EFFECTS OF REACTION TEMPERATURE AND TIME ON FRACTIONATION OF CARBON AND NITROGEN FROM HYDROTHERMAL LIQUEFACTION OF MICROALGA *SPIRULINA SP*

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ABSTRACT

The effects of reaction temperature and reaction time on fractionation of carbon and nitrogen in products derived from hydrothermal liquefaction (HTL) of microalga Spirulina sp. were investigated. Spirulina sp. alga biomass was processed using HTL into four products: biocrude, solid residue, aqueous and gas phases. HTL were performed at reaction temperature of 290, 310, 330, 350 and 370oC at reaction time of 5, 15, 30, 45 and 60 min using biomass of 16w/v% solids. The results showed that decomposition of carbon and nitrogen in the biocrude increased with an increase in reaction temperature and reaction time, in contrast to that for the solid residue. Approximately 51 to 72% elemental carbon were recovered in the biocrude, whereas it was 22 and 35% for nitrogen recovery. For the aqueous phase, the carbon recovery was between 13 and 18% carbon, and 36% nitrogen were recovered. The pH of the aqueous phase varies between 6.6 and 8.6. Less than 10% carbon and 12 to 23% nitrogen were recovered in the gas phase.

Keywords: *Carbon recovery; Hydrothermal liquefaction; Microalgae biomass; Nitrogen recovery; Renewable energy*

1. INTRODUCTION

Fossil fuels downstream and upstream processes and its applications have led to issues such as environmental pollution, global warming and greenhouse gas emission. Hence, the increase research investigations on technologies and renewable energy sources. Renewable energy production from biomass as a carbon source has high potentials for producing chemicals and liquid fuels (Brennan and Owende, 2010; Christi, 2007; Huber *et al*., 2006) to compliment fossil fuels. Hence biomass has been considered as a CO_2 neutral and a source for sustainable energy production (Alba *et al*., 2012). Unlike lignocellulosic plants, microalgae have higher biomass productivity, faster growth rate and does not affect food chain (Lam and Lee, 2006).

Lipid extraction combined with transesterification is the conventional process for liquid fuel biodiesel production from microalgae biomass. However this process utilizes only the lipids components (<30%) of the algae biomass (Meher *et al*., 2006; Vo *et al*., 2016), thus generating upto 70% of valuable organics as waste product. Moreover this conventional process involves drying biomass prior to lipid extraction, leading to significant increase in energy cost due to the dying step.

Hydrothermal liquefaction (HTL) is one of the thermochemical processes considered potentially for producing liquid transportation fuels from microalgae biomass. In addition to capability of HTL processing of whole algae components to liquid fuels, it can also convert wet and dried biomass feedstocks. HTL has been reported as an importantly conversion process, as it avoids use of energy for drying of feedstocks prior to processing. As required for other conversion processes such as pyrolysis and transesterification (Peterson *et al*., 2008; Elliot *et al*., 2015). Although pyrolysis involves shorter reaction times, the oil product (normally referred to as bio-oil) is usually high in moisture and oxygen content when compared with oils (known as biocrude) derived from HTL. HTL produces an energy dense product biocrude (Dote *et al*., 1994) that is upgradable to liquid transportation fuels with similar properties like that of conventional petroleum (Elliot *et al*., 2013).

Typically, HTL is operated at reaction temperature of 200oC-370oC, 8wt% to 20wt% solids loading, reaction time of 5min to 60min, with or without catalyst, and a reaction pressure (Alba *et al*., 2012; Eboibi *et al*., 2014a) which is a function of the temperature (5MPa to 25MPa). The products from HTL are biocrude, solid residue, aqueous and gas phases. The primary product biocrude is dark brown liquid with an energy value of 30MJ/kg to 40MJ/kg, but cannot be used directly as liquid transportation fuels except for firing of boilers (Eboibi *et al*., 2014b). For transportation fuels, the biocrude needs upgrading in order to remove impurities, improving its fuel properties comparable to conventional petroleum. The solid residue is dark ash and can be applied on farmland/fields as alternative fertilizer, though there are limited reports on such applications in the scientific literature. The aqueous phase

has been reported to be rich in nutrients (Bi *et al*., 2018; Edmundson *et al*., 2017) and its recycling for cultivation pond to culture microalgae has been successful (Biller *et al*., 2012). Moreover the gaseous phase mostly contains carbon dioxide (about 98%), and (2%) hydrocarbon such as methane, propane and ethane.

Several research investigations on the influence of various operating conditions ranging from different algae strains, batch and continuous systems, catalyst types, reaction temperatures on yields and quality of products have been performed on HTL of algae (Cheng *et al*., 2017; Eboibi *et al*., 2015; Wang *et al*., 2018). Despite the impressive outcomes of these previous research investigations, there are limited studies on elemental mass balances in products from liquefaction. The fate of elements particularly carbon and nitrogen is very important following HTL of algae (Eboibi *et al*., 2014b; Ross *et al*., 2011). Although there have few reports on carbon and nitrogen fractionation in biocrude, however there are limited data on the effect of reaction temperature and reaction time on distribution of these elements in HTL products. Knowledge of elemental distribution in products enhances understanding of the kinetics and reaction mechanism of HTL (Eboibi, 2018). Specifically it would help to predict the optimum operating conditions in terms of elemental distribution. Therefore the main of this report is to investigate the effects of reaction temperature and reaction time on the fractionation of carbon and nitrogen in derived HTL products.

2 MATERIALS AND METHOD

A freshwater microalga *Spirulina* sp. was used in the present study. The algae was cultivated in open raceway ponds owned and operated by the Biotechnology Division, Aban Infrastructure Pvt. Limited, Chennai, India. Algae biomass was harvested and dewatered using filter press. The harvested algae containing about 16wt% solids was stored at -8°C prior to HTL experiments. A laboratory grade dichloromethane (DCM) was used as solvent.

2.1 Hydrothermal liquefaction

HTL experiments were performed using custom built 1L batch reactor made of Inconel with an inbuilt magnetic stirrer. The reactor has a maximum operating temperature of 500°C and pressure of 350bar. The HTL were performed at reaction temperature of 290°C, 310°C, 330°C, 350°C, and 370°C each for reaction time of 5min, 15min, 30min, 45min and 60min with 350g of algae biomass. Details of heating and cooling reactor, including products separation and quantification have been reported previously (Eboibi *et al*.,

2014a). The HTL product and separation procedures are presented in Fig. 1. All HTL runs were repeated in triplicates and the average yield recorded.
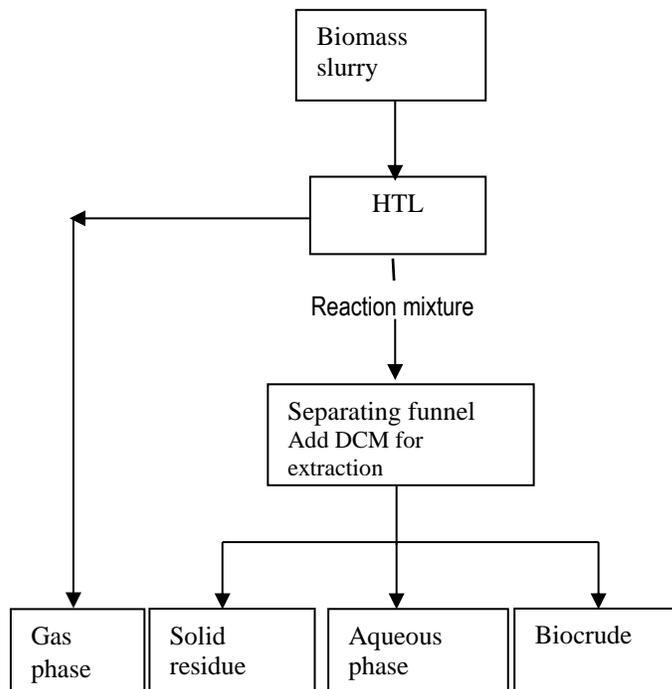
Figure 1: HTL of *Spirulina* sp. microalgae biomass production and separation procedures.

2.2 Analysis

The biochemical (carbohydrate, protein and lipids) and elemental composition of the harvested algae biomass were analysed prior to liquefaction. Carbohydrate, protein and lipids were estimated in accordance to methods explained previously (Eboibi *et al*., 2014). The elemental composition (carbon (C), hydrogen (H), sulfur (S) and nitrogen (N)) of the microalgae biomass, biocrude, solid residue and aqueous phase were determined in accordance to ASTM D-5291 method using an elemental analyser system (VarioEL III GmbH), while the oxygen (O) content was obtained by difference using Eq. (1).

$$Oxygen\ content\ (O) = 100 - (C + H + N + S)w/w\%$$
                                                    1

The higher heating values (HHV) were determined by substituting the CHNSO data into a unified correlation equation (Eq. (2)) proposed by Channiwala and Parikh, (2002).

$$HHV\left(\frac{MJ}{kg}\right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.151N$$
                                                    2

where C, H, N, S and O represent the mass of carbon, hydrogen, nitrogen, sulfur and oxygen, respectively, on a dry weight basis. The composition of the algae biomass used in present study is presented in Table 1.

Table 1: Biochemical and elemental composition of Spirulina sp[a].

Biochemical composition, afdw[b] wt%.	
Carbohydrate	11
Lipids	18
Protein	53
Elemental composition	
Carbon	44
Hydrogen	6.8
Nitrogen	9.0
Sulfur	0.5
Oxygen[c]	39.7
HHV (MJ/kg)	19.2

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

The products yields were calculated according the Eq. (3) (Eboibi *et al*., 2015).

$$Y_i = M_i / M_f \qquad\qquad 3$$

where Y_i represent *the yield* of *i*th fraction, *i* the biocrude, solid residue or aqueous phase, *f* is the initial feed and *M* the mass.

The carbon recovery (CR) in product fractions were estimated using Eq. (4), while Eq, (5) was used for nitrogen recovery (NR). The CR and NR in gaseous phase were calculated by difference of the combined mass of carbon, nitrogen.

$$CR = \frac{Carbon\ in\ product\ \left(\frac{w}{w}\%\right) \times Weight\ of\ product\ (kg)}{Carbon\ in\ feed\ \left(\frac{w}{w}\%\right) \times Weight\ of\ feed\ (kg)} \times 100\% \qquad 4$$

$$NR = \frac{Nitrogen\ in\ product\ \left(\frac{w}{w}\%\right) \times Weight\ of\ product\ (kg)}{Nitrogen\ in\ feed\ \left(\frac{w}{w}\%\right) \times Weight\ of\ feed\ (kg)} \times 100\% \qquad 5$$

3.0 RESULTS AND DISCUSSION

3.1. Effects of reaction temperature and reaction time on CR and NR in biocrude

The amounts of carbon and nitrogen recovered in biocrude after at different reaction temperature and reaction times are presented in Fig. 2. As shown in Fig. 2, carbon and nitrogen fractionated in biocrude were higher than that of the original algae feed. Based on the data presented in Table 1, 44% carbon and 9% nitrogen of raw algae feedstock were found to be generally lower compared to the amount of carbon and nitrogen recovered in biocrude (Fig. 2). This finding suggests that HTL substantially improves the properties of HTL products fractions such as carbon when compared to that of the algae feedstock. In most cases, carbon recovery in the biocrude increase with an increase in reaction temperature and time. For example, at 290oC, 5min, 51% carbon were recovered in the biocrude, and it increases to 64% with further increase in reaction time.

At 310oC, a minimum of 54% and maximum of 67% carbon were recovered in the biocrude. There were increase in carbon fractionation from 64% to 72%, from 5min to 30min at 330oC. However further increase in reaction time led to a gradual decrease from 72% to 66%. At 350oC there were no substantial differences in elemental carbon fractionation in biocrude at the various reaction times. Maximum of 72% carbon was achieved at 60min reaction time, and a minimum of 69% at 45min. At 370oC, carbon content in biocrude gradually decrease from 68% at 5min to 64% at 60min. This was expected as operating close to the critical point of water (374oC) enhances gasification reactions. Thus, it is expected that recovery of carbon in gaseous phase is higher than that in the biocrude phase.

This study has shown that operating HTL at 330oC, 30min could be the optimal operating temperature in terms of achieving maximum. Higher carbon content in biocrude is generally believed to enhance biocrude energy density. Moreover, similar observation occurred in CR in biocrude at 370oC, which reaffirmed operating close to critical point of water favours gaseous reactions. Hence the nitrogenous compounds could have been distributed to other product fractions.

Furthermore, there were general increase in NR in the biocrude with an increase in reaction temperature and residence time (shown in Fig. 2). At 290oC, 5min, about 22% NR was achieved and 30% at 60min. This suggests fractionation of nitrogenous compounds into biocrude during HTL could be relative to reaction temperature and time. Cheng *et al*., (2018) reported higher nitrogen recovery at higher reaction temperature and time. Zhu *et al*., (2017) reported 5% to 15% carbon in biocrude. The differences in carbon recovery is mostly attributed to initial protein content

of the raw feedstock. Moreover, it was found that recovery of nitrogen in the biocrudes collaborates with biocrude yield, as higher biocrude yield led to higher NR.

Similar trend in NR were reported by Alba *et al*., (2012); where about 16% was achieved at 200°C, which further increased to 36wt% (at 250°C), and to 42wt% (at 300°C). However, NR decreased from 42wt% to 39wt% at 375°C and from 39wt% to 22wt% at 450°C with further increase in HTL reaction temperature. Lower NR in biocrude fraction is preferred as nitrogen leads to NO$_x$ emission (Eboibi, 2018; Neveux *et al*., 2014). Nitrogen fractionation in biocrude is mostly due to the high content of protein in the algae (Hu *et al*., 2017). Decomposition of nitrogenous compounds in biocrude has been a challenge in HTL-alga-biocrude. This has led to several research investigations in feedstocks with lower nitrogen, and upgrading studies of resultant biocrude (Cheng *et al*., 2018). In the present study, nitrogen recovery in biocrude followed similar trends as found for carbon. In addition, NR in biocrude were higher at higher reaction temperature when compared to that at lower reaction temperatures.

Conclusively, 51% to 72% were recovered in the biocrude, whereas 22% to 35% for nitrogen recovery, which were within the range of previous research investigations (Alba *et al*., 2012; Biller and Ross, 2011; Eboibi *et al*., 2014a). These previous studies reported up to 83% carbon and 22% to 53% nitrogen in biocrude phase when operating between 300°C to 370°C and 5min to 60min.
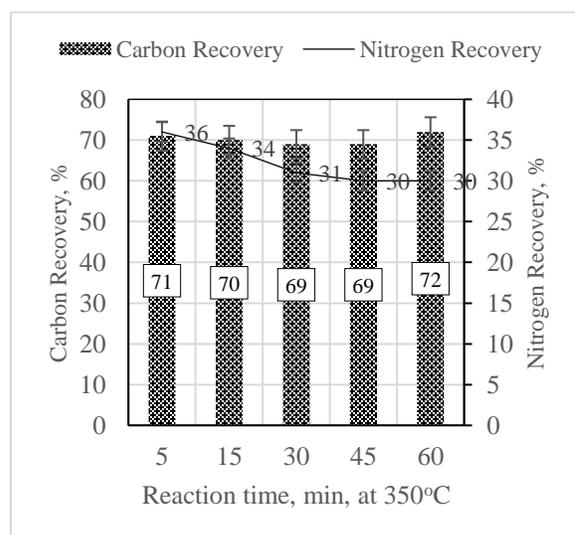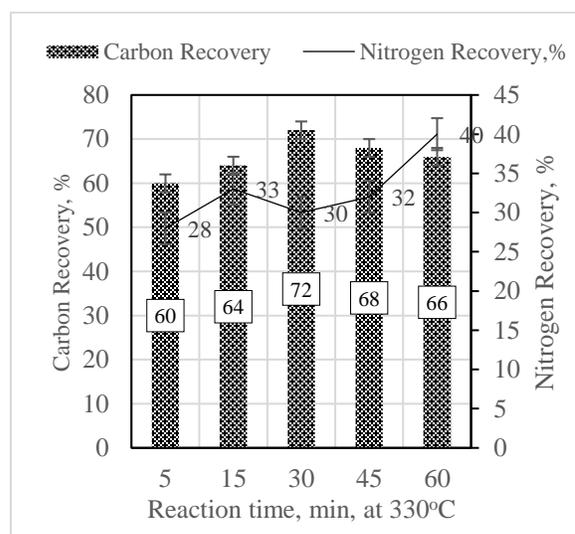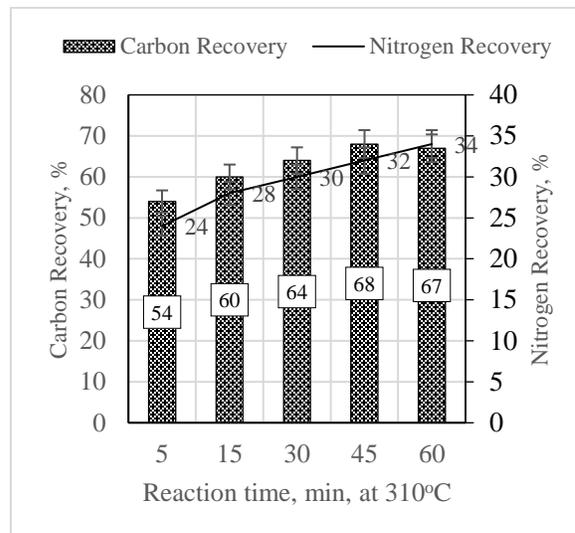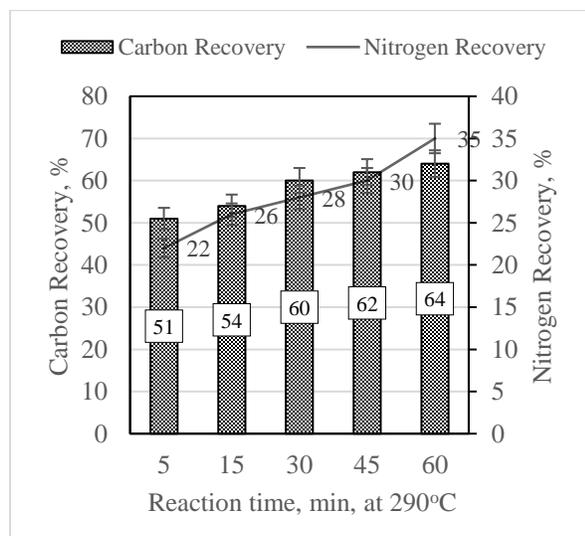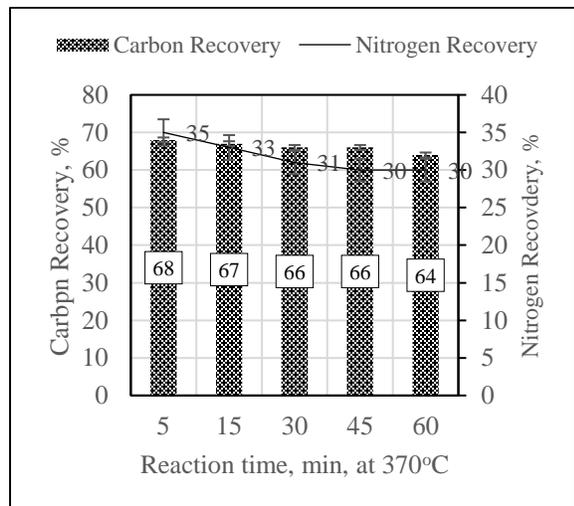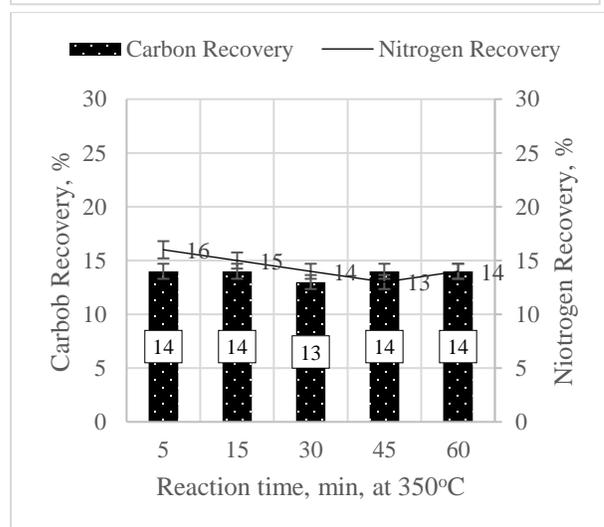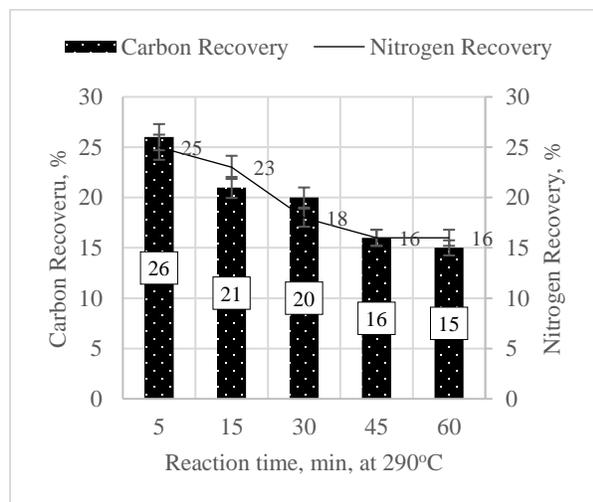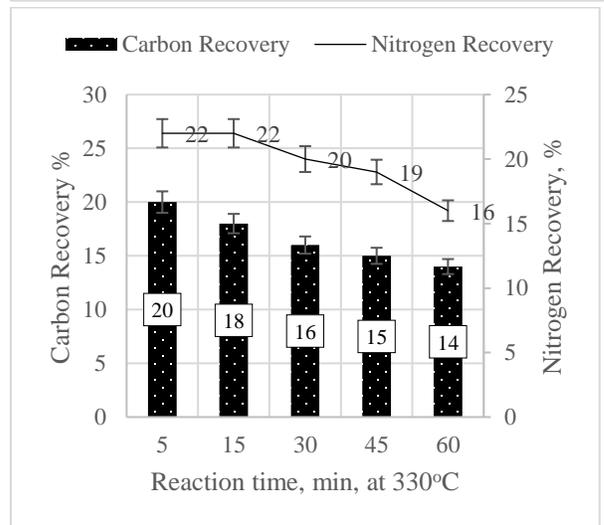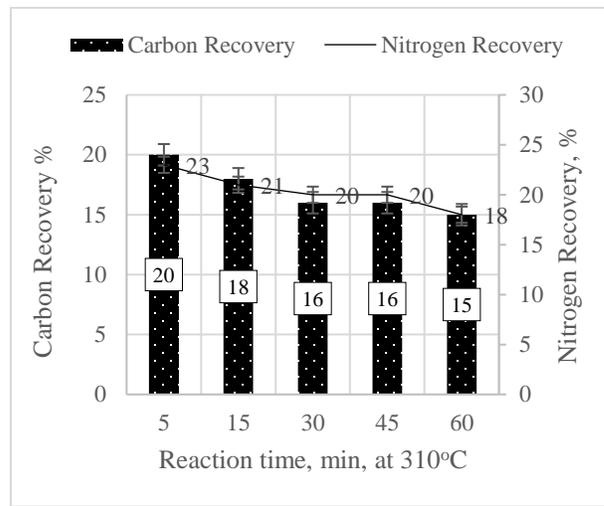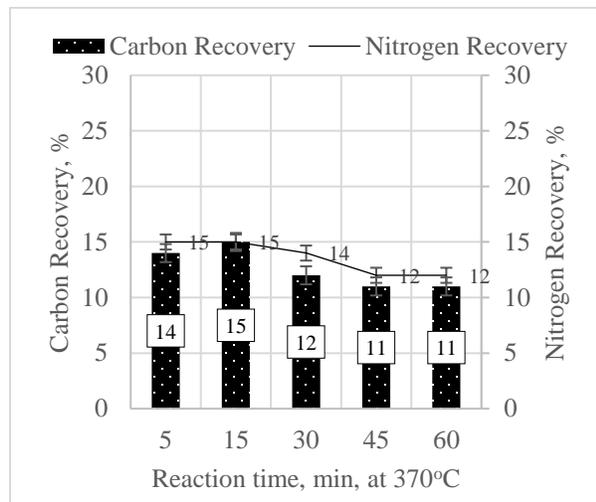
Figure 2: Carbon and nitrogen recovery in biocrude at different reaction temperature and reaction time.

3.2. Effects of reaction temperature and reaction time on CR and NR in solid residue

Carbon and nitrogen recoveries in the solid residue are shown in Fig 3. In contrast to increase in both CR and NR in biocrude with increase in reaction temperature and time (shown in Fig.2), CR and NR in solid residues decreases with increase in temperature and time.

Figure 3: Carbon and nitrogen recovery in solid residue at different reaction temperature and reaction time.

There were no much differences in CR and NR in solid residues at similar operating condition. At 290°C CR in solid residue decreases from 26% to 15%, while NR was from 25% to 16%. Similar trend was achieved for 310°C, 330°C, 350°C and 370°C. At 310°C, CR decrease from 20% to 15% and 23% to 18% for NR. It was found that CR and NR at 310°C were similar to that obtained at 330°C, where CR decreases from 20% to 14% and NR were 22% to 16%.

Further increase in reaction temperature from 330°C to 350°C has substantial influence on CR and NR, It was found that CR decreased from 20% at 330°C to 14% at 350°C at 5min. Operating at the same reaction condition (330°C, 5min), NR reduced from 22% to 16%. However there were no substantial variation in CR and NR with further increase in reaction temperature. This study has shown that 11% to 26% carbon and 12% to 25% nitrogen were fractionated in the solid residue. Suggesting that the residue could be applied on farmland as it contains valuable nutrient. Nitrogen is one of the elements found in fertilizers normally used for cultivation of plants.

3.3. Effects of reaction temperature on CR and NR in aqueous phase

The data obtained for effects reaction temperature on fractionation of carbon and nitrogen as well as pH in the aqueous phase are shown in Fig. 4. As illustrated in Fig 4, the CR were found to decrease from 18% to 13% when reaction temperature was increase from 290°C to 370°C at 5 min. Generally, CR in aqueous phase were lower when compared to CR distribution in biocrude fractions but close to that for solid residue at similar operating conditions. Although, a carbon source is necessary in cultivation pond, minimal is required for growth of algae. High carbon in culture medium favours synthesis of carbohydrate in algae, which is undesired in algae compounds. Hence the lower CR in aqueous phase reported in this study could favour cultivation of additional algae.

Furthermore, NR in the aqueous phase increased from 30% (at 290°C) to 36% at 330°C and gradually decreased to 33% at 370°C. This finding shows that reaction temperature had substantial effects on NR during liquefaction of algae. Decomposition of nitrogen were higher at high reaction temperatures when compared to lower temperatures. Interestingly, NR in the aqueous phase were higher when compared to CR. NR were generally higher than CR with 12% to 21%.
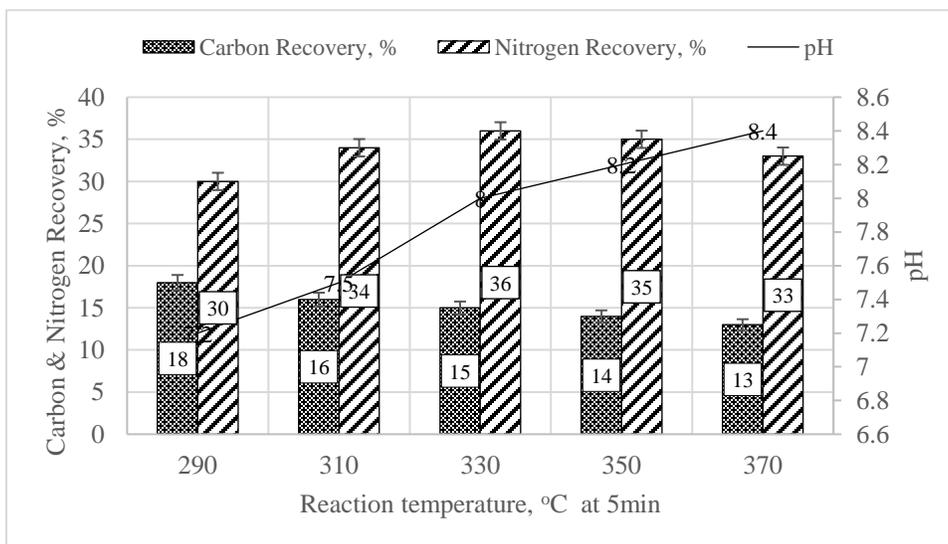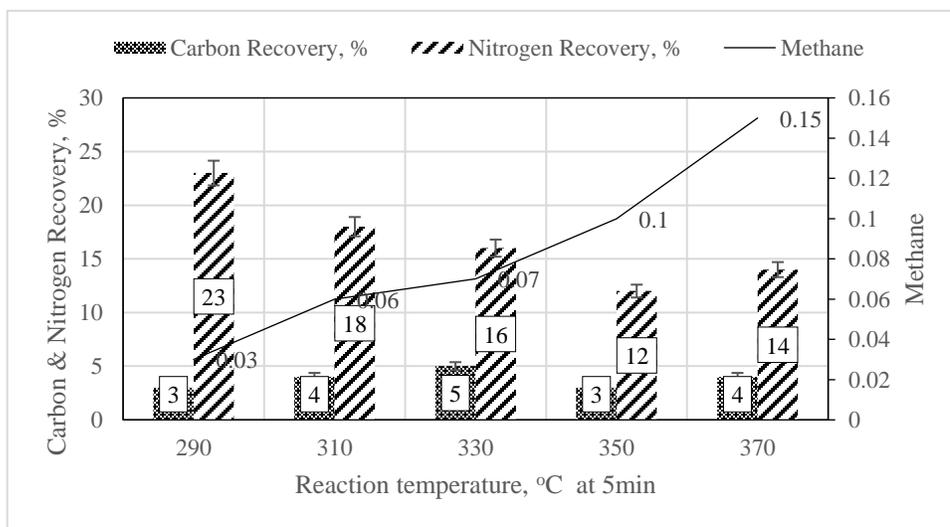
Figure 4: Carbon recovery, nitrogen recovery and pH at different reaction temperature at reaction time of 5min

NR in aqueous phase were marginally higher when compared to nitrogen recoveries in other product fractions. Maximum 36% nitrogen fractionated in the aqueous phase which is within range of 39.7% reported by Yu *et al*., (2011), but lower than 10% to 70% reported by Zhu *et al*., (2017). Recovery of nutrient such as nitrogen in aqueous phase, as mentioned previously favours algae cultivation, as nitrogen is one of the important nutrient for algae growth (Jose *et al*., 2017; Tran, 2016).

Also shown in Fig. 4, is the pH of the aqueous phase at different reaction temperature. The pH changes from being close to neutral pH to alkaline. The changed in pH from 6.6 to 8.6, suggests that reaction has occurred. Cheng *et al*., (2018) reported pH of 7.7 to 8.8 and concluded that high alkalinity could be mostly due to high protein content in initial algae. However, high alkalinity of the aqueous phase needs to be neutralize before being used for further applications such as in algae culturing. This finding is important as very few studies have reported on the pH level of wastewater (known as aqueous phase).

3.4. Effects of reaction temperature on CR and NR in gas phase

The amount of carbon and nitrogen including methane recovered in the gas phase are shown in Fig. 5. As presented in Fig. 5, CR and NR in the gas phase were between 3% and 5%, whereas 12% and 22% as achieved for nitrogen. NR were found to be dominant in the gas phase when compared to CR. The variations in CR and NR in this fraction is not clear, though they were obtained by differences. Methane production in gas phase varies between 0.02% and 0.16%. Based on the data presented in Fig. 5, the production of gaseous compounds increase with an increase in reaction temperature. This reaffirms that operating close to critical point of water favours gasification reactions, as mentioned previously. Yu e*t al*., (2011) reported the presence of other carbon sources such as CO, CO_2, and CH_4, where CO_2 was also found to be higher. It was reported that carbon recovery increased from 0.1% to 8.7% with an increased in reaction temperature. Moreover, Brown and Savage, (2011) and Yang *et al*., (2004) reported that the gas phase contains more of CO_2 at relatively lower reaction temperatures during HTL process.

Figure 5: Carbon recovery, nitrogen recovery and methane yield in gas phase at different reaction temperature at 5min

CONCLUSION

This study reported on the effects of reaction temperature and time on fractionation of carbon and nitrogen in products derived from hydrothermal liquefaction of microalga *Spirulina* sp. Carbon recovery and nitrogen recovery in biocrude increase with an increase in reaction temperature. In contrast, recoveries in carbon and nitrogen in solid residue were lower with an increase in reaction temperature. Reaction temperature had more substantial effect than reaction time on the elemental distributions. Importantly, recovery of carbon and nitrogen elements corroborates with the obtained fractional yields.

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