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Influence of potassium carbonate (K_2CO_3) as catalyst on biocrude oil yield and properties via hydrothermal liquefaction of *Spirulina platensis*

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Abstract

This study is relevant to developing biomass, specifically microalgae, as a source for biofuel production through hydrothermal liquefaction (HTL). Hydrothermal liquefaction (HTL) is a thermochemical conversion that requires no drying of the feedstock because the whole microalgae biomass is decomposed and converted in hot compressed water. A biocrude oil is obtained as the main product, along with gaseous, aqueous and solid by-products. It was observed in different studies that catalysts, particularly alkali catalysts, improve liquefaction efficiency. This study investigated the effects of potassium carbonate (K_2CO_3) on the yield and properties of biocrude oil. Different amounts of catalysts used were 5, 7.5, and 10 wt. %, respectively. Biocrude oil was produced from hydrothermal liquefaction of *Arthrospira platensis* (formerly referred to as *Spirulina platensis*) in a micro-reactor at 280 and 350 degrees Celsius for two levels of residence time, 15 and 45 minutes. The biocrude produced under these different conditions were analyzed for C, H, O, and N content. Biocrude oil yield and its calorific value were also determined. The highest biocrude oil yield with catalyst (32.18 wt. %) was obtained at 280 °C with 15 minutes residence time and 5 wt. % K_2CO_3. Highest HHV of 39.17 MJ/kg was obtained with the addition of 10 wt. % K_2CO_3 at 280 °C and 45 minutes residence time. Biocrude oil obtained from the experiment runs had almost similar H/C, and O/C values to that of biodiesel and plant oil and was better than biomass pyrolysis oil. The N/C ratios of the biocrude oil ranged between 0.03 to 0.09.

Keywords: Hydrothermal liquefaction, potassium carbonate, Spirulina, biocrude oil

1. Introduction

There is an increase in worldwide interest on renewable energy sources such as biofuels. The major drivers for bioenergy development are the important issues on shortage of fossil fuels, increasing crude oil price, energy security, and rapid global warming.

One of the possible means of climate change mitigation is the development of sustainable biofuels. By converting CO_2, H_2O and sunlight to biomass, microalgae effectively capture carbon from the atmosphere. Therefore, upon combustion there is no additional carbon added to the atmosphere [1]. Hydrothermal liquefaction (HTL) is an approach that requires no drying of the feedstock because the whole microalgae biomass is decomposed and converted in hot compressed water. A biocrude oil is obtained as the main product, along with gaseous, aqueous and solid by-products. Upon combustion, this biocrude oil has low sulfur emissions and its low ash content results in reduced emissions of particulates, although it may lead to high NOx emissions, due to the high amounts of nitrogen in chlorophyll and proteins, very abundant in microalgae cells. This last issue is one of the most challenging issues that HTL will need to overcome in order to become a real alternative for biofuel production from microalgae [2]. Catalytic hydrothermal liquefaction (HTL) involves the addition of catalyst in the conversion of biomass to biocrude oil for the purpose of improving biocrude oil yield and properties. Catalytic HTL lowers the activation energy leading to an increase in a specific product particularly biocrude oil. It also leads to a high degree of

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oxygen removal or reduction of a wide range of oxygenated compounds. Most research studies on the effect of catalyst during HTL of microalgae have mostly made use of homogeneous catalyst, of which Na_2CO_3 has mainly been applied [3].

The main objective of this study is to evaluate the influence of potassium carbonate (K_2CO_3) on the yield and properties of the biocrude oil specifically the C, H, N, and higher heating value.

2. Materials and Methods

2.1. Materials

The experiments were performed using *Spirulina* powder obtained from online commercial source, Superfood Grocer, where they are traded as heath food supplements. Table 1 gives the composition and higher heating value (HHV) of the microalgae used in this study. *Spirulina* is a strain of microalgae with low lipid and high protein content. Deionized water was used for all of the experiment runs. Anhydrous potassium carbonate (K_2CO_3) powder and a reagent grade dichloromethane (DCM) were also used.

Table 1. Proximate analysis and elemental analysis of *Spirulina* biomass used in the hydrothermal liquefaction study

Proximate analysis (wt. %)		**Elemental Analysis (wt. %)**	
Moisture	5.86		
Volatile Combustible Matter	79.1	C	45.4
Ash	6.76	H	6.82
Fixed Carbon	14.1	N	9.19
Sulfur	0.632	O[a]	38.59
Higher Heating Value (MJ/kg)	20.21		

[a]Determined by difference

2.2. Apparatus and experimental procedure

Hydrothermal liquefaction has been performed in a 5 ml Swagelok microbatch reactor, loaded with biomass and deionized water containing K_2CO_3 catalyst. The reactor design is an unstirred bomb type made from 316 stainless steel. Liquefaction experiments have been performed at two temperatures, 280 ℃ and 350 ℃ for 15 minutes and 45 minutes residence time, the heating rate of the reactor is approximately 5 ℃ per minute. Operating parameters included 350 ℃ processing temperature with a corresponding pressure of ~20.5 MPa [4]. In each case approximately 1.5 g of microalgae has been mixed with 3 ml of catalyst solution. Microalgae is added to the reactor pre-mixed as a slurry. The reactor was tightly sealed, and heated to the desired reaction temperature using an electrical sand bath heater. Fluke Hydra Logger software was used to log temperature during operation through the use of a K-Type thermocouple connected to a Fluke Data Logger. The reactor was maintained within 5 ℃ of the process set-point temperature for the desired residence time. The start of the residence time was set when the reactor has attained the desired reaction temperature and stopped at the completion of the desired residence time. The reactors were removed from the sand bath and quenched by immersion in a water bath. However, measuring and monitoring the temperature in those small reactors are very difficult; therefore, most of the previous studies assumed the temperature inside the reactor would reach the equilibrium with the sand/salt bath in a short time, which may introduce some uncertainties [5].

The gas was vented after the reactor had cooled. The reaction mixture was first filtered without the addition of dichloromethane (DCM) by gravity filtration using a Whatman 41 ashless filter paper

(Whatman, CAT No. 1441-125). Stepwise addition of DCM solvent was used to remove the biocrude oils stuck in the wall and lid of the reactor. Two-phase mixture (water with organic matter dissolved in it and biocrude oil dissolved in DCM) was formed in the filtrate. The upper layer (aqueous product) was collected with a syringe and transferred to a separate vial. The bottom layer, which is the biocrude oil dissolved in DCM, was also transferred in another container. The mass of biocrude oil yield was determined after DCM solvent evaporation and a constant weight was already attained.

3. Results and Discussion

3.1. Biocrude Oil Yield

The HTL mass yields obtained are presented in Fig. 1. All experiment conditions were repeated in duplicate and a mean value is reported. The data show that highest yield was obtained with 5 wt. % catalyst with process temperature of 280 ℃ and 15 minutes residence time. Potassium carbonate did not yield a higher biocrude fraction when used as a catalyst at larger concentration. Similar results as Anastasakis and Ross [6] on the HTL of Laminaria saccharina showed that the use of potassium hydroxide in concentrations of 0-100 wt. % loading consistently decreased the biocrude oil yield and increased the amount of water soluble products. Results found are also consistent with the study of Biller and Ross [7] wherein they confirmed that the liquefaction of Spirulina, which has a protein content of 65%, produced a biocrude oil yield that is 17-18% with catalyst. A further study by Zou et al. [8] obtained similar results to previous researchers with the use of different sodium carbonate loadings on the HTL of D. tertiolecta; the increase in bio-crude was <5 wt. %, parameters such as temperature and holding time were shown to have much larger effects. Using more than 5 wt. % of potassium carbonate is not recommended as biocrude yield obtained from processing did not improve in most instances.

Fig. 1. Biocrude oil yield (wt. %)

3.2. Elemental Analysis of Biocrude Oil

Table 2. Elemental analysis results of biocrude oil

Temperature (℃)	Residence Time (min)	% Catalyst	% w/w			
			C	H	N	O
280	15	5	65.2	9	6.02	19.78
280	15	7.5	65.1	8.91	5.73	20.26
280	15	10	66.3	8.9	4.61	20.19
280	45	5	68.6	10.3	6.89	14.21
280	45	7.5	71.7	10.2	6.68	11.42
280	45	10	74.3	10.9	6.54	8.26
350	15	5	72.8	10.3	2.48	14.42
350	15	7.5	69.6	9.87	2.14	18.39
350	15	10	73.4	9.57	2.31	14.72
350	45	5	68.8	8.32	2.35	20.53
350	45	7.5	63.4	9.89	3.78	22.93
350	45	10	62.5	7.24	2.46	27.8

Generally, biocrude oil obtained at all the runs had higher carbon and hydrogen content (62.5–74.3% and 7.24–10.9%, respectively), and lower oxygen content than that of the original feedstock (45.4% and 6.82%, respectively).

3.3. Higher Heating Value of Biocrude Oil

Table 3. Higher heating values at different parameter conditions

Temperature (℃)	Residence Time (min)	% Catalyst	HHV (MJ/kg)
280	15	5	31.34
280	15	7.5	31.09
280	15	10	31.50
280	45	5	35.33
280	45	7.5	36.73
280	45	10	39.17
350	15	5	36.71
350	15	7.5	34.31
350	15	10	35.82
350	45	5	31.46
350	45	7.5	31.44
350	45	10	26.50

Higher heating values of the biocrude oil using various catalyst concentration and parameter conditions are provided in Table 3. Biocrude oil produced in all of the experiment runs were with higher heating value in the range of 26.50 to 39.17 MJ/kg, which were significantly higher than the original feedstock (20.21 MJ/kg). The highest HHV of 39.17 MJ/kg for the biocrude oil was obtained using 10 wt. % potassium carbonate (K_2CO_3), process temperature of 280 ℃, and residence time of 45 minutes. This HHV was 91.3% of the energy content of petroleum crude (42.9 MJ/kg).

3.4. Atomic H/C, O/C, and N/C Ratio

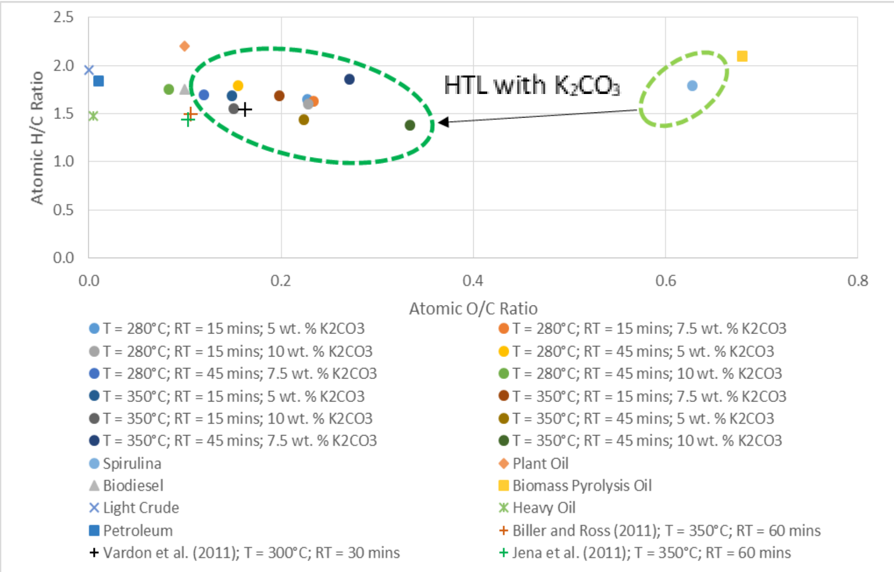

Fig. 2 Van Krevelen diagram: the atomic ratios H/C and O/C of the biocrude oil obtained from HTL of *Spirulina*

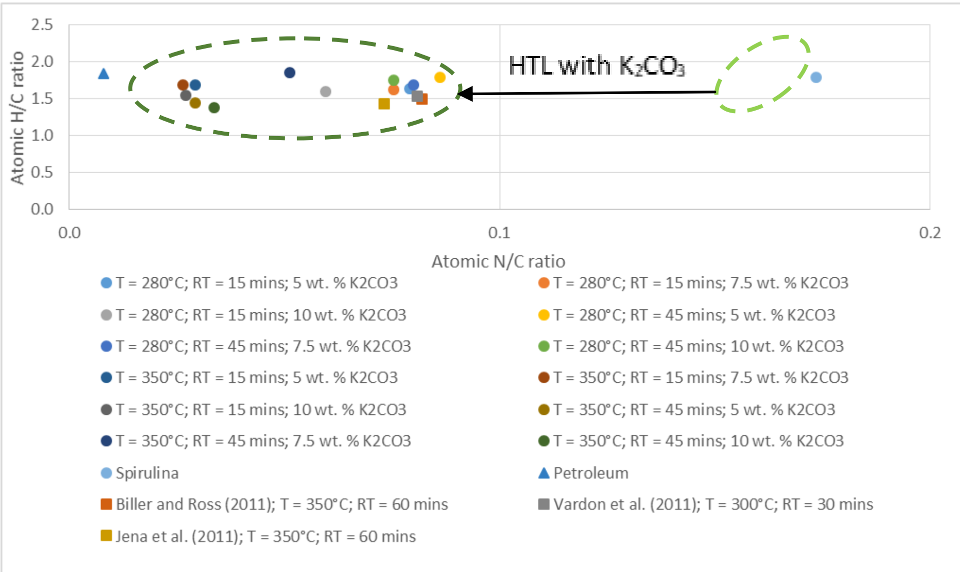

Fig. 3 Van Krevelen diagram: the atomic ratios H/C and N/C of the biocrude oil obtained from HTL of *Spirulina*

Comparisons to other fuel oils are made in the van Krevelen diagrams shown in Fig. 2 and 3. Biocrude oil obtained from the experiment runs had almost similar H/C, and O/C values to that of biodiesel and plant oil and was better than biomass pyrolysis oil. Generally, biocrude oils from HTL had higher carbon and hydrogen content and lower oxygen content than the original feedstock which had 45.4% carbon and 37.96 % oxygen.

4. Conclusions

The highest biocrude oil yield was obtained with 5 wt. % catalyst with process temperature of 280 ℃ and 15 minutes residence time. However, a higher biocrude fraction was not produced when catalyst loading was increased to 7.5 wt. % and 10 wt. %. Biocrude oil produced in all of the experiment runs were with higher heating values in the range of 26.50 to 39.17 MJ/kg, which were significantly higher than the original feedstock (20.21 MJ/kg). The highest HHV of 39.17 MJ/kg for the biocrude oil was obtained using 10 wt. % potassium carbonate (K_2CO_3), process temperature of 280 ℃, and residence time of 45 minutes. This HHV was 91.3% of the energy content of petroleum crude (42.9 MJ/kg). Biocrude oil obtained from the experiment runs had almost similar H/C, and O/C values to that of biodiesel and plant oil and was better than biomass pyrolysis oil. The N/C ratios of the biocrude oil ranged between 0.03 to 0.09.

Further studies are needed to confirm these results by performing more replicates with the use of a high volume reactor capable of handling larger sample sizes. Larger sample sizes would limit the variability seen in small volumes of feedstock and minimize the effects of oil masses lost to the reactor. Additionally, further studies should involve testing at varying parameters such as temperatures and residence to potentially determine optimum parameters for the conversion process of particular catalysts and feedstocks. Fractional distillation of the biocrude could also be done to further characterize the product.

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