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PREDICTIVE MODEL FOR BIOCRUDE YIELD FROM HYDROTHERMAL LIQUEFACTION OF MICROALGAE

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Abstract
Despite several scientific research investigations on hydrothermal liquefaction of microalgae, there is limited study on predictive models. In this paper a model predicting biocrude yield for hydrothermal liquefaction of microalgae was developed, allowing interaction of carbohydrates, lipids and proteins. The results showed that the developed model could predict biocrude yield from experimental HTL of *Nannochloropsis* sp., *Spirulina* sp. and *Tetraselmis* sp., accounting for differences in biochemical composition. The model corroborates with HTL experimental data; that algae high in lipids and proteins leads to higher biocrude yield than microalgae high in carbohydrates.

Keywords: Biocrude; Energy; Hydrothermal liquefaction; Microalgae; Predictive model

1.0 Introduction

In the last decade renewable energy liquid fuel production from hydrothermal liquefaction (HTL) of microalgae has attracted extensive research investigations. HTL is a thermochemical process, conducted under subcritical hot compressed water at reaction temperature of 200^{o}C to 370^{o}C, 5MPa to 20MPa, 5min to 60min reaction time and with solids loading up to 20wt%. Importantly, eliminating the energy-intensive drying step (Elliott *et al*., 2013).
Despite numerous research investigations on factors affecting algal cell composition during culturing and reports on effects of operating conditions (Arun *et al*., 2017; Elliott *et al*., 2016); specific strain parameters (Cheng *et al*., 2018; Liang *et al*., 2017), solvents (Caporgno *et al*., 2016; Hu *et al*., 2018); catalysts (Wang *et al*. 2017; Wang *et al*., 2018), hydrothermal upgrading (Xu and Savage, 2018; Yang *et al*., 2017); and techno-economic and life-cycle assessment (Pedersen *et al*., 2018; Yoo *et al*., 2015) of HTL products relative to algal cell content, there are limited studies on models to predict biocrude yields from HTL.

One of the challenges on HTL predictive model is the complex nature of algae cell, having carbohydrate, lipids and protein as main biochemical compounds. The composition of these compounds varies even in same microalga specie. The variations in biochemical compounds and algal species has been reported to affect yield and quality of HTL product fractions, and energy return on investment (Barreiro *et al*., 2013; Shakya *et al*., 2017; Yoo *et al*., 2015).
Biller and Ross, (2011) and Terri *et al*., (2012) in separates report developed a model to predict biocrude yield from hydrothermal liquefaction of biomass feedstock based on composition of carbohydrate, lipids and protein. The developed models could predict biocrude yield, however non-algae model compounds were used as feedstocks, and the developed model unable to give accurate estimated yields of other algae species. Accordingly, Leow *et al*., (2015); Valdez *et al*., (2012, 2014) and Vo *et al*., (2016) developed quantitative kinetic models to assess the trends in decomposition of biochemical components during HTL of algae. These kinetic models were able to determine the kinetic rate constants for formation of HTL products from decomposition of carbohydrates, lipids and proteins. Still, non- microalga base model compounds and in some cases defatted algae (which should have changed actual cell structure) were used, which differ from natural microalgae. Consequently the models were unable to give accurate prediction of yields in biocrude of other species of microalgae. Nevertheless, these previous studies have shown concept of processing microalgae having combined components of carbohydrate, lipids and protein which could be a useful tool for modelling.

Therefore, the main objective of this present study is to develop a component additive model to predict biocrude yield and elucidate influence of variable biochemical contents on fractional yields.

2.0 Material and methods

2.1 Materials

Freeze-dried samples of *Nannocholoropsis* sp., *Spirulina* sp. algae biomass were provided by Aban Infrastructures Pty Ltd, Chennai, India while *Tetraselmis* sp. biomass was provided by Muradel Pvt Limited, Adelaide, South Australia. All algae biomass samples were stored in an airtight packages at room temperature before HTL experimental runs. Prior to experimental runs, the biomass biochemical composition (carbohydrate, lipids, and proteins) were determined. The carbohydrate content were estimated in accordance to the method of Green and Popa (2010), while the lipids and proteins contents by Folch *et al*., (1956) and Lowry *et al*., (1951) methods, respectively.

2.1.1 Hydrothermal liquefaction.

Details of HTL experiment and separation procedures have been described in previous reports (Eboibi *et al*., 2015; Eboibi *et al*., 2014a). Briefly, HTL of algae biomass were conducted in 1000mL custom built Inconel high-pressure, electrical jacket heated closed reactor vessel with an inbuilt magnetic stirrer. Based on literature data (for optimum biocrude yields), HTL experiments were conducted at 350^{o}C and 5mins reaction time using 350g of alga slurry with ~16wt% solids loading. The slurry were obtained from mixing 300mL deionised water with 60g alga biomass. All HTL experimental runs were in triplicate, and the average yield reported.

The yields in biocrude, solid residue, and aqueous phase were estimated according to Eq. (1)

$$Yield_i\,(wt\%) = \frac{Mass\ of\ Product\ after\ liquefaction}{Mass\ of\ alga\ loaded\ in\ reactor} \times 100\% \quad (1)$$

where *i* is biocrude, solid residue or aqueous phase. Yield in gas phase was estimated by difference, using calculated yields of combined remaining fractions

2.1.2Model derivation

The predictive model allows predicting biocrude yield of any microalgae strain. A reaction pathway for decomposition of algae compounds into product fractions is presented in Fig. 1. As shown in Fig. 1, the rate constants $k_{A,l}$, $k_{A,p}, k_{A,c}, k_{B,l}, k_{B,p}, k_{B,c}$were used to describe breakdown of microalgae biochemical compounds (carbohydrate, lipids and protein) during HTL

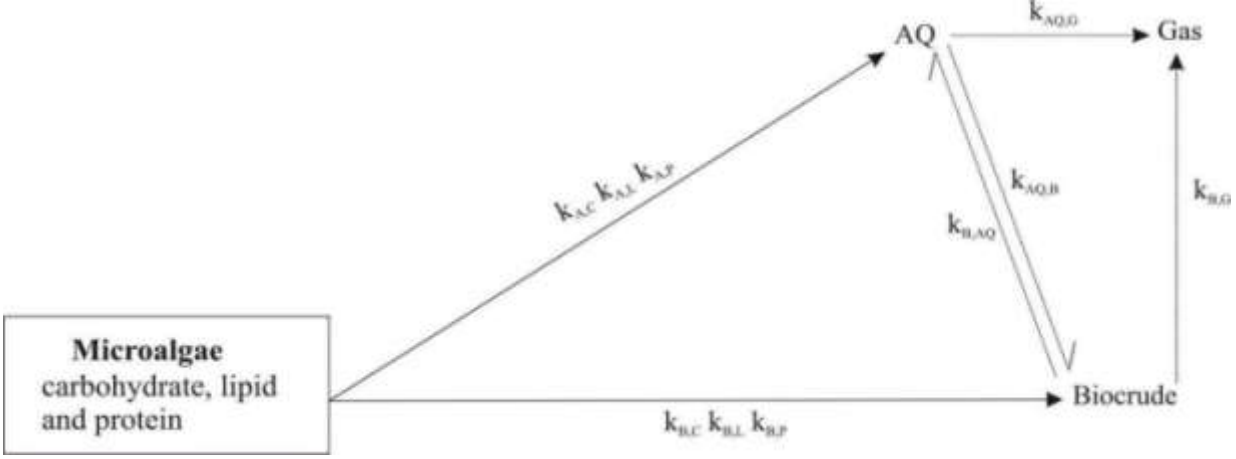

Fig. 1: Reaction pathways for hydrothermal liquefaction of microalgae (Adapted from Valdez *et al*., 2014).AQ: Aqueous phase. k_n: is rate constants. $_C$: carbohydrate. $_L$: lipid. $_P$: protein. $_B$: Biocrude. $_G$: Gas

A set of differential equations (Eq. (2) to Eq.(4)) were solved using direct integration method, assuming a first order derivative in order to get linear equation (Eq. 12, Eq. 18 and Eq. 25) where the rate constants (Valdez *et al*., 2014) optimized value at the given temperature can be substituted. Having treated each reaction pathway in Fig.1 as 1storder reaction lead to the basis for the reaction model.

$$Protien: \frac{dx_{1,p}}{dt} = -\left(k_{A,p} + k_{B,p}\right)x_{A,p} \quad (2)$$

$$Lipids: \frac{dx_{1,l}}{dt} = \left(k_{A,l} + k_{B,lp}\right)x_{A,l} \quad (3)$$

$$Carbohydrates: \frac{dx_{1,c}}{dt} = -\left(k_{A,c} + k_{B,c}\right)x_{A,c} \quad (4)$$

where p = proteins, l= lipids, c = carbohydrates, k_A and k_B= are rate constants (0 – 0.35min^{-1}), x_A= dry ash free solids (Valdez *et al*., 2014). Yield coefficients x, y *and* z are for lipids, proteins and carbohydrates, respectively, were obtained after solving the differential Eq. 2 to 4).Due to the interactions of algae compound during HTL (Toor *et al*., 2011; Torri *et al*., 2012) led to the development of Eq. (5) (Biller and Ross, 2011).

$$Biocrude\ yield\ (\%) = x * L + y * P + z * C \quad (5)$$

Using direct integration method to differentiate in respect to lipid (l:

$$x = \int \frac{dx_{1,l}}{dt} = \int (k_{A,l} + k_{B,l}) \int x_{A,l} \quad (6)$$

$$x = -\left(\frac{k_A^2}{2} l + \frac{k_B^2}{2} l\right) l(\frac{x_A^2}{2}) \quad (7)$$

$$x = -l\left(\frac{k_A^2}{2} + \frac{k_B^2}{2}\right) l(\frac{x_A^2}{2}) \quad (8)$$

Multiplying right hand side of Eq. 8 by 2 to eliminate the denominator gives:

$$x = -l(2)\left((2)\left(\frac{k_A^2}{2}\right) + (2)\left(\frac{k_B^2}{2}\right)\right) l * (2)(\frac{x_A^2}{2}) x = -l({k^2}_A + {k^2}_B) l({x^2}_A) \quad (9)$$

Eliminating (l) from the right hand side of Eq. 9

$$x = ({k^2}_A + {k^2}_B){x^2}_A \quad (10)$$

Assuming $x_A$is negligible and introducing factor 1 for pure mathematical convenience, Eq. (10) becomes

$$x = 1 - ({k^2}_A + {k^2}_B) \quad (11)$$

Substituting rate constants (optimized values for lipids: k_1= 0.33 and k_2 = 0.35; proteins: k_1 = 0.28 and k_2 = 0.32 and for carbohydrates: k_1 = 0.10 and k_2 = 0.26 (Valdez *et al*., 2014)) into Eq. (11).

$x = 1 - (0.33^2 - 0.35^2) = 0.77$. Therefore the yield coefficient of lipid (x) = 0.77.

Similarly for protein:

$$y = \int \frac{dx_{1,p}}{dt} = -\int (k_{A,p} + k_{B,p}) \int x_{A,p} \quad (12)$$

$$y = -\left(\frac{k_A^2}{2} p + \frac{k_B^2}{2} p\right) p(\frac{x_A^2}{2}) \quad (13)$$

$$y = -p\left(\frac{k_A^2}{2} + \frac{k_B^2}{2}\right) p(\frac{x_A^2}{2}) \quad (14)$$

Multiplying right hand side of Eq. (14) by 2 in order to remove the denominator gives:

$$y = -p(2)\left((2)\left(\frac{k_A^2}{2}\right) + (2)\left(\frac{k_B^2}{2}\right)\right) p * ((2)\left(\frac{x_A^2}{2}\right)) \quad (15)$$

$$y = -p({k^2}_A + {k^2}_B) p({x^2}_A) \quad (16)$$

Eliminating p from the right hand side and assuming x_A is negligible, Eq. (16) becomes

$$y = ({k^2}_A + {k^2}_B) \quad (17)$$

Substituting rate constant of protein:

$y = (0.28^2 + 0.32^2) = 0.18$. Therefore the yield coefficient of protein (y) = 0.18.

Similarly for carbohydrate:

$$z = \frac{dx_{A,c}}{dt} = -\left(k_{A,c} + k_{B,c}\right)x_{A,c} \quad (18)$$

$$z = \int \frac{dx_{1,c}}{dt} = -\int (k_{A,c} + k_{B,c}) \int x_{A,c} \quad (19)$$

$$z = -\left(\frac{k_A^2}{2} c + \frac{k_B^2}{2} c\right) c(\frac{x_A^2}{2}) \quad (20)$$

$$z = -c\left(\frac{k_A^2}{2} + \frac{k_B^2}{2}\right) c(\frac{x_A^2}{2}) \quad (21)$$

Multiplying right hand side of Eq. 21 by 2 in order to eliminate the denominator

$$z = -c(2)\left((2)\left(\frac{k_A^2}{2}\right) + (2)\left(\frac{k_B^2}{2}\right)\right) c * (2)(\frac{x_A^2}{2}) \quad (22)$$

$$z = -c({k^2}_A + {k^2}_B) c({x^2}_A) \quad (23)$$

Eliminating c, and x_A being negligible, Eq. (23) becomes

$$z = ({k^2}_A + {k^2}_B) \quad (24)$$

Substituting the rate constants of carbohydrates into Eq. (24) gives carbohydrate coefficient $(z) = (0.10 = 0.10^2 + 0.26^2 = 0.08$.
Finally substituting all generated values for yield coefficients $(x, y\ and\ z)$ into Eq. (5) gave the predictive model equation of the present study as

$$Predictive\ biocrude\ yield\ (wt.\%dw) = 0.77 * L + 0.18 * P + 0.08 * C \quad (25)$$

2.1.3 Model simulation

The model was simulated using Microsoft Office Excel 2007 by Monte Carlo's application. The model upon simulation was able to predict yields in biocrude of any microalgae strain and as well plot charts comparing experimental and predicted biocrude yields.

2.1.4 Model validation

The validation of the developed predictive model was achieved by comparing predicted yields based on experimental observations with reported data in HTL algae literature. Data on yields were obtained from 18 peer-reviewed published journal papers for freshwater and marine algae species.

3. Result and Discussions

3.1 Feedstock

In this reported study freshwater (*Spirulina* sp.) and marine species (*Tetraselmis* sp., *Nannochloropsis* sp.) were used. The biochemical composition of algae feedstock is presented in Table 1. As shown in Table 1, the algae biochemical composition were found to be within the range of previous reports (Xue and Savage, (2018), Wang *et al*., 2017). Protein contents were relatively closer (between 53wt% and 58wt %) unlike for lipids and carbohydrate contents. *Tetraselmis* sp. had higher carbohydrate content (22wt %) when compare to 14wt% and 11wt% for *Nannochloropsis* sp. and *Spirulina* sp., respectively. Nevertheless, the similar proteins and variation in lipids and carbohydrate biochemical content of these species may give reason to test whether freshwater and a marine alga behaves differently during liquefaction.

Table 1: Biochemical composition of *Nannochloropsis* sp., *Spirulina* sp., and *Tetraselmis* sp. microalgae

Microalgae species	**Biochemical Composition, wt.% daf[a]**			**Reference**
	Carbohydrate	**Lipids**	**Protein**	
Nannochloropsis sp.	20	28	59	Xue and Savage, 2018
Spirulina sp.	24	10	66	Wang *et al*., 2017
Nannochloropsis sp.	14	28	54	Present study
Spirulina sp[b].	11	18	53	Present study
Tetraselmis sp[b].	22	14	58	Present study

[a]: dry ash free. [b]: Eboibi *et al*., (2014b).

3.2. HTL yields

The fractional yields obtained from liquefaction of *Nannochloropsis* sp., *Spirulina* sp., and *Tetraselmis* sp. are presented in Fig. 2. As shown in Fig. 2, there were substantial variations in yields. Generally, biocrude yields derived from marine algae *Nannochloropsis* sp. (56wt%) and *Tetraselmis* sp.(52wt%) were higher than 42wt% for freshwater algae *Spirulina* sp. Biocrude yields obtained from the respective algae were higher than their respective lipids content (Table 1). Suggesting that it is not only the lipids that produce biocrude but as a result of interactions of the biomolecules. This is in agreement with previous reports (Biller and Ross, 2011); Changi *et al*., (2012); Shakya *et al*., 2017; and Torri *et al*., (2012) investigating effects of algae compounds on biocrude yields, that interaction of carbohydrates and proteins led to formation of products classified as biocrude, arising from the production of alsphatenes, diketopiperazine, melanoidins, and water soluble compounds. In the present study, the higher carbohydrate content in *Tetraselmis* sp. could be a factor that led to lower formation of biocrude, in favour of solid residues production.

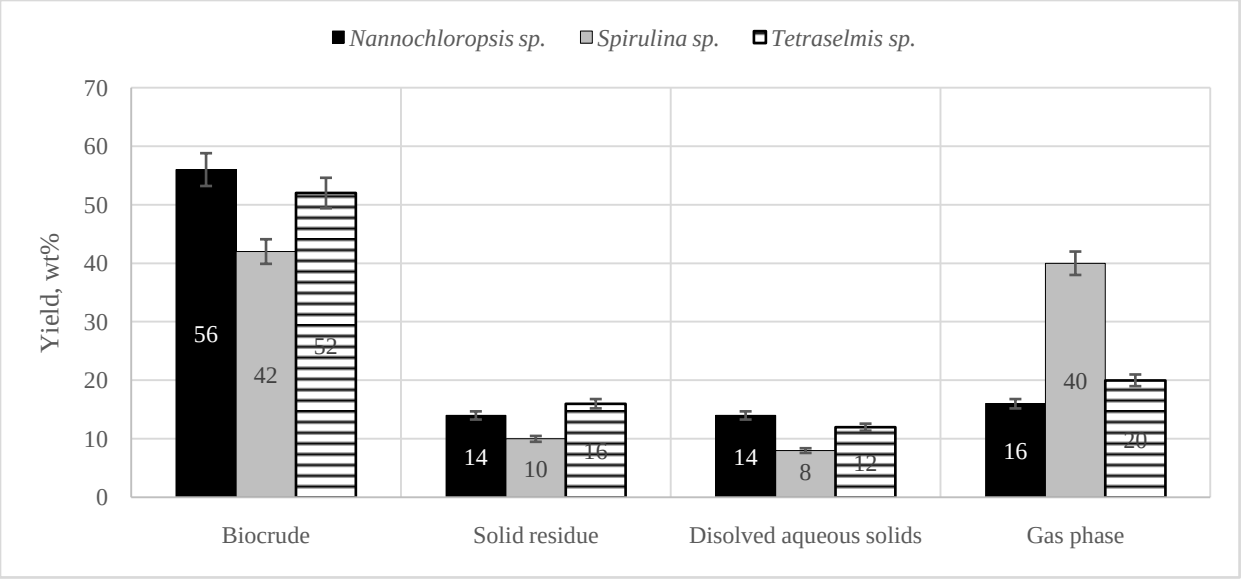

Fig.2: Fractional yields of products from HTL of *Nannochloropsis* sp., *Spirulina* sp., and *Tetraselmis* sp. microalgae

Due to higher carbohydrates, *Tetraselmis* sp. numerically has higher solid residue of 16wt% when compared to 14wt% *Nannochloropsis* sp. and 10wt% for *Spirulina* sp. The higher solid residues for marine algae could be mostly due to their higher salt content when compared to freshwater algae. As marine alga has been reported to be high in salt content (Biller and Ross, 2011). Similarly, marine algae has higher dissolved solids residue:14wt% for *Nannochlroposis* sp. and 12wt% for *Tetraselmis* sp. compared to 8wt% for *Spirulina* sp. *Spirulina* sp. has higher yields in gas phase (40wt%)when compared to 16wt% and 20wt% for *Nannochloropsis* sp. and *Tetraselmis* sp. In conclusion, microalgae containing large amount of non-protein and non-lipid components could be considered as poor feedstock for HTL.

3.3. Predictive model for biocrude yield and comparison with experimental yields

The coefficients of the developed model were found to be within the range of previous models, (shown in Table 2) (Biller and Ross, (2011), Torri *et al*. (2012) and Leow *et al*., (2015)).

Table 2: Comparison of developed model with previous additive models

Predictive model for biocrude yield	References
$Biocrude\ yield = 0.80L + 0.18P + 0.06C$	Biller and Ross, (2011)
$Biocrude\ yield = 0.95L + 0.33P + 0.06C$	Teri *et al*., (2012)
$Biocrude\ yield = 0.97L + 0.42P + 0.17C$	Leow *et al*., (2015)
$Biocrude\ yield = 0.77L + 0.18P + 0.08C$	Present study

L: lipids. P: protein. C: carbohydrate.

These previous models were calibrated using data derived from liquefaction of either model compounds and/or defatted algae feedstocks. It is envisaged that such feedstocks would not give true scenario of predicted models on algae of different biochemical compounds. In this study, the feedstocks used were untreated prior to liquefaction, hence their cell components were intact. In addition the data used for the model is believed to provide a clearer understating of predicted yields arising from the variation of algae biochemical contents.

The model correlation based on data from HTL experiment of each microalgae at 350^{o}C, 5min is shown in Fig. 3. As illustrated in Fig. 3, the generalized predictive model was able to describe biocrude yields from HTL of *Nannochloropsis* sp., *Spirulina* sp. and *Tetraselmis* sp. As there were no much differences between experimental and predictive yields. Experimental yields for *Nannochloroposis* sp. was 56wt%, 52wt% for *Tetraselmis* sp. and 42wt% for *Spirulina* sp. when compared to predictive yields of 54wt%, 46wt% and 40wt%, respectively. Therefore it could

be inferred that the developed model applied herein seems capable to capture variations in HTL behaviour of algae with differences in their biochemical contents.

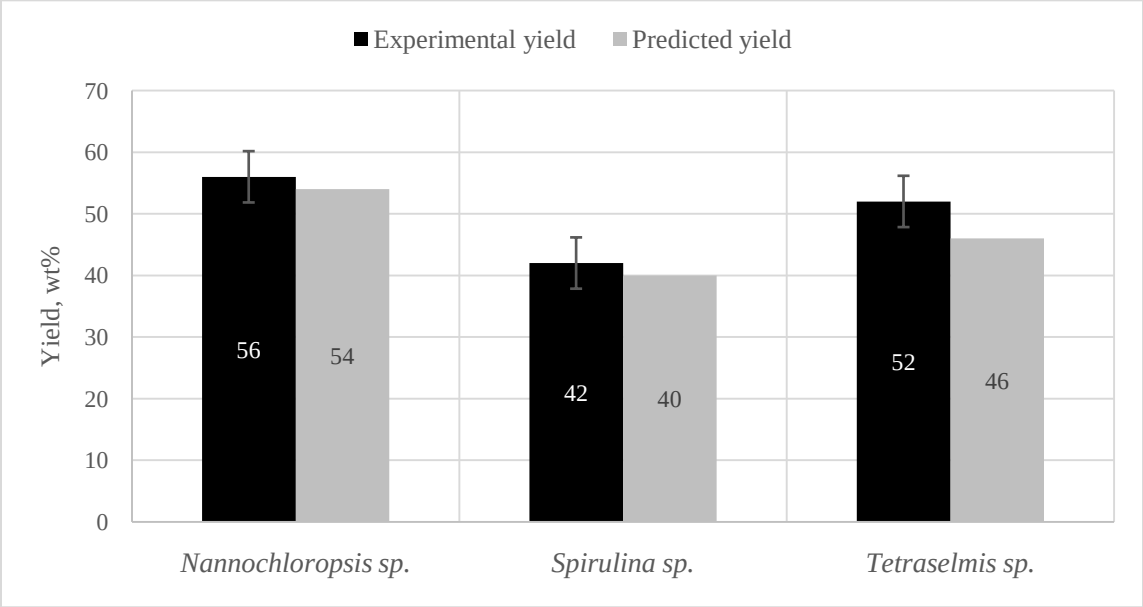

Figure 3: Comparison of HTL experimental yields and model predicted yields.

Furthermore, the model developed in this study was applied to literature data on HTL yield from both freshwater and marine alga species, shown in Fig. 4 to Fig. 10. The predictive yield and experimental yield for *Chlorella* sp. is presented in in Fig. 4. The predicted yield were very close to the experimental data in previous reports, except for Ross *et al*., (2010) that reported 13.6wt% compared to 30wt% predictive yield.

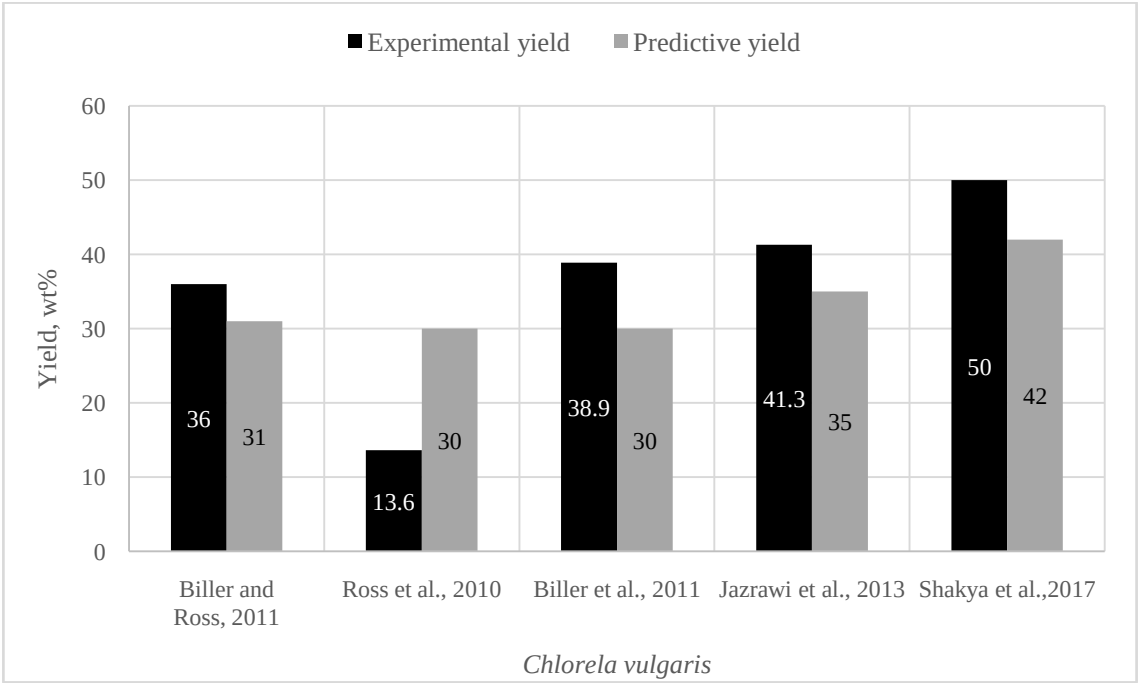

Fig. 4: Comparison of experimental and predictive yield for *Chlorella* sp.

The predictive and experiemnatl yield for *Dunaiella tertiolecta* is presentd in Fig. 5. The predictive yield were in the range of 29wt% to 55.3wt% compared to experimental yield of 425.8wt% to 55.3wt%. Due to differences in the biochemical componets and HTL experiemnatl conditions led to variation in the respective yields. Even algae of same species have differencesin biochemical contents (shown in Table 2) arising from culturing and envrionemntral factors, which of course influences experimental (Fig. 2) and consequently predictive yields.

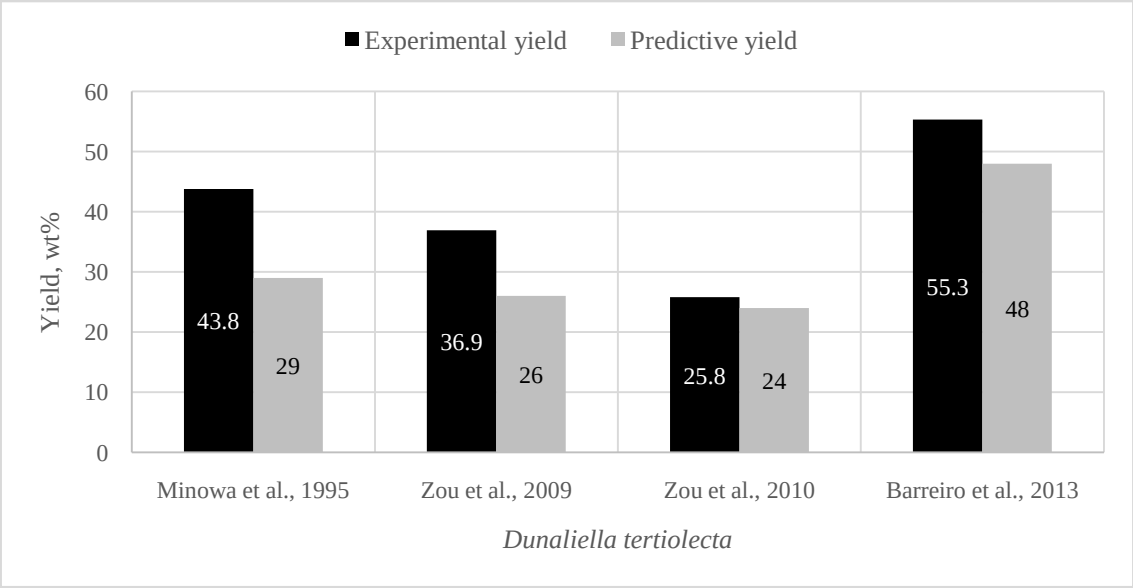

Fig. 5: Comparison of experimental and predictive yield for*Dunaiella tertiolecta.*

Nannochloropsis sp. predictive and experimental yield is presented in Fig. 6. As shown in Fig. 6, the model was able to capture differences in biocheical content of the algae (shown in Table 2) with respect to biocrude yields. For example Brown et al., (2010) and Duan and Savage, (2011) reported 43wt% and 57wt% biocrude yields, respectively, however 41wt% was predicted. Cheng et al., (2017) reported experiemental biocrude yield of 59wt%, but 35wt% was predicted, substantially lower than 41wt%. The differences in predicted yields, though from same specie is due to variation in biochemical contnet (Table 2). Brown et al., (2010) and Duan and Savage, (2011) used Nannochloropsis alga containing 12wt% carbohydrates, 28wt% lipids and 52wt% protein contents, but Cheng et al., (2017) used alga of higher carbohydrates (22.9wt%), 19.7wt% lipids and low protein (13.5wt%). This finding confirms that algae with high carbohydrates and low-lipids and low-proteins may be considered as poor feedstock HTL.

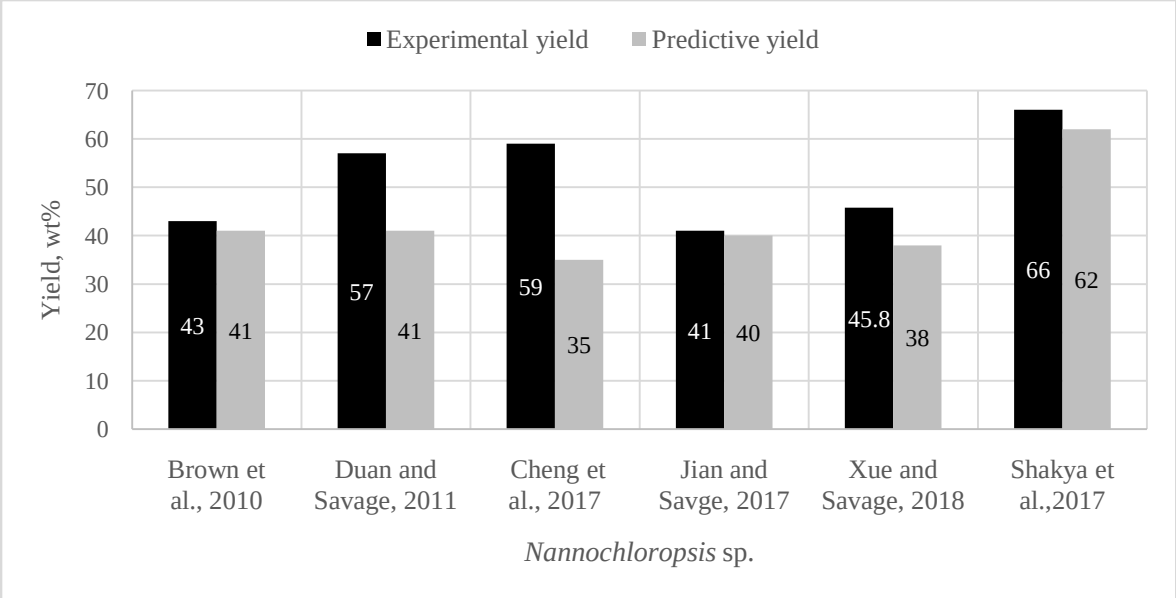

Fig. 6: Comparison of experimental and predictive yield for *Nannochloropsis*sp.

Furthermore, the experimental and predictive yields for *Scenedesmus* sp. is illustrated in Fig. 7. Based on data presented in Fig. 7, similar trends were observed for *Nannochloropsis* sp. with respect to carbohydrates, lipids and protein contents, as explained previously.

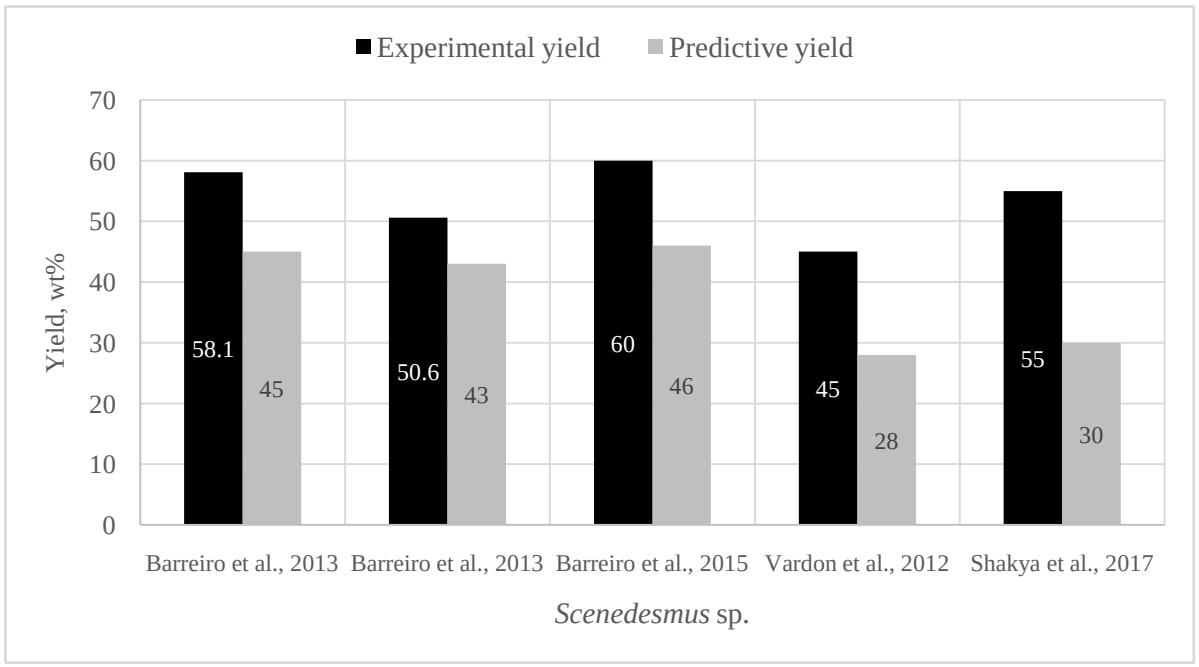

Fig. 7: Comparison of experimental and predictive yield for *Scenedesmus* sp.

The experiemntal yields were in the range of 45wt% to 60wt% while it was 28wt% to 45wt%. Besides differences in biochemical composition and reaction temperature, other factors that influences biocrude yield during HTL is catalyst, which is not capture in the model. Catalyst has been reported to reduce HTL activation energy, consequently improving biocrude yields up to 10wt%, depending on catalyst type (Eboibi *et al*., 2014b; Jena *et al*., 2012). Nevertheless, this study has demonstrated that the predictive model could quantitatively assess effects of

differences in biochemical content on biocrude yields. However further research is necessary on improving the model, incoporating variation in reaction time and reaction temperature, catalyst, and solids loading.

Literature data on freshwater *Spirulina* sp biochemical compounds has high carbohydrates, moderate lipids and protein contents (see Table 3). As expected moderate yields in biocrude were obtained from liquefaction of *Spirulina* sp., consequently low yields were predicted using a generalized model (shown in Fig. 8). Due to its high carbohydrates, *Spirulina* sp has an average predictive biocrude yield of 31.5wt%, the lowest amongst both freshwater and marine algae. Others in descending order were 38.4wt% for *Scenedesmus* sp., 33.6wt% (*Chlorella* sp.), 33.5wt% (*Phaeodactylum triornutum),* 33wt% (*Porphyridium cruentum*), and 31.8wt% for *Dunaliella tertiolecta*. The average yields for freshwater algae were found lower than that of the marine algas species which were in the range of 42.8wt% to 44wt%. This finding suggests that marine algae species maybe more suitable feedstocks for HTL-biofuel production, in addition to saving freshwater for cultivation.

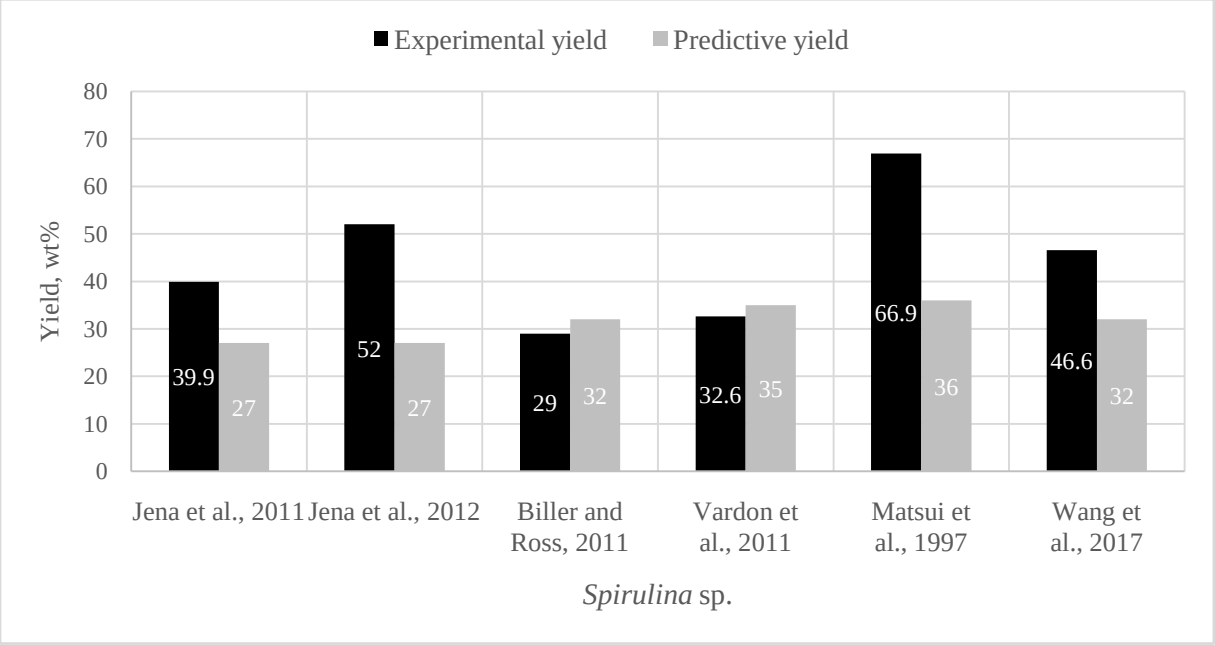

Fig. 8: Comparison of experimental and predictive yield for *Spirulina* sp.

The experimental and predicted yields for *Tetraselmis* sp. is presented in Fig. 9. As shown in Fig. 9. the predicted value for *Tetraselmis* sp was 46wt% and 42wt% (Eboibi *et al*., (2014a)) and Barrerio *et al*., (2013), respectively. This suggests that the model does a good job by predicting yield based on the biochemical data used. In addition 46wt% predicted yield for *Tetraselmis* sp was second highest to 55wt% of *Nannochloropsis* sp. *Crypt*. sp. and *Galdierasu* has predicted value of 38wt% and 28wt% as against observed yield of 68.9wt% and 31wt%, respectively (not shown). It is important to state that aside differences in operating conditions in previous reports, the experimental yields were obtained using different separation protocols in present study, though similar. It could have been possible certain errors were encountered. As there is yet to be developed standard separation procedures for HTL of algae.

Table 3: Properties of microalgae species and HTL experimental condition

Microalgae	Biochemical composition			HTL experimental condition			References
	Carbohydrate	Lipids	Protein	T °C	Time, min	Catalyst	
Chlorella vulgaris	25	9	55	350	30	Pt/Al	Biller *et al*.,2011
Chlorella vulgaris	25	4	60	350	3	-	Jazrawi *et a*l., 2013
Chlorella vulgaris	49.7	30.3	14.6	320	30	-	Shakya *et al*., 2017
Dunaliella tertiolecta	14.7	20.5	61.3	300	5	Na_2CO_3	Minowa *et al*., 1995
Dunaliella tertiolecta	21.7	2.9	61.3	360	50	H_2SO_4	Zou *et al*., 2009
Dunaliella tertiolecta	20.2	22.2	32.3	360	50	-	Zou *et al*., 2010
Dunaliella tertiolecta	20.2*	23.4	50.8	375	5	-	Barreiro *et al*., 2013
Nannochloropsis sp.	12	28	52	350	60	-	Brown *et al*., 2010
Nannochloropsis sp	12	28	52	350	60	Pt/C	Duan and Savage, 2011
Nannochloropsis sp.	22.9	19.7	13.5	310	60	-	Cheng *et al*., 2017
Nannochloropsis sp.	12*	28*	52*	400	60	-	Jian and Savage, 2017
Nannochloropsis sp.	20	59	28	400	60	Pt/C	Xue and Savage, 2018
Nannochloropsis sp	12.4	55.4	12.9	320	30	-	Shakya *et al*.,2017
Spirulina sp.	31	11	49	350	60	Na_2CO_3	Jena *et al*., 2012
Spirulina sp.	20	5	65	350	60	Na_2CO_3	Biller and Ross, 2011
Spirulina sp.	21	5	64	350	60	-	Vardon *et al*., 2011
Spirulina sp.	5	12	57	350		$Fe(CO)_5$-S	Matsui *et al*., 1997
Spirulina sp.	23.7	10.3	66	230	30	Montmorillonite	Wang *et al*., 2017
Tetraselmis sp.	22	14	58	350	5	-	Eboibi *et al*., (2014a)
Tetraselmis sp.	22*	19.5	43.6	375	5	-	Barreiro *et al*., 2013
Porphyridium cruentum	40	8	43	350	60	Na_2CO_3, HCOOH	Biller and Ross, 2011
Phaeodactylum tr.	30*	21.9	37.5	375	5	-	Barreiro *et al*., 2013
Phaeodactylum tr.	30*	20	38*	350	15	-	Christensen *et al*., 2014
Galdieria su.	14.5	5.5	45.3	375	5	-	Cheng *et al*., 2017
Scenedesmus almeriensis	25*	21.8	51.7	375	5	-	Barreiro *et al*., 2013
Scenedesmus almeriensis	25*	13.1	30	350	15	-	Barreiro *et al*., 2015
Scenedesmus almeriensis	25	13	56	300	30	-	Vardon *et al*., 2012
Scenedesmus almeriensis	54.7	17.8	30.1	320	30	-	Shakya *et al*., 2017

*: assumed based on available literature data.

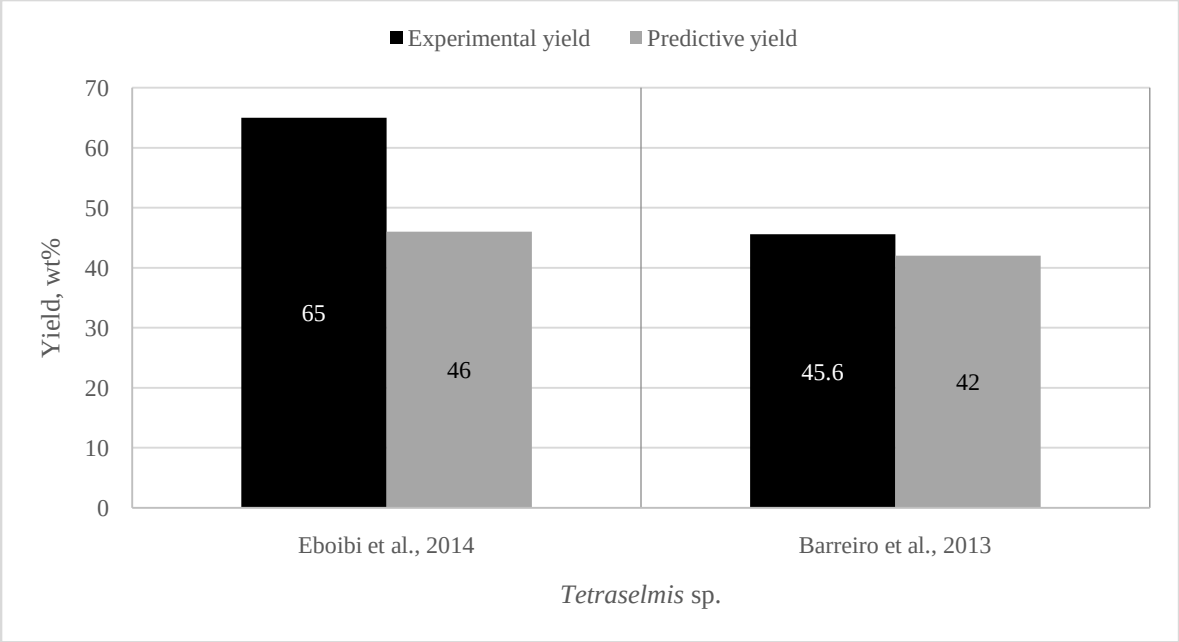

Fig. 9: Comparison of experimental and predictive yield for *Tetraselmis* sp.

Finally, the predicted yields and experimental observation for *Porphyridium cruentum* and *Phaeodactylum tricornutum* are presnted in Fig. 10. Based on the data presented in Fig. 10, *Porphyridium cruentum* and *Phaeodactylum tricornutum* has an average predicted yield of 33wt% and 33.5wt%, respectively. Again Biller and Ross, (2011) reported an experimental yield of 20wt% for *Porphyridium cruentum* but lower than 28wt% predicted. So irrespetive of separation procedure used to obtain biocrude yields, the model developed in this present study is capable to predict yields relative to the algae biochemical composition.

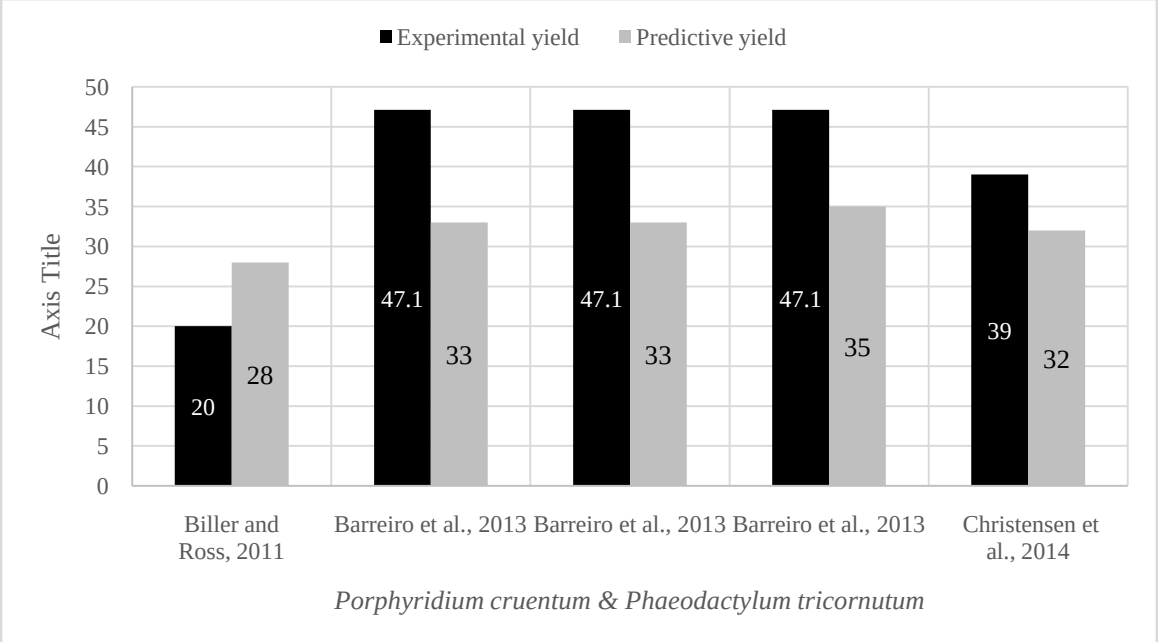

Fig. 10: Comparison of experimental and predictive yield for *Porphyridium cruentum and Phaeodactylum triornutum.*

4.0. Conclusion

This study has shown the effects of algae biochemical composition on product fractions from HTL. The developed addictive predictive model could correlate influence of carbohydrates, lipids and proteins on yields of biocrude from hydrothermal liquefaction of microalgae. Based on HTL product fractions and model data, lipids- and proteins-rich algae could produce higher biocrude yields than algae richer in carbohydrates.

5.0 Recommendation

Additional study is needed to understand the effects of other parameters such as reaction temperature, reaction time and algal solid loading on biocrude yield. In addition to biochemical composition, a comprehensive study on coupled effects of mentioned reaction parameters to determine biocrude quality and quantity would be an interesting future work.

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