kg}\right) = 0.3491C + 1.1783H + 0.1005S - 0.10340 - 0.0151N - 0.0211 \quad (2)$$

The amount of energy recovered in biocrude were calculated using Eq. (3).

$$ER = \frac{HHV_b \; x \; M_b}{HHV_f \; x \; M_f} \; x \; 100\% \quad (3)$$

where ER represents energy recovered; HHV_b and HHV_f is the higher heating values of biorude and feedstock, respectively; Mb is the mass of biocrude and Mf the mass of feedstock.

The atomic ratios of hydrogen-to-carbon (H/C), oxygen-to-carbon (O/C) and nitrogen-to-carbon (N/C) were calculated using Eq. (4a), Eq. (4b) and Eq. (4c), respectively.

$$H/C = \frac{H(\frac{w}{w}\%) \; x \; MW_C}{C(\frac{w}{w}\%) \; x \; MW_H} \quad (4a)$$

$$O/C = \frac{O(\frac{w}{w}\%) \; x \; MW_C}{C(\frac{w}{w}\%) \; x \; MW_O} \quad (4b)$$

$$N/C = \frac{N(\frac{w}{w}\%) \; x \; MW_C}{C(\frac{w}{w}\%) \; x \; MW_N} \quad (4c)$$

where $H(w/w\%)$ and $C(w/w\%)$, $O(w/w\%)$ are weight percentages of hydrogen, carbon, and oxygen, respectively, MW_C is the molecular weight of carbon, and MW_H the molecular weight of hydrogen. MW_O represents molecular weight of oxygen and MW_N the molecular weight of nitrogen.

III RESULTS AND DISCUSSION

This section discusses the results obtained from HTL of *Tetraselmis* sp. alga with and without catalyst and differing solids loading. Also, the analytical data obtained following analysis of the primary product biocrude are discussed extensively.

A. HTL Product Yields: Catalysed and Non-Catalysed Reactions

The yields in biocrude, solid residue gas and aqueous phases derived from HTL of *Tetraselmis* sp. with or without Na_2CO_3 catalyst are presented in Figure 1. Irrespective of catalysed or non-catalysed reaction, biocrude yields increase from 36wt% to 66wt% when reaction temperature increased from 310ºC to 350ºC. However, further increase in reaction temperature to 370ºC led to decrease in yields.

B. HTL Product Yields: Effect of Different Solids Loading

To avoid clogging of reactor parts with alga solids, high biocrude yields and issues of energy input, it is important to know suitable organic solids favourable for higher biocrude yield. The HTL yields; biocrude, residue, gas and aqueous phases obtained from differing solids loading are presented in Figure 2. As illustrated in the figure, the minimum biocrude yield of 45wt% was obtained at 10%w/w% solids loading, maximum of 61wt% biocrude yield at 20%w/w solids loading. However, the biocrude yields were relatively constant with further increase in solids loading above 20%w/w.

The combined co-product mass yields gradually reduced from 55wt% to 39wt% when solids loading increased from 10%w/w to 20%w/w. However, the coproduct mass yields steadily increased from 39wt% to 45wt% with an increased in solids loading above 20%w/w. Due to unconverted alga the solid residue fraction gradually increased from 14wt% to 17wt% with an increased in solids loading from 20%w/w to 45%w/w. The trend in increase and decrease in organic solids loading were found to correspond with the biocrude yields.

There could be several reasons that led to variation in biocrude yields with respective organic solids loading. Some possible reasons could be due to presence of optimum amount of organics to H^+ and OH^- ions in HTL reactions at higher solids loading (Jena et al., 2011). Also, the amount of water available in the medium could have effects in the disruption of algal cellular cells. As higher amount of media (suggesting lower solids loading) leads to lower biocrude yields, while lower amount (high solids loading) may lead to decrease in biocrude yield. It therefore suggests HTL of alga feedstocks with solids approximately 20%w/w favour higher biocrude yield. However, slurry of lower organic solids, apparently with more water content is more energy-intensive (Biller and Ross, 2011; Jazwari et al., 2013).

C. Effect of Catalysed and Non-Catalysed HTL Reactions on Resultant Biocrude Properties

Data obtained from the elemental analysis of bicrude is presented in Table 2. Although, there were no substantial increase in biocrude yield with applied Na_2CO_3 catalyst (shown in Figure 2), the quality of biocrude improved. Applied Na_2CO_3 catalyst showed quantitative nitrogen and sulfur removal. Also, there were reductions in oxygen content except at 310ºC, resulting in minimal improvement in biocrude energy density. Suggesting that the applied catalyst favour deoxygenation reactions. Due to deoxygenation, there were improved hydrogen-to-carbon ratios of resultant biocrude. The HHVs of biocrude generally improved, gaining additional 2.7MJ/kg when compared with non-catalysed reactions. Moreover, biocrude obtained with Na_2CO_3 catalyst had lower O/C and N/C atomic ratios. At optimum reaction temperature of 350ºC, the biocrude has an HHV of 35.7 MJ/kg, H/C ratio of 2.0, O/C and N/C of 0.12 and 0.04, respectively.

Despite improved biocrude properties with applied catalyst, there is still need to upgrade HTL-biocrude to petroleum crude standard. As shown in Table 2, the resultant biocrude is still below par for direct application for transportation fuel. The obtained biocrudes are still characterised with high levels of heteroatoms, hence further upgrading studies are required. Since upgrading of biocrude is still necessary, then it would be unnecessary to apply catalyst for liquefaction, though could be useful for laboratory-scale

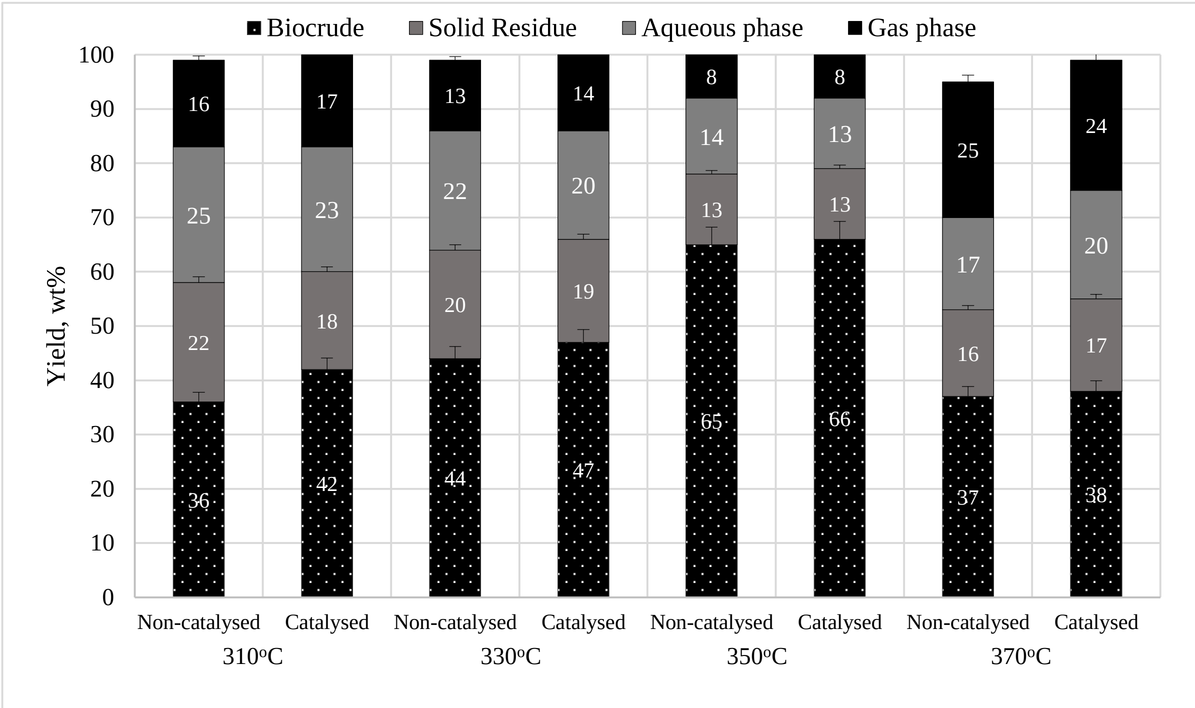

Figure 1: Products derived from HTL of microalgae with and without catalyst at different reaction temperature.

studies. This would reduce production cost in future commercialization of HTL-alga-biorefinery.

D. Effect of Solids Loading on Biocrude Elemental Content

The elemental carbon, hydrogen, nitrogen, sulfur, and oxygen of biocrude obtained from differing solids loading are presented in Figure 3. Although, solids loading has been found to influence biocrude yield, there were no substantial effect on its elemental content. As shown in Figure 3, the elemental content of carbon was between 71w/w% and 73w/w%, hydrogen remain fairly constant (between 8w/w% and 9w/w%), nitrogen (3w/w% and 3.5w/w%) and between 0.8w/w% and 1.2w/w% for sulfur. The oxygen content was found to have higher numerical variation (between 13.1w/w% and 16.7w/w%), however, it showed no clear trend. Also, and as expected there were no much differences in the HHVs, which varied between 33MJ/kg and 34.5MJ/kg. These finding confirms that solids loading have no substantial impact on the properties of resultant biocrude but only on its yield.

Comparing with previous report, Jena et al., (2011) who investigated different solids loading from HTL of Spirulina sp., reported no substantial differences in elemental composition of biocrude produced. At 350^{o}C, they reported 73.7% for carbon content, 8.9% for hydrogen, 6.3% for nitrogen, 0.9% for sulfur and 10.7% for oxygen content, while the HHV was 35.2MJ/kg. Jazwari et al., (2013) reported no differences in elemental content and HHVs for biocrude from HTL of Chlorella sp. at different solids loading. At 10% solids loading operating at 350^{o}C, they reported 70.7% carbon content, 8.8% hydrogen

Table 2: Properties of biocrude obtained with catalysed and non-catalysed HTL of *Tetraselmis* sp.

HTL reaction conditions		Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	HHV (MJ/kg)	Atomic ratios		
								H/C	O/C	N/C
310ºC	Non Catalysed	69.7	8.9	5	0.6	15.8	33.1	2.0	0.17	0.06
	Catalysed	70.0	9.4	3.8	0.4	16.4	33.8	2.1	0.17	0.04
330ºC	Non Catalysed	70.1	7.7	5.4	0.5	16.3	31.8	1.7	0.17	0.06
	Catalysed	73.5	8.7	4.8	0.3	12.7	34.5	1.8	0.12	0.05
350ºC	Non Catalysed	69.7	8.5	5.1	0.5	16.2	32.6	1.9	0.17	0.06
	Catalysed	74.2	9.4	4.3	0.2	11.9	35.7	2.0	0.12	0.04
370ºC	Non Catalysed	68.6	9.1	5.3	0.7	16.3	32.9	2.1	0.17	0.06
	Catalysed	72.2	8.9	4.8	0.4	13.7	34.2	1.9	0.14	0.05
Petroleum crude[a]	-	83-81	10-14	0.1-2	0.05-6	0.05-1.5	40-44	1.4-1.9	0.01	0.05

[a]: Speight, 1999.

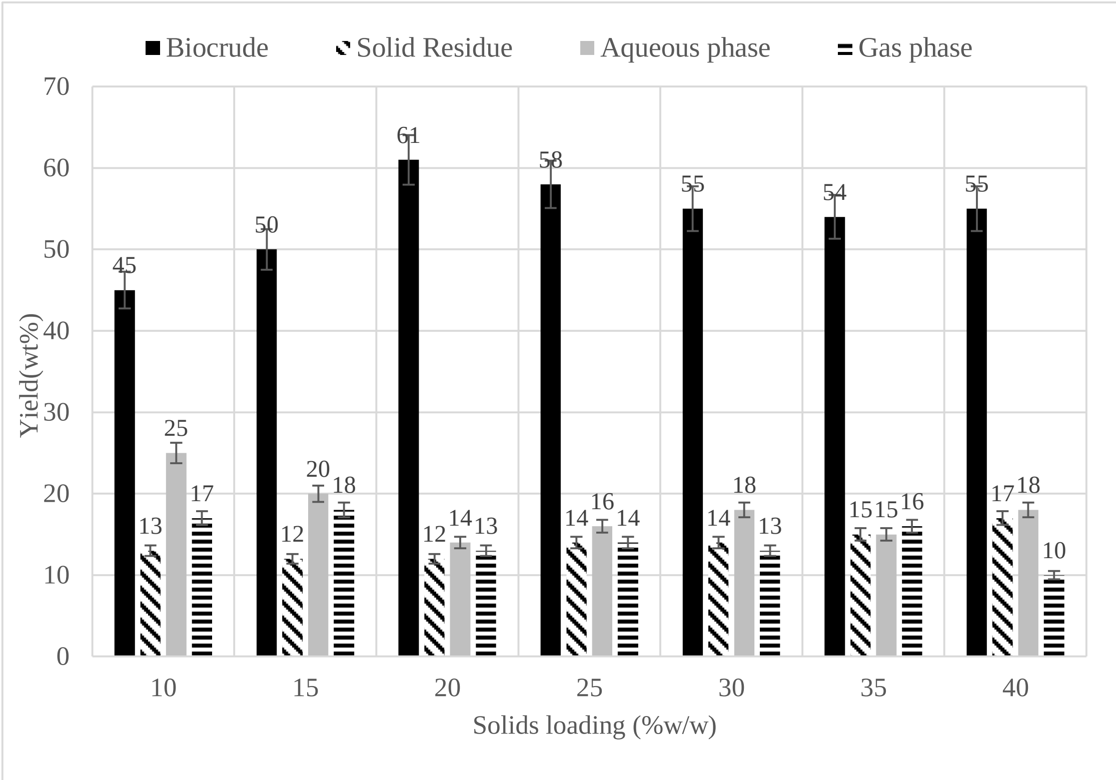

Figure 2: Phase yields obtained from HTL of halophytic *Tetraselmis* sp. microalga at different solids loading at 350ºC.

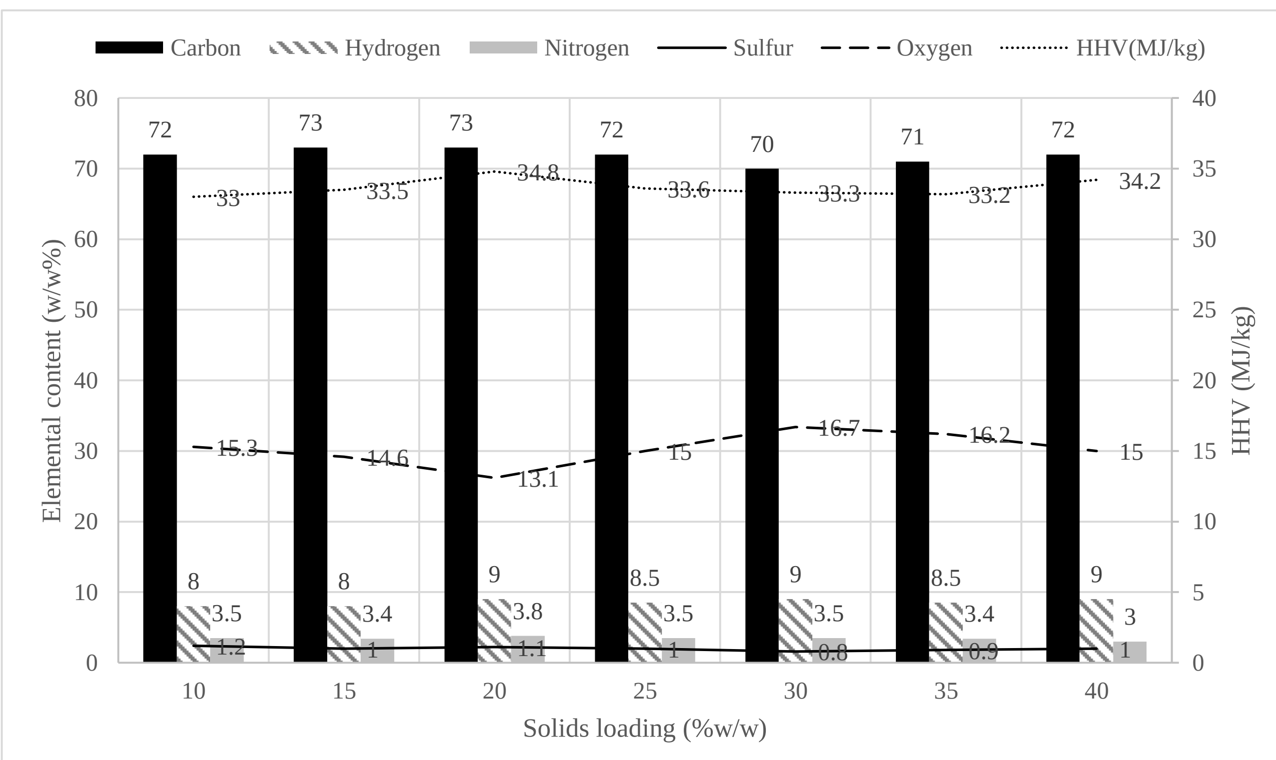

Figure 3: Elemental content and energy density of biocrude after HTL of halophytic *Tetraselmis* sp. microalga at different solids loading at 350ºC.

content, 7.7% nitrogen content, 0.8% sulfur content and 12% as oxygen content, while 33.8MJ/kg for HHV.

At 5% solids loading at 350ºC reaction temperature, they reported 67.9%, 8.9%, 7.9, 15.3% and 32.5MJ/kg for carbon, hydrogen, nitrogen, oxygen and HHV, respectively. Therefore, the data in present study is in good agreement with previous report, as solids loading have no substantial effect on elemental composition of biocrude.

It should be noted that the results obtained in this study may only be applicable to the microalga *Tetraselmis* sp. As the yield and properties may be differ with other algae species, mostly due to differing biochemical composition. The biochemical components has been reported to have substantial effect on yield and characteristics of HTL of algae (Biller and Ross, 2011; Toor et al., 2012), hence the variations in scientific literature data.

E. Energy Analysis for Solids Loading

Some of the important factors to determine biocrude quality regarding energy density is the amount of energy recovered (ER) in biocrude, and hydrogen-to-carbon (H/C) atomic ratio and higher heating values. As a result, the amount of ER, H/C and HHV were evaluated following HTL of alga at different solids loading. The data obtained for HHVs have been presented in Figure 3, while ER and H/C are illustrated in Figure 4.

Based on the data shown in Figure 4, at 10%w/w solids loading, the ER initially increased from 52% to 76% at 20%w/w solids loading. However, further increase in solids loading from 20%w/w to 45%w/w led to decrease in ER from 76% to 48%. The trend in energy recovered in biocrude was found to correspond with the biocrude yield, shown in Figure 2. The hydrogen-to-carbon atomic ratios varied between 1.7 and 2.0, which are within acceptable limits for biofuel precursors (Speight, 1999).

IV. CONCLUSION

The product fractions from HTL of *Tetraselmis* sp. alga in catalysed, non-catalysed at different reaction temperatures, under different organic solids loading and the characteristics of biocrude were reported in this paper. The result showed that applied catalyst had very little changes in yield with substantial improvement in quality of biocrude. Maximum biocrude yield of 61wt% and minimum of 45wt% were obtained at 20%w/w and 10%w/w solids loading respectively. Biocrude yield at above organic solids loading of 20%w/w remained fairly constant with higher residual product. There were slight improvement in energy density of the resultant biocrude, enhancing the quality of biocrude.

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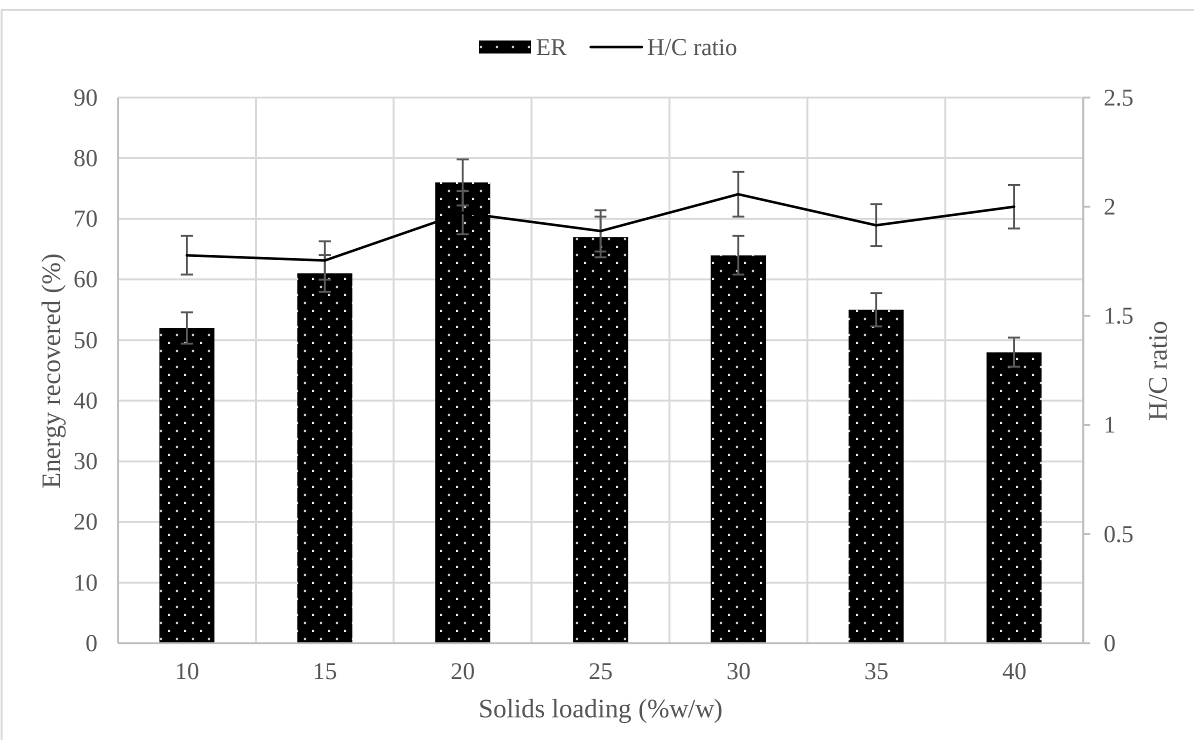

Figure 4: Energy recovered and H/C ratio in biocrude obtained at different solids loading.

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