Bio-Oil Production from the Pyrolysis of Blue-Green Algae for Sustainability Alternative Fuels

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Abstract

Pyrolysis experiments of blue-green algae (*Arthrospira platensis)* were carried out in a custom-built tube reactor to determine the pyrolysis conditions which was affected by the production of pyrolysis oil. The effects of process variables; the operating temperature (400-600°C), raw material federate (0.4-3.0 kg h^{-1}), particle size (150-800 µm) and N_2 flowing rate (50-250 cm^3 min^{-1}) were also investigated. The maximum bio-oil yield of 46.19 %wt. was obtained at process conditions of 500 °C feed rate of 0.6 kg h^{-1}, the N_2 flow rate of 200 cm^3 min^{-1} where using a feedstock by an average particle size of 500 µm. The oily and aqueous phase also were separated, the bio-oil yield was obtained, and their characteristics were investigated using GC-MS technique, and FT-IR also was confirmed the functional group of bio-oil which acquired of phenol, amide and carboxylic acid. The physicochemical analysis shows that bio-oils that have a higher calorific value of 29.12 $MJkg^{-1}$ are promising alternative fuels, whereas the high level of acidity of 46.78 mg_{KOH}/g required an upgrading before used as a fuels

Keywords: pyrolysis, bio-oil, Spirulina

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Introduction

During the last few decades, the depletion of the reserved conventional fossil fuels where the energy consumption had continuously been increasing, energy price crisis, the dramatical increase of CO_2 emission and raising awareness of global warming has drawn more has encouraged the interest in alternative sources on the predictions of bioenergy (Lee, et al., 2010; Lie, et al., 2012; Plis, et al., 2015; Anand, et al., 2016). Biomass is one of the most preferred sources of sustainable energy with the properties similar to fossil fuels depend on its characteristics and their conversion processes into bioenergy (Lee, et al., 2010; Duman, et al., 2011; Aysu et al., 2014). Biomass including lignocellulosic, wood, and algae that a potential candidate to produce clean fuels (Moralı, et al.,2015) Nevertheless, biomass is particularly prominent in that it not only enhances fuels diversification but also mitigates the environmental pollution and global warming due to the emission of carbon dioxide neutral (Charusiri, et al., 2017).

Algae have proven to be a viable biomass feedstock for conversion to fuel intermediates due to their high energy content and ability to grow autotrophically using carbon dioxide and sunlight. Also, algae's high biomass yield and ability to accumulate large quantities of neutral lipid and protein that promising as a source of energy production (Thangalazhy-Gopakuma, et al., 2012; Hsieh, et al., 2014) Currently, conventional algae have been considered for use as a bioenergy resource for biofuel production either biochemical sub derided into trans-esterification for biodiesel production has been accessible in the past ten years (Hu, et al., 2013). However, one limitation of this production of biodiesel is the use of many chemicals and produces waste from many production processes such as wastewater and chemical residues. However, the thermochemical conversion process such as pyrolysis is among the most promising methods for producing liquid fuels from algae can be attained both thermal and catalytic conversion in which algae is decomposed by thermal on the absence of oxygen atmospheric, to obtained of char, gaseous, bio-oil, and its value chemicals (Lie, et al., 2012; Cao, et al., 2013; Wang, et al., 2013; Yan, et al., 2017). In slow and fast pyrolysis was mainly a difference in the amount of products, on slow reaction gave char production maximized whereas fast pyrolysis gave bio-oil as mostly liquid products is one most valuable chemicals (Duman, et al., 2011).

In this study, *Arthrospira platensis* (*Spirulina platensis*), commonly known as spirulina, is among the most popular blue-green algae species, which is cultivated on a large scale (Chaiwong, et al., 2013; Anand, et al., 2016) This species is primarily utilized for the production of bio-nutrients and food supplements. Nevertheless, it has been considered for use as a bioenergy resource for biofuel production either biochemical sub derided into trans-esterification or thermochemical via fast pyrolysis reaction. to produced bio-oil. The emphasized of this study to optimization the operating parameters of pyrolysis bio-oil production from Spirulina in small pyrolyzer. Also, the analysis by the gas chromatography-mass spectrometry to understand the composition of chemical constituents formed during pyrolysis studies. Product yield, the composition of bio-oil and tar phase and the most relevant physicochemical properties also were obtained.

Materials and Methods

Arthrospira platensis (Spirulina algae) was collected, then dried in open air for seven days and sieved by a Retsch AS200 sieved shaker according to ASTM E11 to classified into desire sizing of feedstock about of the three series average size including below 250 μm, 500 μm and 750 μm. The proximate analysis included the measurement of moisture, volatile matter and ash content were determined to investigate according to ASTM E-871-82, ASTM E-872, and ASTM E-1755-01, respectively. The ultimate analysis was performed using CHN-600 analyzer (LECO, USA.) to carried out, the carbon, hydrogen, and nitrogen content. Heating value and bio-oil product were obtained following ASTM D2015 using a LECO AC350 (LECO, USA.). Thermal gravimetric analyzer Netzch 409 Simultaneous STA (NETZSCH-Geratebau GmbH, Selb, Germany) was used examine the thermal decomposition behavior of Spirulina and to provide a reference for operational parameters.

The pyrolysis of Spirulina was performed in custom-built stainless steel (SS316) that illustrated in Figure 1. Spirulina was contained in the biomass hopper and fed into the pyrolyzer by under-screw feeder with a nitrogen gases flow rate of 50-250 cm^3min^{-1}. The temperature of pyrolysis was explored under 400 to 600 °C. Reactor screw feeder controlled the detention time at a feeding rate of 120 to 240 rpm represented of detention time of 0.5 – 2.5 $kg\ h^{-1}$. The higher speed (rpm) cause the lower detention time and conversely. Furthermore, the average particle size also determined by ranging from 100 – 1000 μm. After the reaction, the yield of bio-oil, non-condensable gas and bio-char also were calculated.

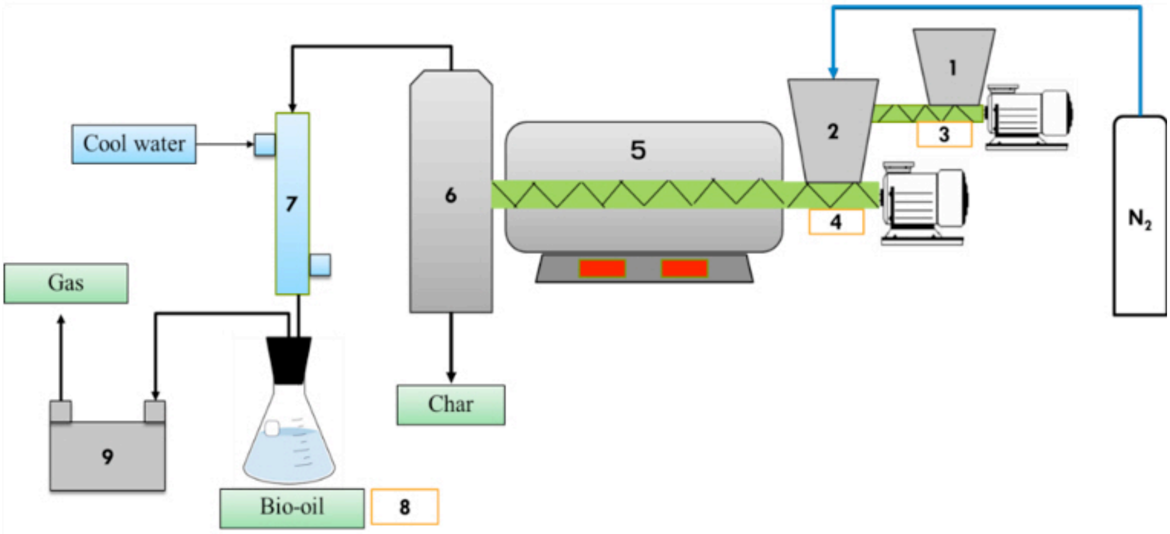

Figure 1. Schematic diagram of the pyrolysis reaction (❶biomass hopper ❷the 2nd hopper ❸screwing feeder ❹under-screw feeder ❺a custom-built tube pyrolysis reactor ❻cyclone ❼cooling condenser ❽bio-oil collector ❾gas hopper

Pyrolysis oil products are usually very complicated mixtures with organic and aqueous phases. A liquid pyrolysis oil phases were separated and analyzed with an Agilent 7890B/5977A (Agilent, USA) GC-mass spectrometer (MS) equipped with both a flame ionization detector (FID), and a thermal conductivity detector (TCD), a split/splitless injection unit and an HP-5MS capillary column (30 m x 0.25 mm x 0.25 µm). The chemical constituents were identified by comparison with the MS database in the National Institute of Standard and Technology (NIST) library. The physicochemical properties of the pyrolysis oil obtained from Spirulina pyrolysis were determined according to the ASTM standard as follows: density, kinematic viscosity, and HHV according to ASTM D369, ASTM D445, and ASTM D240, respectively. The modification acid number (MAN) was determined using an 840-Trinoplus automated titration (Metrohm, UK) according to ASTM D664, and the ultimate components of pyrolysis oil from the Spirulina were determined using a LECO CHN-200 (LECO, USA). The peaks identified in the GC-MS confirmed the identities of the chemical compounds.The ultimate analyses and physicochemical property determination revealed that the properties of the algae pyrosis oil for use to the sustainable energy and its value chemicals.

Result and Discussion

Table 1. illustrated the analyses of proximate and ultimate of Spirulina algae, as can see in the table, high amounts of volatile matter led to easier decomposition of the biomass during the pyrolysis reaction. Moreover, Spirulina of highly volatile matter has preferential properties for its application in the pyrolyzer. The proximate analysis showed that the volatile matter content of Spirulina is also higher whereas the fixed carbon and ash are lower and lower than the comparison with the several lignocellulosic biomass (Chaiwong, et al., 2013, Anand, et al., 2016). The ultimate analysis shows that Spirulina was found to have a high carbon content of 26.36 %wt. on a dry basis and the content of H/C ration and O/C ratio were quite different to the other algae. Also the nitrogen content of 5.84 %wt. was higher for the sample due to the protein component.

Table 1. Proximate and ultimate analysis of Spirulina algae

Proximate analysis	
Moisture (% wt.)	8.84
Volatile matter (% wt.)	78.74
Ash (% wt.)	7.39
Fixed carbon (% wt.) by different	5.03
Ultimate analysis	
Carbon (% wt.)	26.36
Hydrogen (% wt.)	4.82
Nitrogen (% wt.)	5.84
Oxygen (% wt.) by different	18.27
H/C ratio	2.19
O/C ratio	0.52
Composition	
Cellulose (% wt.)	5.10 ± .92
Hemicellulose (% wt.)	1.381 ± .23
Carbohydrate (% wt.)	20.46
Protein (% wt.)	63.65
Lipid (% wt.)	6.18

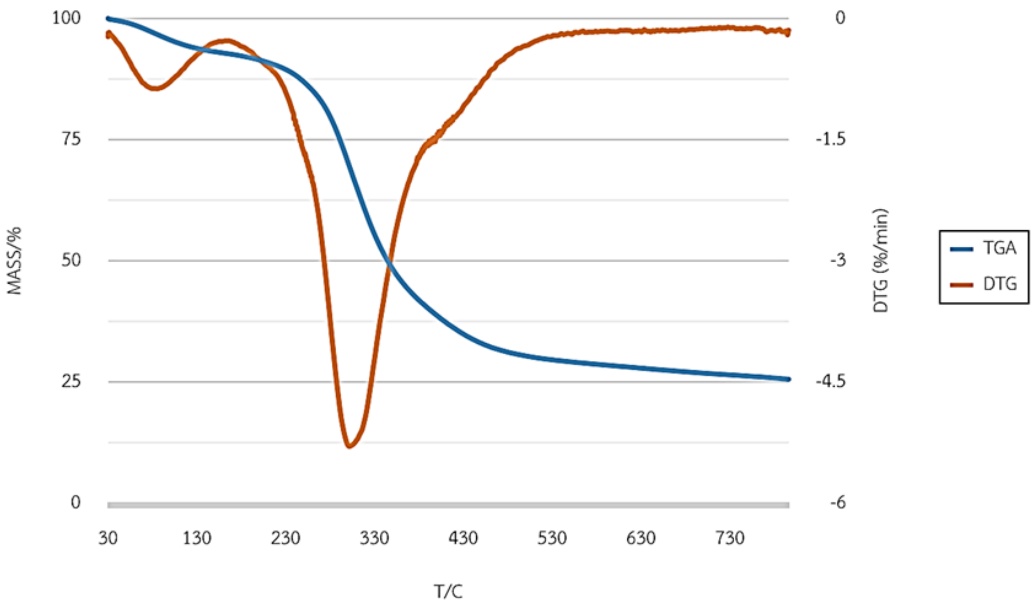

Figure 2. TG-DTG of the degradation process of Spirulina at a heating rate of 10 K min^{-1}

Figure 2**.** illustrated that he thermogravimatric analysis of Spirulina at the heating rate of 10 K min^{-1} in the N_2 atmosphere **(**feeding rate of 50 cm^3min^{-1}**)**, the result shown that the thermal decomposition of algae was 3 stage; an initial to 108 °C is the moisture removal from the microalgae, the second step is the temperature of 250 °C is the devolatileization of volatile matter and some lipid, the final step is the carbon decomposition to char and ash at the temperature above of 550 °C**.** Nevertheless, the temperature decomposition of algae also highest at the temperature of 300 to 550 °C after this operating temperature**.**

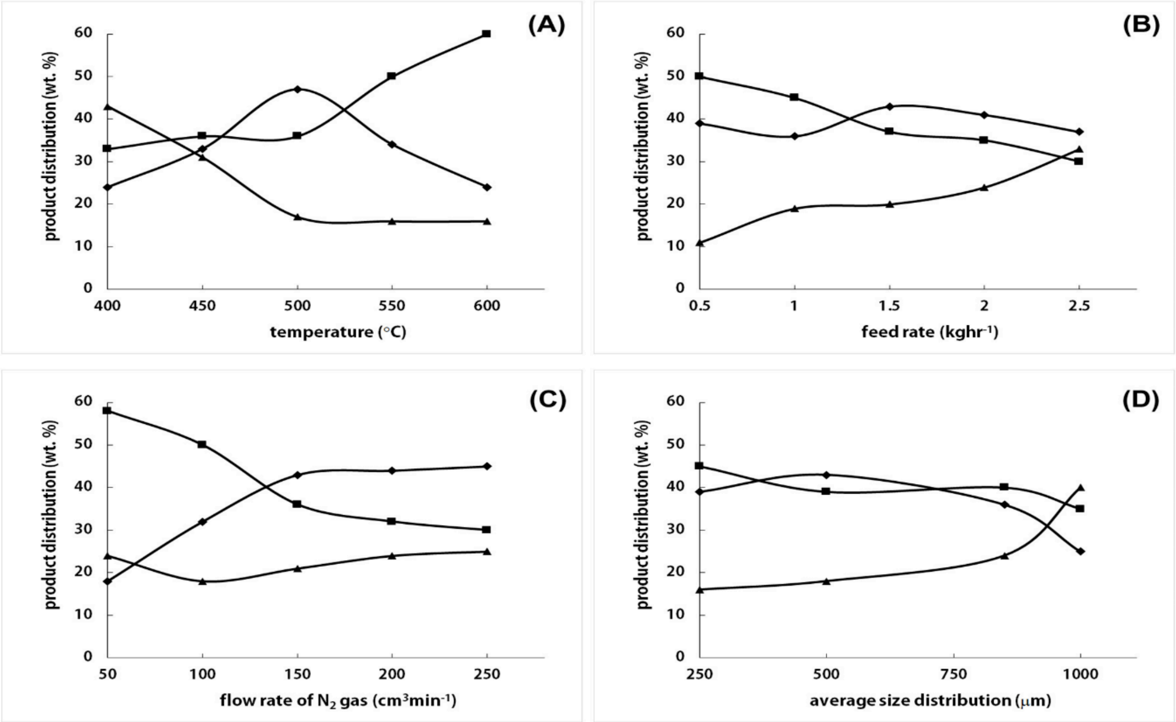

Figure 3. Product distribution of the pyrolysis of Spirulina [■ gas; ♦ bio-oil ;▲ bio-char]

Several studies of the influence of pyrolysis temperature on products distribution and obtained the likely results**.** To maximize high**-**grade bio**-**oil production from lignocellulosic biomass and algae, the following typically conditions consisted of rapid heating**-**up rate, moderate reaction temperature, and short residence time **(**Aysu. Et al., 2014: Moralı, et al., 2015; Charusiri, et al., 2017)

The effect of temperature

Figure 3**(**A**)** illustrates the effect of temperature on product distribution of the pyrolysis of Spirulina**.** At the higher temperature, the thermal degradation can still decompose the small gaseous components into incondensable gases, thus decreasing the bio**-**oil yield, although the temperature continued to increase over the optimal conditions **(**Lee, et al**.**, 2010; Aysu. Et al., 2014) The result reveals that a coupling of the high temperature and a high residence time with a slow biomass feed rate are the primary factors affecting the bio**-**oil conversion**.**

The effect of feed rate

The results demonstrated in Figure 3(B) shown that the Spirulina feed rate significantly influenced the bio-char yield. Whereas when the feed rate was increased, the biochar yield also gradually rose to a maximum bio-char yield. This observation also implied that the secondary reaction of volatile vapor and the thermal decomposition of tar were significant (Luo, et al., 2013; Aysu. Et al., 2014; Moralı et al., 2015) when the Spirulina feed rate was high. Additionally, low feed rates did not significantly affect the liquid bio-oil yield. Thus, the bio-oil was not formed entirely from the primary and secondary reactions due to insufficient heat carriers and transfer for the volatile vapor decomposition reaction

The effect of the N_2 sweeping

As can see from Figure 3**(**C**)**, the bio**-**oil yield increased with a long residence reaction time along with a low feedstock feed rate and low nitrogen sweeping gas flow rate**.** A higher nitrogen flow rate reduced the residence time, whereas an increasing temperature caused the decomposition of volatile matter, with the second pyrolysis reaction of more massive hydrocarbon compound after that converted to small hydrocarbon compound **(**Luo, et al., 2013); this process affected by thermal degradation

The effect of particle size distribution

The particle size of the algae feedstock subjected to the pyrolysis process is another parameter that affects the product distribution. Figure 3(D) represented the particle size affects the mass and heat transfer to the feedstock, the decomposition biomass, devolatilization to volatile vapors and the thermal decomposition of tar during the pyrolysis reaction. In addition, as the particle size increased, the pyrolysis of Spirulina mainly occurred on the algae surface, and the mass and heat transfers were affected by the average size distribution and uniformity and more significant to the liquid product than increasing the average particle size because the temperature inside may have been insufficient to complete the thermal decomposition reaction during the primary pyrolysis stage (Charusiri, et al., 2017).

Characterization of the pyrolysis bio-*oil of Spirulina algae*

The maximum bio-oil yield of 46.19 %wt. was obtained at process conditions of 500 °C feed rate of 0.6 kg h^{-1}, the N_2 flow rate of 200 cm^3 min^{-1} where using a feedstock by an average particle size of 500 μm. In order to quantify the compounds using a GC/MS technique, the bio-oil compositions were identified at several retention times, and the percentages of the peak area, chemical formulas, and molecular weights are listed in Table 2. The organic compounds were analyzed and classified mostly of phenol, aliphatic hydrocarbon including decane, pentadecane, hexadecane as well, some carboxylic acid and oxygenate compounds and others. These chemical compounds were produced by the thermal decomposition of cellulose, hemicellulose and protein and lipid.

Table 2. Chemical compound in bio-oil fraction by Gas Chromatograph–Mass Spectrometry

RT (min)	Peak area	Formula	Compound
3.685	2.27	C_6H_5OH	Phenol
4.435	1.64	C_7H_8O	p-Cresol
5.15	1.16	$C_8H_{10}O$	Phenol, 4-ethyl-
5.757	0.9	C_9H_9N	Benzenpropaneitrile
6.152	2.7	C_8H_7N	Indole
6.516	2.12	$C_8H_{10}O_3$	Phenol, 2,6-dimethoxy-
6.603	0.97	$C_{13}H_{16}$	Benzene, 1-methyl-4-[(1-methylethylidene]cyclopropyl]-
6.793	1.13	C_9H_9N	1H-Indole, 3-methyl-
7.144	1.43	$C_9H_{12}O_3$	1,2,3-Trimethoxybenzene
7.183	1.14	$C_{10}H_{12}O_2$	trans-Isoeugenol
7.426	1.09	$C_{15}H_{32}$	Pentadecane
7.647	1.38	$C_9H_{10}O_4$	Ethanone, 1-(2,6-dihydroxy-4-methoxyphenyl)
7.699	1.18	$C_7H_6O_3$	Benzaldehyde, 2,4-dihydroxy
7.786	1.65	$C_{11}H_{16}O_2$	2(4H)-Benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl
7.92	1.81	$C_{11}H_{17}NO$	2-Cyclohexen-1-one, 2-methyl-5-(1-methylethenyl)-, O-methyloxime, (+)-
8.519	1.17	$C_{21}H_{29}NO_5$	1-Ethylamino-3-(2-methoxy-4-methyl-phenoxy)-propan-2-ol
8.61	11.34	$C_{17}H_{36}$	Heptadecane
8.644	1.01	$C_8H_{10}S$	Benzene, 1-methyl-4-(methylthio)-
8.931	1.04	$C_{13}H_{20}O_2$	Olivetol, dimethyl ether
9.373	8.49	$C_{18}H_{36}$	9-Octadecyne
9.407	1.27	$C_{20}H_{40}$	2-Hexadecene, 2,6,10,14-tetramethyl-

RT (min)	Peak area	Formula	Compound
9.503	0.93	$C_{20}H_{40}O$	3,7,11,15-Tetramethyl-2-hexadecen-1-ol
9.598	3.77	$C_{16}H_{32}O$	Hexadecanal
9.707	3.1	$C_{15}H_{29}N$	Pentadecanenitrile
9.893	1.38	$C_{16}H_{30}O_2$	Palmitoleic acid
9.993	17.2	$C_{16}H_{32}O_2$	n-Hexadecanoic acid
10.582	1.16	$C_{14}H_{24}O$	2(1H)-Naphthalenone
10.734	1.1	$C_{20}H_{40}O$	Phytol
10.764	1.95	$C_{18}H_{30}O_2$	Gamolenic Acid
10.821	6.12	$C_{18}H_{32}O_2$	9,12-Octadecadienoic acid (Z,Z)-
10.933	1.2	$C_{18}H_{36}O_2$	Octadecanoic acid
10.968	1.14	$C_{18}H_{35}NO$	9-Octadecenamide, (Z)-
11.046	7.04	$C_{16}H_{33}NO$	Hexadecanamide
11.831	2.43	$C_{18}H_{32}O_2$	Methyl 9,12-heptadecadienoate
12.425	3.52	$C_{19}H_{38}O_4$	Glycerol 1-palmitate

Table 3. Ultimate analyses of pyrolyzed product

Composition	Aqueous phase	Bio-oil phase	Bio-char
Carbon (% wt.)	1.17	4.93	5.47
Hydrogen (% wt.)	11.62	11.47	4.46
Nitrogen (% wt.)	0.43	0.66	0.74
Oxygen* (% wt.)	4.27	1.26	3.07
H/C ratio**	9.94	2.33	0.82
O/C ratio**	3.65	0.26	0.56

*by different
** by calculation

The physicochemical properties of the pyrolysis oil are presented in Table 3 and Table 4. The elemental analyses revealed that the H/C and O/C values are lower than those of the algae feedstock. The thermal decomposition and gasification reaction formed a condensable bio-oil product, and CO and CO_2 were removed from the first stage of the thermal decomposition of the algae feedstock. The HHV of pyrolysis oil was between 29.12 $MJkg^{-1}$ As mentioned above, the HHV of the pyrolysis oil also increased after the pyrolysis process, potentially due to the significant influences of the temperature and residence time on moisture removal and the dehydration, devolatilization, and depolymerization reactions that condense the volatile vapors into the pyrolysis bio-oil. The density (1008.7 kgm^{-3}) and kinematic viscosity (4.13 mm^2s^{-1}) were measured using ASTM D369 and ASTM D445, respectively. Whereas the high level of the modification acid number of 46.78 mg_{KOH}/g according to ASTM D664 also determined investigate.

Table 4. Physicochemical analyses on pyrolyzed product

Physicochemical analysis	Bio-oil from Spirulina
Density @15 °C (kg/m^3)	1008.7
Kinematic @ 40 °C (mm^2/s)	4.13
Ash (% wt.)	0.68
Total solid (% wt.)	0.007
Acidity (mgKOH/g)	46.78

Conclusion

The pyrolysis of Spirulina algae under the custom-built pyrolysis reactor obtained the optimum reaction condition of the maximum bio-oil product yield of 49.19 %wt. was obtained at a final temperature of 500 °C, the feeding rate of biomass 200 rpm at a nitrogen gas flow rate of 200 cm^3min^{-1} and using the raw material at the average particle size of 750 μm. The GC/MS results, confirmed the bio-oil contain complex compounds mostly composed of aromatic, aliphatic hydrocarbon including decane and pentadecane and hexadecane as well, some acid and oxygenated compounds. The physicochemical properties of bio-oil shown the heating value and the acidity which were not suitable to direct used as transportation fuels substitution unless it is upgraded through catalytic cracking and hydrogenation similar to petroleum diesel fuel.

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References

Anand, V., Sunjeev, V., Vinu, R. (2016) Catalytic fast pyrolysis of *Arthrospira plantensis* (spirulina) algae using zeolite. *Journal of Analytical and Applied Pyrolysis*, 118, 298-307.

Aysu, T., Maşuk. Küçük, M. (2014) Biomass pyrolysis in a fixed-bed reactor: Effects of pyrolysis parameters on product yields and characterization of products. *Energy*, 64, 1002-1025.

Cao, J.P., at al. (2013) Nitrogen transformations during fast pyrolysis of sewage sludge. *Fuel,* 104, 1–6.

Charusiri, W., Tividsant, V. (2017) Upgrading bio-oil produced from the catalytic pyrolysis of sugarcane (*Saccharum officinarum* L) straw using calcined dolomite. *Sustainable Chemistry and Pharmacy*, 6, 114-123.

Chaiwong, K. et al. (2013) Study of bio-oil and bio-char production from algae by slow pyrolysis. *Biomass and Bioenergy*, 56,600-606.

Duman, G., et al., (2011) The slow and fast pyrolysis of cherry seed. *Bioresource Technology*, 102, 1869-1878.

Hsieh, P.Y., et al., (2014) Chemical and thermophysical characterization of an algae-based hydrotreated renewable diesel fuel. *Energy and Fuels*, 28, 3192-3205.

Hu, Z., et al., (2013) Bio-oil production through pyrolysis of blue-green algae blooms (BGAB): product distribution and bio-oil characterization. *Energy*, 52, 119-125.

Lee, M.K., et al., (2010) Pyrolysis of napier grass in an induction-heating reactor. *Journal of Analytical and Applied Pyrolysis*, 88, 110-116.

Lie, D., et al., (2012) Preparation and characteristic of bio-oil from the marine brown alga *Sargassum patens* C. Agaedh. *Bioresource Technology,* 104, 737-742.

Luo, S., Yi, C., Zhou, Y. (2013). Bio-oil production by pyrolysis of biomass using hot blast furnace slag. *Renewable Energy*, 50, 373-377.

Moralı, U., Şensöz, S. (2015). Pyrolysis of hornbeam shell (*Carpinus betulus* L.) in a fixed bed reactor: Characterization of bio-oil and bio-char. *Fuel*, 150, 672–678.

Plis, A., et al. (2015) Thermochemical and kinetic analysis of the pyrolysis process in *Cldaohora glomerata* algae. *Journal of Analytical and Applied Pyrolysis*, 115, 166-174.

Thangalazhy-Gopakuma, S, et al. (2012) Catalytic pyrolysis of green algae for hydrocarbon production using H^+ZSM-5 catalyst. *Bioresource Technology*, 118, 150-157.

Yan, W.H., et al. (2017) Catalytic hydropyrolysis and co-hydropyrolysis of algae and used engine oil for production of hydrocarbon-rich fuel. *Energy*, 113, 1153-1162.

Wang, K., Brown, R.C. (2013) Catalytic pyrolysis of microalgae for production of aromatics and ammonia. *Green Chemistry*, 15, 675-681.

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