Assessing Yield and Properties of Distillate from Biocrude and Blend after Hydrothermal Liquefaction of Microalgae

EBOIBI, BE

Department of Chemical Engineering, Delta State University, Oleh Campus, P.M.B. 22, Oleh, Delta State, Nigeria.
Email: blessingeboibi@gmail.com

ABSTRACT: This paper is on assessing yield and properties of distillate derived from biocrude, and blend stream of biocrude and conventional petroleum. Biocrude was produced from hydrothermal liquefaction of a halophytic microalga *Tetraselmis* sp. at 350ºC, 5min with 16w/v% solids content. The resultant biocrude was coprocessed with petroleum using fractional distillation. The result of the study shows that similar yield and quality distillate were obtained from petroleum and blended stream. Distillate fraction obtained from the blend had similar properties such as higher heating values (HHV), H/C atomic ratio and elemental composition to those of petroleum crude. The energy density of biocrude-distillate significantly improved from 72.4MJ/kg to 86.9MJ/kg with about 97% reduction in oxygen content. Recovery of gasoline fractions with normal boiling point range of 190ºC to 290ºC were found higher in petroleum and blend compared to biocrude. This finding is important as coprocessing blend of biocrude and petroleum would address the issues with heteroatoms, which could be of great economic importance. However further studies are necessary on distillate fractions, in order to assure compatibility with petroleum derived fuels.

Hydrothermal liquefaction (HTL) is a novel promising technology for the complete conversion of whole algae to feedstock upgradable to drop-in fuels. Importantly, it avoids energy-intensive (Cheng *et al*., 2018; Wagner *et al*., 2017) normally applied to processes such as transesterification and pyrolysis for biofuels production. HTL of microalgae is carried out at subcritical operating conditions (200ºC to 374ºC), pressures 5-25MPa, using biomass of 10wt% to 20wt% solids, with/or without catalyst and water acting as both solvent and catalyst, at vary reaction times (Wang *et al*., 2018; Fushimi and Umeda, 2016). HTL products include biocrude, solid residue, aqueous phase and gas phase. Research investigation has shown that the primary product, biocrude fall short of conventional refining limit, hence cannot be used directly as transportation fuels (Xu and Savage, 2018). Hence, biocrude requires further upgrading to improve its fuel properties. The aqueous phase can be recycled to algae cultivation pond, while the gas phase contains up to 90% carbon dioxide and traces of hydrocarbon gases. The solid residue contains nutrient which could be used as substitute to fertilizer, although no literature has been reported on its application. A review of the scientific literature shows that numerous research investigations have been carried out in HTL of microalgae within the last decade. Research investigations on various algae strains (for high lipid and stress resistance and growth rate) (Barreiro *et al*., 2013; Cheng *et al*., 2017), different operating reaction conditions (reaction temperature, reaction time, solvents and catalyst) (Xu and Savage, 2015; Eboibi *et*

al., 2014a) and several review papers have put together research on HTL of algae-to-biofuel (Vlaskin *et al*., 2017; Barreiro *et al*., 2013; Guo *et al*., 2015). In addition, there have been reports on the life cycle assessments and techno-economic analyses (LCA & TEA) of HTL-algae-to-biofuels (Pedersen *et al*., 2018; Delrue *et al*., 2013; Frank *et al*., 2012; Liu *et al*., 2013). Based on these studies, HTL has better energy return on investment (ERoI), lower greenhouse gas (GHG) emission and higher economic potentials compared with the conventional lipid extraction and transesterification processes from microalgae (Biller *et al*., 2015; Eboibi *et al*., 2015).

Due to issues on heteroatoms impurity, led to further processing of resultant biocrude by upgrading with catalytic hydro-processing or catalytic and/or non-catalytic hydrothermal in batch/continuous reactors (Bai *et al*., 2014; Biller *et al*., 2015; Elliot *et al.*, 2013; Li and Savage, 2013; Roussis *et al*., 2012). Although, these studies reported improved biocrude yield, enhanced energy density, higher energy recovery in the upgraded biocrude, the heteroatoms, particularly N content were still higher with at least 2w/w% to 4w/w% compared to petroleum (Eboibi *et al*., 2015). In addition, the outcomes of these studies have shown that complete replacement of fossil fuels by HTL-derived-biofuels is not feasible in the near future (Lavanya *et al*., 2016). If that being the case, how would HTL-algae biofuels be achieved, could there be any modality for gradual introduction of biocrude to existing refinery? The 'bottom-line' is that further

Email: blessingeboibi@gmail.com

studies are needed to be able to achieve drop-in-fuels production from HTL of algae. Like petroleum, HTL-biocrude needs upgrading and refining in order to produce transportation fuels (Liang *et al*., 2017). One of the potential approach is blending biocrude with petroleum feedstocks (Jiang and Savage, 2017). The few reports of investigations of related studies on blending of pyrolysis derived oils with petroleum shows promising outcomes. Foster *et al*., (2012) reported coprocessing of pyrolysis oil with standard gas oil to achieve drop-in-fuels. Blending of wood derived oil with diesel fuel were reported by (Nabi *et al*., (2015). In 2011, De Miguel *et al*., investigated coprocessing of deoxygenated pyrolysis oils with straight runs gas oil. Generally, the outcomes of these previous reports are promising; considering that similar yields were obtained for blended feeds and pure petroleum. The blends have insignificant effects in engine performance. These studies shows promising result, hence it would be of interest to elucidate yield and characteristics of products obtained from blending of HTL-derived biocrude with petroleum. Therefore the main aim of this reported study is on the feasibility of blending HTL-algal-biocrude with petroleum, to elucidate the energy density and distribution of heteroatoms in distillate products.

MATERIALS AND METHODS

Feedstock: A halophytic microalga *Tetraslmis* sp. was used in this present study. The algal was cultured and harvested from open raceway ponds owned and operated by Muradel Pty Limited, in Karatha, Australia. After harvesting and dewatering, the algal biomass was stored at -8ºC. Freeze-dried biomass (at -48ºC and pressure 0.133mBar using 18L Labcono FreeZone drier) were transported to India for the studies. HTL and fractionating experimental studies were performed at Biotechnology Division, Aban Infrastructure Pvt. Limited, Chennai, India.

Table 1: Properties of *Tetraselmis* sp. biomass

Biochemical composition[a], wt% afdw[b]	
Proteins	58
Lipids	14
carbohydrate	22
Elemental composition, w/w%	
Carbon	42
Hydrogen	6.8
Nitrogen	8
Sulfur	3
Oxygen[c]	40.5
Higher heating value (MJ/kg)	19.2

[a]: *Eboibi et al., (2015).* [b]*afdw: ash free dry weight.*[c]*: obtained by difference*

The microalga biochemical composition: protein, lipids and carbohydrate were determined according the methods of Lowry *et al*., (1951); Folch *et al*., (1956) and Dubois *et al*., (1956), respectively. The algal biomass properties (biochemical and elemental composition) are presented in Table 1. The conventional petroleum was obtained from WRPC and use as received.

Hydrothermal liquefaction: HTL were carried out using a custom built 1L high pressure-temperature batch reactor with an inbuilt magnetic stirrer. HTL of *Tetraselmis* sp. was performed at 350ºC, 5min with ~16w/v% solids loading. Heating of the reactor was provided by an inbuilt electrical heater. The reactor set-up is shown in Fig. 1. The reactor was loaded with 360g algal slurry obtained by mixing 60g of algal biomass with 300g of deionised water. Then the reactor was sealed and heated to 350ºC reaction temperature using an electrical heater. This temperature was maintained (±4ºC) for 5min reaction time. During liquefaction the reactant was stirred continuously at 300rpm for homogeneous reaction. The reaction time was set after attaining 350ºC, and stopped after completing 5min. After complete reaction, the reactor was cooled to room temperature, followed with product separation and recovery.

Product separation and recovery: After cooling the produced gas were vented via gas relief valves. Then the reactor content referred to as product mixture were transferred to a separating funnel, and subsequently diluted with equal volumes of dichloromethane to the amount of product mixture. About 50ml each of water and dichloromethane were used to rinse the magnetic stirrer and reactor walls. The resultant rinse solution were transferred to the separating funnel containing the rest product mixture. This was followed by manually agitating the separating funnel for about 5min, in order to improve extraction. Then the separating funnel was allowed to sit for up to 12hr for phase separation, which led to formation of three phases. An upper phase referred to as aqueous phase; middle layer the biocrude phase containing DCM; and bottom phase, the solid residue fraction. These phases were decanted to separate beakers. The aqueous phase and residue fractions were again washed 2 to 3 times with 100ml DCM in order to extract residual biocrude. The resultant DCM fractions were added to the biocrude phase containing DCM. The combined biocrude phase were subjected to 40ºC to evaporate DCM and water, the remnant defined as biocrude (Sheng *et al*., 2018). The aqueous and residue were quantified after drying at 100ºC in accordance to (Eboibi *et al*., 2014a; Yang *et al*., 2017).

Fractional distillation of petroleum, produced biocrude and the blend were conducted in accordance to ASTM D1160. The blended stream was made up of 10% of biocrude and 90% petroleum. Distillation experimental runs on feedstocks to obtain distillate, residue and loss were conducted in triplicate and the average yield reported with less than 5% error. Similarly triplicate runs were performed for fractional yields at different temperature.

Fig. 1: HTL and Fractional distillation process. (a) HTL reactor set-up. (b) Products recovery and separation procedures

1: Reactor. 2: Electrical heater. 3: Power supply. 4: Pressure sensor. 5: Thermocouple. 6: Magetic stirrer. 7: Contorl box, 8: Valves. HTL: Hydrothermal liquefaction. DCM: Dichloromethane. AP: Aqueous phase. SR: solid residue.

Yields: The yields were determined by relating the mass of products (distillate, residue) to initial mass of feedstock, while loss was determined by difference (100 − (distillate + residue) wt%). Similarly the

fractional yields at different temperatures were determined by relating recovered mass to initial weight of feed.

Elemental analysis: The elemental (carbon, hydrogen, nitrogen, and sulfur (CHNS)) composition were determined using VarioEL III elemental analyser system according to ASTM D-5291 and D 3176 methods. The elemental oxygen content was determined by difference (O = 100-(C+H+N+S)) w/w%). Data obtained for CHNS analyses were used to calculate the higher heating values (HHV) MJ/kg using the unified correlation (Eq. (1)) proposed by Channiwala and Parikh, (2002).

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

Where C, H, N, S, O and A are the respective mass of carbon, hydrogen, sulfur, oxygen, nitrogen and ash, on a dry weight basis. Atomic hydrogen-to-carbon, nitrogen-to-carbon, and oxygen-to-carbon ratios were obtained from the CHNSO data and molecular weight of respective elements.
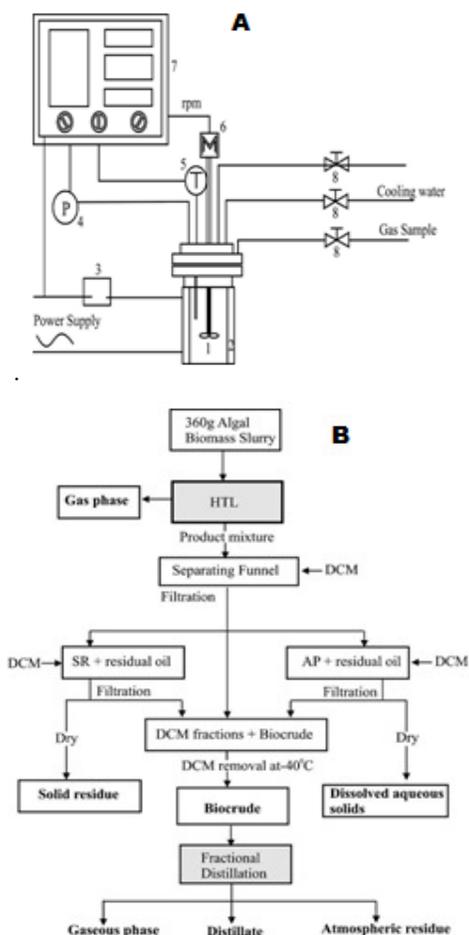
Energy recovery and specie mass balance: Energy recovery (ER) is a term used to describe the amount of energy recovered in product from initial feedstock. ER were calculated using Eq. (2) (Biller and Ross, 2011; Jena *et al*. 2011). Using a similar equation (Eq. 2), the species mass balances were calculated but after replacing the higher heating values of product and feedstocks with the elemental composition of a particular specie (Eboibi *et al*., 2014b; Neveuz *et al*., 2014)

$$ER = \frac{HHV\ of\ product\left(\frac{MJ}{kg}\right)x\ Mass\ of\ product\ (kg)}{HHV\ of\ feedstock\left(\frac{MJ}{kg}\right)x\ Mass\ of\ feedstock\ (kg)}\ x\ 100\% \quad (2)$$

Boiling point distribution-Simulated distillation (SimDist): The boiling point distribution of distillates and raw feeds of petroleum, biocrude, and blend were analysed according to ASTM 7169 method, using gas chromatography equipped with a flame ionisation detector (GC-FID). All samples for SimDist were prepared in accordance to the ASTM 2887 method.

RESULTS AND DISCUSSION
HTL yield: The results of the study shows 65wt% biocrude, solid residue of 15wt%, 12wt% aqueous phase and 8wt% gas phase were derived from algal initial feedstock. The biocrude yield of 65wt% was found higher than 14wt% lipids of algal biomass, suggesting the importance of HTL when compared to

conventional transesterification for biofuel production. Transesterification processes normally extract only the algal lipids component which is converted to biofuel. Based on reported data suggests that using HTL higher products recovery are obtained.

FD yield of petroleum, biocrude and blend: The yields obtained following fractional distillation were 70wt% for petroleum and 71wt% for the blend. However, the distillate yields from biocrude were lower with ~6wt% compared with petroleum and blend. In addition, there were insignificant differences in residue yields and loss for petroleum and blend. An atmospheric residue of 15wt% and 16wt% were obtained for petroleum and blend, respectively. This finding suggests that blending of petroleum and HTL-algal biocrude would have no effects on yields, however further studies on properties of the distillate are necessary.

The residue obtained from the present study were found to be about 5wt% to 14wt% higher compared to that derived from vacuum distillation in a previous report (Eboibi *et al*., 2014b), where 10wt% residue were reported under optimum operating condition. The variation could be due to the fact that fractional distillation being a unit operation is mostly meant for distillation of low boiling compounds. Whereas vacuum distillation which normally follows fractional distillation is meant for processing of heavier molecular weight compounds that failed to distil using fractional distillation. Hence more distillate could be obtained from the residue if channelled to vacuum distillation.

Interestingly, 15wt% gas phase (including loss and water) were obtained from raw petroleum, and 13wt% for biocrude. This suggests that raw petroleum could contain more gaseous compounds when compared to biocrude. There could be other reasons for this variation in gaseous yields. One of the possible reasons corroborated with the separation processes involved in recovery of biocrude after production. It could be possible some light fractions were evaporated during evaporation of dichloromethane (at ~40°C) from the mixture of biocrude and DCM, as shown in Fig. 1b. Bai *et al*., (2014) has shown further processing of biocrude leads to an average ~10wt% conversion into gas, where they reported gas yield ranging from 7wt% to 14wt%. The presence of methane, ethane and ammonia has been reported as gaseous compounds following treatment of biocrude. As expected biocrude led to higher residue of 24wt% compared to 15wt% for petroleum and ~16wt% for the blend, which could be due to higher salt content and heavier molecular weight fractions. Such residue fractions could be

further process for other useful products, as practiced in conventional refinery. The biocrude used in the present study was produced from a marine halophytic *Tetraselmis* sp. algal, known to contain salt (Eboibi *et al*., 2015).

Comparing with previous research, the yields of distillate obtained in this present study were found to be within the range of previous studies investigating processing of biocrude to drop-in fuels. Sarman and Konwer, (2005) reported 89wt% distillate yield from blending biocrude with petroleum, and 79wt% from biocrude following distillation. De Miguel *et al*., (2011) reported that similar yields were achieved for pure petroleum and blended feed. However, it was found that the residue (16wt%) obtained in this present study were lower, except for biocrude residue compared to 22wt% for marine algal HTL-biocrude blend with petroleum and 24wt% for freshwater algal biocrude blend with petroleum (Lavnaya *et al*., 2016). A residue of 61wt% for Maya crude, 57wt% for Arab heavy crude and 23.6wt% for Narimanam crude was reported. The wide differences in atmospheric residue yields could be mostly due to variations in operating conditions and type of crude/biocrude. As there are light, heavy crude, while others are paraffinic and aromatic; having varying characteristics and geographic origin dependent. In addition, it was observed that the distillate were more viscous and wax formation were noticed in the condenser at higher boiling points. Wax were higher during distillation of biocrude compared to petroleum and blend, which could be due to fatty acids compounds of the original feedstock. The wax build up could be reduced with an increase in temperature, reduction in or temporary stoppage of cooling water (Jensen and Rasmussen, 2014). Furthermore, one of the important terms in conventional refining is the distillation profile, which is one of the focus of analytical result of FD.
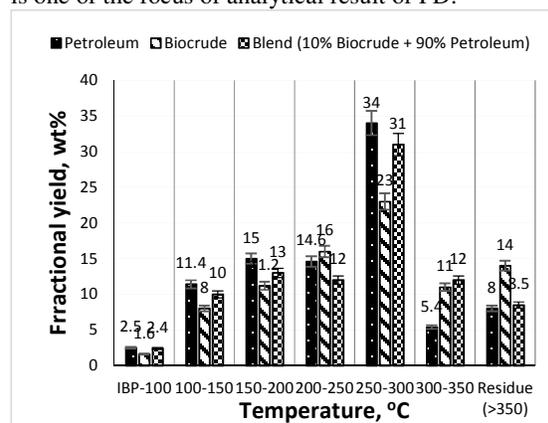

Fig. 2: Fractional distillate yield of petroleum, biocrude and blend obtained at different temperature

The profile describes the mass fraction and/or volume distilled at specific boiling temperature range. In fact it is the function of the boiling point distribution in terms of temperature. The distillate fractional yields derived from petroleum, biocrude and blend at different temperature is shown in Fig. 2. As illustrated in Fig. 2 the distillates were collected at IBP-100°C, 100-150°C, 150-200°C, 200-250°C, 250-300°C, and 300-350°C with > 350°C for residue. There were no much differences in fractional yields for petroleum and the blend at different distillate temperatures.

At lower temperature (IBP-100°C), similar yields were obtained for blend and petroleum, higher compared to biocrude. As mentioned previously, the blend and petroleum contained more gaseous product compared to biocrude. All the feedstocks seems to follow similar trends in fractional yields except at 200-250°C and >350°C, where biocrude had higher yields. This reaffirms that biocrude had higher heavier molecular compounds that could not cracked at lower operating temperature, hence the higher residue fraction.

This reported study has shown that blending of biocrude with petroleum had no significant effects on yields. Importantly, the blend and petroleum had similar residual fractional yield of 8wt% and 8.5wt%, respectively. This is a valuable information for both the refiner and biocrude producer, as blending could address the issue of fossil crisis in the future. One of the viewpoint of biocrude producer is that, the major advantage of blending or coprocessing is reduction in investment costs relating to refining. Due to varying composition of biomass, a potential biorefinery requires several processing units, in order to produce specific liquid transportation fuels. Thus blending biocrude with petroleum seems to be an option for production of drop-in fuels.

Elemental composition of raw feedstock and distillates of petroleum, biocrude and blend: The elemental composition of feedstock and distillates from petroleum, biocrude and blend is presented in Fig. 3. Generally, there were no significant variations in the elemental composition of the distillates and the raw feedstocks for petroleum and the blend, where differences exist, it is only very little. The carbon content for raw petroleum was 85wt%, with numerical increased to 89wt% for its distillate. For the blend, the carbon content increased from 84wt% (for raw blend) to 87wt% following distillation. This finding suggests that the quality of petroleum and biocrude blend could still be maintained, having found to have similar carbon content with raw petroleum. Moreover, the mild increased observed between raw petroleum and

its distillate, suggest the necessity of upgrading for improved fuel properties. For biocrude, there were significant variations for raw biocrude and its distillates, as the carbon content increased from 72.4w/w% to 86.9w/w%.

Currently, there are no reported research studies on the distribution of carbon of distillates obtained from FD of HTL-algal- biocrude and blends with petroleum. Though in a related study, Eboibi *et al*., (2014) reported an increase in carbon content of 68.5wt% to 85.2wt% and 70.5wt% to 85.7wt% for vacuum distilled biocrudes derived from *Tetraselmis* sp. and *Spirulina* sp., respectively. Importantly, the 84wt% carbon content of blend and 87wt% distillate was found to be within range of most raw petroleum and upgraded HTL-biocrudes. For example Biller *et al*., (2015) reported 79% to 85% carbon content for upgraded biocrude oils. Speight, (1999) reported that the carbon content of different petroleum are in the range of 83wt% to 87wt%. Suggesting that blending of HTL-biocrude with petroleum would have no negative effects on the carbon content.

Furthermore, the hydrogen content of all distillates obtained from petroleum, biocrude and the blend numerically decreased with 0.5wt% to 1wt%. This is not surprising because loss of hydrogen atoms were expected, since hydrogen was not added during the process as practised in large scale. In fact consumption of hydrogen is an issue worth considering for hydroprocessing, even more for cohydroprocessing because hydrogen consumption is expected for complete removal of oxygen presence in the feedstocks (Chen *et al*., 2013). As a result the decrease in hydrogen content led to reduction/removal of oxygen content with eventual increased in higher heating values of distillate product, which will be discussed later. The nitrogen of the blend reduced from 1.2w/w% (for raw blend) to 0.2w/w% for distillate, biocrude reduced from 4.7w/w% (raw biocrude) to ~1.2w/w% for distillate, while it was 0.4wt% (raw petroleum) to ~ 0.14w/w% for distillate. Accounting for 63% to 75% reduction in nitrogen content for distillates when compared with respective raw feedstocks. Chen *et al*., (2013) reported 55% (at 360°C) hydrodenitrogenation (HDN) conversion during coprocessing of a blend of canola oil and heavy vacuum gas oil and 95% conversion at 395°C. Suggesting HDN conversion is temperature dependent. Moreover, the data obtained for the distillate nitrogen content was found to be within the range for petroleum (0.1w/w% to 2w/w%) (Speight, 1999). The nitrogen content of biocrude has been one of the important challenges in HTL-microalgae-

biocrude, and its reduction to comparable fuel standard has led to several investigations (Eboibi *et al*., 2015; Elliot *et al*., 2013). Based on the data reported in this present study particularly nitrogen content of biocrude and petroleum blend, suggests blending and coprocessing of biocrude and petroleum could be one of the available options to produce drop-in fuels from HTL-algae-biocrude. Nevertheless further investigation on the distillate fuel fractions for other properties is necessary, in order to ensure compatibility with conventional fossil derived fuels.

The sulfur content for blend had 58% reduction in both distillates derived from petroleum and blend, and 55% for biocrude distillates. The reduction in sulfur content could be attributed to loss of hydrogen atom producing hydrogen sulphide. Generally the sulfur content in all distillates was found to be within fuel specifications of marine and jet, and considerably below that of petroleum crude. As the average sulfur content in petroleum crude oils employed in United State refineries is above 1.4wt% (Jessen and Ramussen, 2014). Hence giving biocrude and/or blending of HTL-algae-biocrude an additional value compared to petroleum.

Furthermore, the oxygen content was found to have maximum reduction in distillates compared to other impurities such as nitrogen and oxygen. There were no significant differences in oxygen content reduction in petroleum and blend distillates. Deoxygenation occurs during decarboxylation and dehydration reactions, where oxygen is removed in the form of CO_2 and H_2S (Fogassy *et al*., 2010; Toor *et al*., 2011). Remarkably, biocrude distillates had 96.8w/w% oxygen content removal, similar to 83w/w% to 96.8w/w% in oxygen reductions in previous report (Eboibi *et al*.., 2014b). The distillates of petroleum and blend had similar oxygen content of 1.1w/w% and 1.2w/w%, respectively, and was 0.4w/w% for both distillates derived from their raw feedstocks. This reduction accounts for 55% and 66% for petroleum and blend distillates, respectively. Although, oxygen content reductions were below 100%, the remaining could be in heavier oxygenate compounds. Nevertheless, the data obtained is satisfactory considering relatively mild operating conditions in present study.

Beside heteroatoms content, the energy density also referred to as higher heating value (HHV) is one of the important data to determine the quality of biocrude. Of which this comparison is mostly made with conventional petroleum. Due to the high amount of oxygen removal in the biocrude, the HHV increased from 35.2MJ/kg to 40.3MJ/kg. The HHV of the blend numerically increased from 43.2MJ/kg (raw feed) to

44MJ/kg (distillate). Similar trend was observed for petroleum, increasing from 44MJ/kg (raw petroleum) to 45MJ/kg (distillate). One of the important outcomes of this present study is that there were no substantial differences in quality of the blend when compared with petroleum. Thus, this study has demonstrated that blending of HTL-algal-biocrude had no negative effects on the energy density. Suggesting coprocessing of biocrude with petroleum in existing refineries could be possible in near future. This would be of great economic promise, with significant reduction in carbon footprint compared to petroleum.

The atomic ratios is also an important factor normally considered to access the energy density and quality of fuel. The hydrogen to carbon ratios of distillates product were generally lower compared to that of feedstocks. The H/C ratios of the distillates were 1.7, 1.2 and 1.6 for petroleum, biocrude and blend, respectively. The decrease in H/C ratios reaffirms the loss of hydrogen and carbon molecules towards the removal of oxygenates during decarboxylation and deoxygenation reactions. Hydrogen-to-carbon ratio of the blend and petroleum were found to be similar (1.7 for petroleum and 1.6 for the blend). Previous research has reported hydrogen consumption and decrease in H/C atomic ratios during upgrading of biocrude (Biller *et al*., 2015; Li and Savage, 2013; Duan and Savage, 2011). They reported that the decrease could be due to the high operating temperatures. Nevertheless, hydrogen is normally supplied during industrial processing of crude oils, hence the issue of atomic loss would not be a challenge.

Carbon and energy recovery: It is important that majority of energy and carbon are recovered in primary product following distillation. The carbon and energy recovered in the distillate, residue and loss is presented in Fig. 4. As illustrated in Fig. 4, 86% of the initial carbon was recovered in distillate obtained from the blended stream, similar to 88% for petroleum. For biocrude 78% carbon was recovered in its distillate.

There were no much difference in carbon recovered in residues from petroleum (8%), biocrude (12%) and 10% for the blend. Higher amount of carbon was however recovered in loss fraction obtained from biocrude (10%) compared to 4% for petroleum as well as blend. Similarly, more than 83% of the feedstock energy were recovered in distillate fractions, as shown in Fig. 4. Although, the energy recovery was not closed, the other remaining amount could have been distributed to the residue and loss fractions.
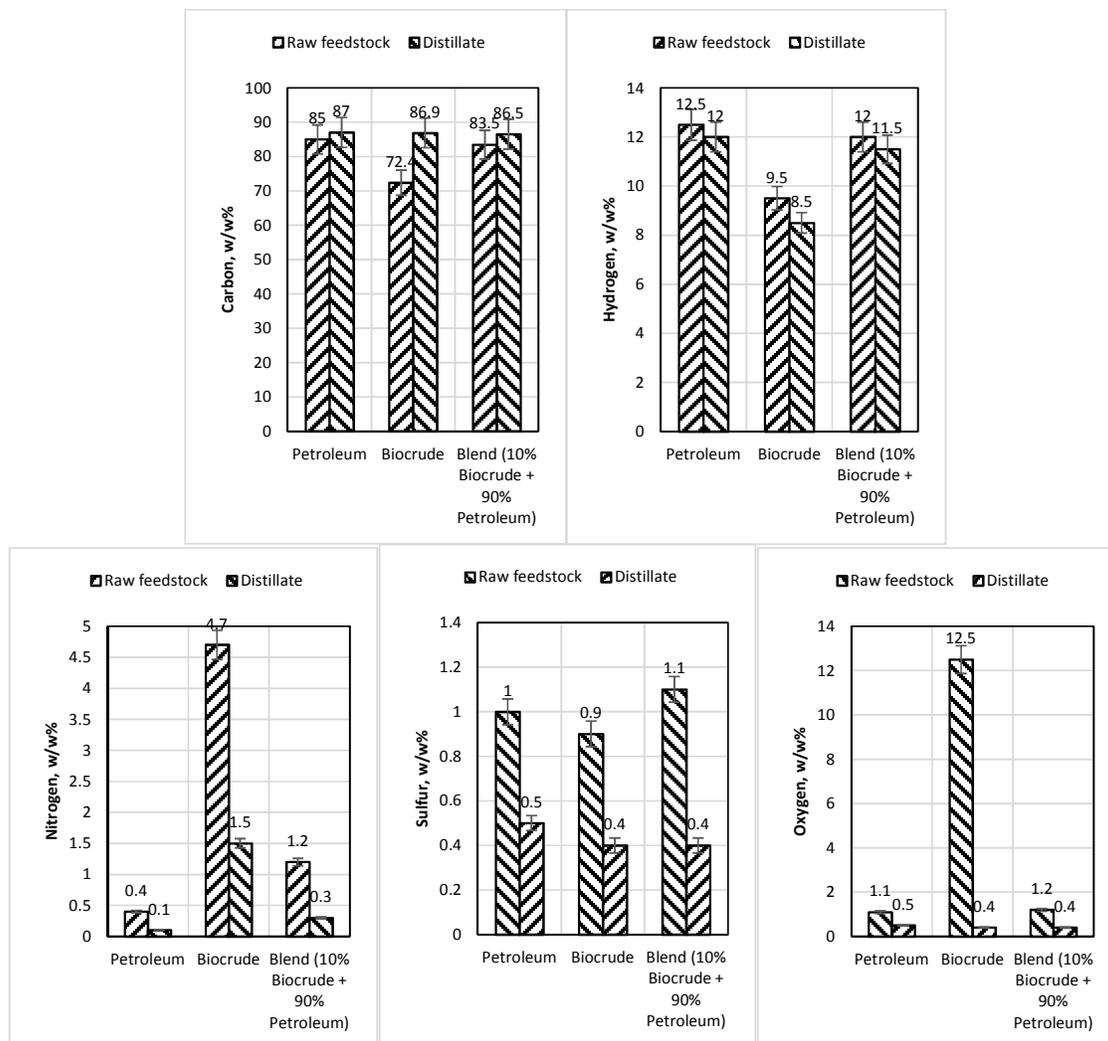
Fig. 3: Elemental composition of raw feedstock and fractional distillate of petroleum, biocrude and blend (of 10% biocrude and 90% petroleum)

Conclusively, having similar and larger energy and carbon recovery in distillates obtained for the blend and petroleum, further shows coprocessing of biocrude with petroleum would have insignificant effect on its quality of derived fuels.

Simulated distillation (SimDist) of raw feedstock and distillates: The SimDist data obtained for raw feeds and distillates of petroleum, biocrude and blend is presented in Fig 5. As shown in Fig. 5, there wide differences among the raw feedstock and distillates. The boiling point (bp) fractions of raw feedstocks; petroleum (30%), biocrude (54%), and blend (34%)) were mostly within the range of heavy vacuum gas oil (340-538°C) (Fig 5a). In contrast the percentage recovery at 340-538°C boiling points had an average 50% decreased for the distillates (Fig. 5b).

However, heavy naptha fractions increased with 38.5%, 71.4% and 42% for petroleum, biocrude and blend, respectively. This finding corroborate with earlier observation that petroleum comprises of lower bp compounds when compared with biocrude. Generally, distillates recovery were larger in low bp compounds (<340°C) corresponding to gas oil, kerosene and heavy naphtha fractions. About 68% of total petroleum, 62% blend and 44% biocrude feeds were recovered in heavy naphtha and kerosine fractions, maximum recovered was for kerosine fractions. Moreover, the residues fractions reduced from 14% to 5% for petroleum, 16% to 12% for biocrude and 14% to 7% for blended stream. Similar trends were observed for both petroleum and blended feed. Conclusively, this study has shown that there is no distinct fractional yields and quality between petroleum and blend.
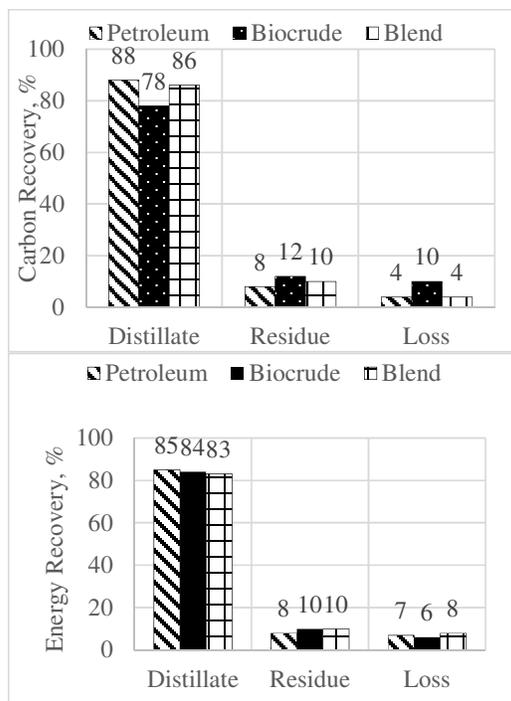
Fig. 4: Carbon and energy recovery after fractional distillation
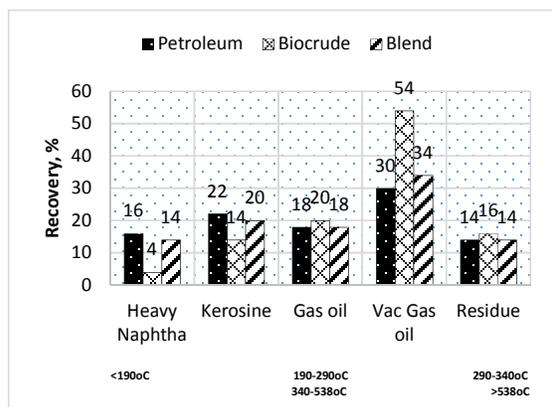

Fig. 5a: Simulated distillation of raw feedstock and distillates of petroleum, biocrude and blend (a) Raw feedstocks (b) distillates

Conclusion: This study has demonstrated the feasibility of blending and coprocessing HTL-algal biocrude with petroleum. Coprocessing of biocrude with petroleum feeds could therefore be an option to address issues on heteroatoms, limiting its usage to production of liquid transportations fuels. Fractional distillation of bicorude significantly improved the quality of biocrude. Nevertheless, in addition to optimal studies, more research investigations are needed, particularly on the distillate fractions to assure compatibility with petroleum derived fuels.
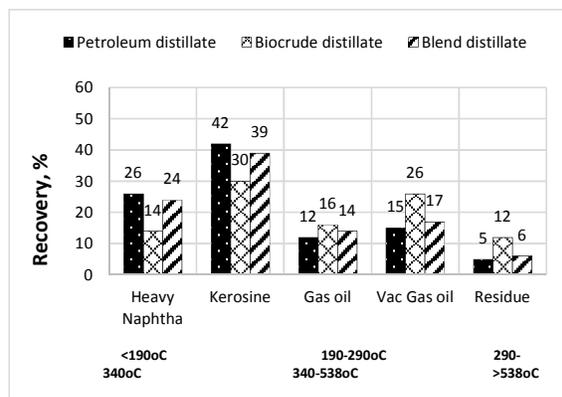

Fig. 5b: Simulated distillation of raw feedstock and distillates of petroleum, biocrude and blend (a) Raw feedstocks (b) distillates

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