Biodiesel Production from Macro Algae as a Green Fuel for Diesel Engine

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Abstract

Transesterification is an effective method to produce significant levels of biodiesel from renewable resources like plant oils and animal fats. Macroalgae is one of the inexpensive sources of oil feedstock for biodiesel production which is abundantly available in the sea areas. In this study algae oil was extracted from several types of macroalgae species namely *L. Epiphytic, Cladophora, Agardhiella, Gracilaria, Spirogyra and Bryopsis Pennata*. And their oils were then converted into biodiesel by the transesterification process. The extraction of algae oil from macroalgae was accomplished through Soxhlet method. The fuel properties of biodiesel was characterized through FTIR analysis and found to be similar chemical composition as to petroleum diesel. In addition, the highest yield was found (92%) at methanol to oil ratio 4:1, catalyst 1.0 wt% (KOH) in heating with stirring.

***Keywords*:** biodiesel, FTIR, macroalgae, renewable, transesterification.

I. Introduction

DUE to the depletion of fossil fuel reserve and environmental concerns, a search for alternative fuels have gain significant attention over the years. A number of studies have shown that triglycerides of vegetable oils can be used as diesel fuels as discussed by Fukuda [1,2]. Consequently, considerable efforts have been made to develop alternative diesel fuels that have the properties and performance as the petroleum-based diesel fuels, and the most promising way is the transesterification of triglycerides to fatty acid alkyl esters, chemically alters organically derived oils in forming biodiesel fuel. This process has been widely used to reduce the viscosity of vegetable oils (triglycerides). In transesterification, triglycerides in vegetable oil will react with alcohol to form mixture of fatty acid alkyl esters and glycerol.

Biodiesel produced from vegetable oils can be used as an alternative to diesel fuels because the characteristics of biodiesel are close to petroleum-based diesel fuels. Several works have shown that biodiesel produced from various vegetable oils have viscosity close to petroleum-based diesel fuel. Their gross heating values are a little lower, but they have high cetane and flash points as investigated by Fukuda [1]. If methanol is used in transesterification, the obtained biodiesel will be fatty acid methyl esters (FAMEs) [3].

Among biomass, algae usually have a higher photosynthetic efficiency than other biomass [4]. Algae are tiny biological factories that use photosynthesis to transform carbon dioxide and sunlight into energy so efficiently that they can double their weight several times a day [5]. As part of the photosynthesis process algae produce oil and can generate 15 times more oil per acre than other plants used for biofuels, such as corn and switchgrass [6]. Resulting algae oil can be used to produce biodiesel through the transesterification process [7].

Several macroalgae species are abundantly available in Sarawak and mostly the species are situated along coastline region [8]. In addition, the climate in Sarawak is fit for algae cultivation and with this benefit it would be easier to produce large amount of oil for biodiesel production [9]. Many studies have been carried out on biodiesel production from various algae

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species and using different esterifications process [1,2]. Little work, however, has been devoted to Sarawak macroalgae species and their biodiesel production with transesterification method [9,10].

In the present work, six species of selected Sarawakin macroalgae species namely *L. Epiphytic, Cladophora, Agardhiella, Gracilaria, Spirogyra and Bryopsis Pennata* were used to biodiesel production. Therefore, the main aim of this study is to produce biodiesel from several macroalage species and characterization of their properties.

2. MATERIALS AND METHOD

2.1 Macro Algae

Six species of selected macroalgae were collected from different places of Kuching and Kota Samarahan for this study. The macroalgae species were *Leathesia Epiphytic, Cladophora, Agardhiella, Gracilaria, Spirogyra* and *Bryopsis Pennata.* The fresh water algae like *Leathesia Epiphytic, Cladophora* and *Spirogyra* were collected from Desa Ilmu, Kota Samarahan area. Whereas, the marine algae species- *Agardhiella, Gracilaria* and *Bryopsis Pennata* were collected from Marine Research Institute, Kuching, Sarawak.

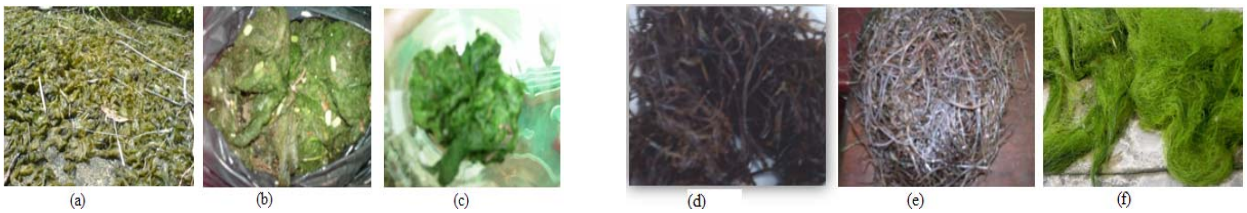

Figure 1 Macroalgae species of: (a) *Leathesia Epiphytic*; (b) *Cladophora*; (c) *Spirogyra*; (d) *Agardhiella*; (e) *Gracilaria*; and (f) *Bryopsis Pennata*

2.2 Oil Extraction

Oil extraction from algae species was carried out by Soxhlet method. In this process the macroalgae species were fully dried in oven dryer and in sun light. The dried macroalgae were then grinded to powder form. The powder macroalgae (70 gm) were placed in the thimble of soxhlet. In bottom flask, 400 ml n-hexane solvent was taken to extract the oil. The extracted oil in solvent was separated by rotary vacuum distillation.

2.3 Biodiesel Production

The extracted Algae oil from six algae species were collected and converted into biodiesel. 20 mg of oil was taken in a beaker. Potassium hydroxide (KOH) and methanol (CH_3OH) with proper ratio were taken in another beaker and dissolved by heating with stirrer to produced methoxide. Then the methoxide was mixed with oil and followed three different processes- Heating with stirring, Orbital shaker and Auto Clave.

After completed the reaction the solution was kept in separating funnel for 24 h to settle the biodiesel and glycerine layers. The bottom heavy layer of glycerine was first poured in a small beaker and the biodiesel layer was remained in the separating funnel for purification. The remaining biodiesel layer was washed to remove the unreacted components with hot water repeatedly until it becomes clean and pH about 8.0. The pure biodiesel was dried by heating gently, measured by measuring cylinder and stored in a glass bottle for test.

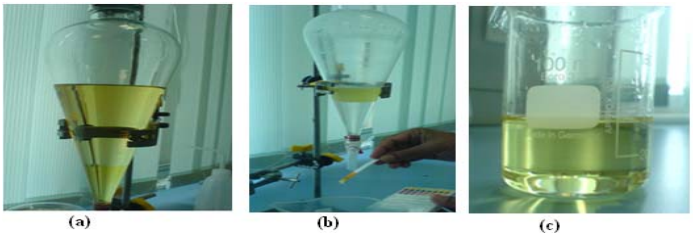

Figure 2 Pure biodiesel after purification

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of the biodiesel samples were recorded on a Shimadzu Fourier Transform Infrared Spectroscopy (FTIR) 81001 Spectrophotometer. The transmittance range of the scan was 370 to 4000 cm^{-1}. The obtained spectra are described in the results and discussions section.

3. RESULTS AND DISCUSSION

3.1 Optimization of Biodiesel Production

The extracted oil from all species of algae was collected and converted into biodiesel production in selected process. It can be found from table 1 and figure 3 that the conversion efficient of algal oil to biodiesel depends on different parameters such as time, temperature, pH etc. In the first step for each 20 ml of algal oil, amount of methanol varied from 40 ml to 140ml, amount of KOH 0.2 gm, reaction time 30 minutes, RPM 150, temperature below 60^0C and pH around 8 were maintained (Table 1). In Figure 3, it was shown that maximum biodiesel 18.6 gm that is 93.0 % produced in methanol to oil ratio at 4:1, remaining other parameters unchanged.

Table 1 Biodiesel production changing methanol to oil ratio

Batch	Oil (ml)	Methanol (ml)	KOH (gm)	Time (min)	RPM	Temperature (^{0}C)	pH	Biodiesel (ml)
1	20	40	0.2	30	150	50~60	7~8	13.4
2	20	60	0.2	30	150	50~60	7~8	16.4
3	20	80	0.2	30	150	50~60	7~8	18.6
4	20	100	0.2	30	150	50~60	7~8	17.2
5	20	120	0.2	30	150	50~60	7~8	16.2
6	20	140	0.2	30	150	50~60	7~8	14.8

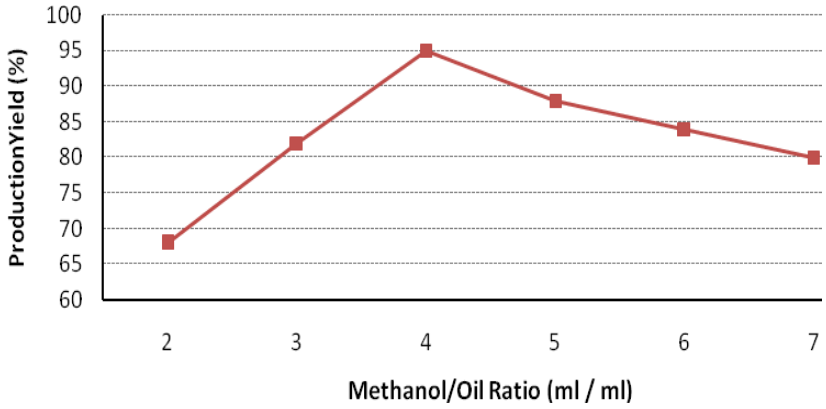

Figure 3 Effect of methanol to oil ratio on the production yield

From Table 2 and Figure 4, it was shown the effect of concentration of KOH on the production yield of biodiesel at CH_3OH to Oil ratio of 4:1 and other parameter remain same. The reaction yields were optimum, when the KOH ranges from 0.6 wt% to 1.2 wt%.

Table 2 Biodiesel production changing the percentages of catalyst

Batch	Oil (ml)	Methanol (ml)	KOH (wt %)	Time (min)	RPM	Temperature (^{0}C)	pH	Biodiesel (ml)
1	20	80	0.2	30	150	50~60	7~8	17.9
2	20	80	0.4	30	150	50~60	7~8	18.2
3	20	80	0.6	30	150	50~60	7~8	18.4
4	20	80	0.8	30	150	50~60	7~8	18.7
5	20	80	1.0	30	150	50~60	7~8	18.5
6	20	80	1.2	30	150	50~60	7~8	18.3

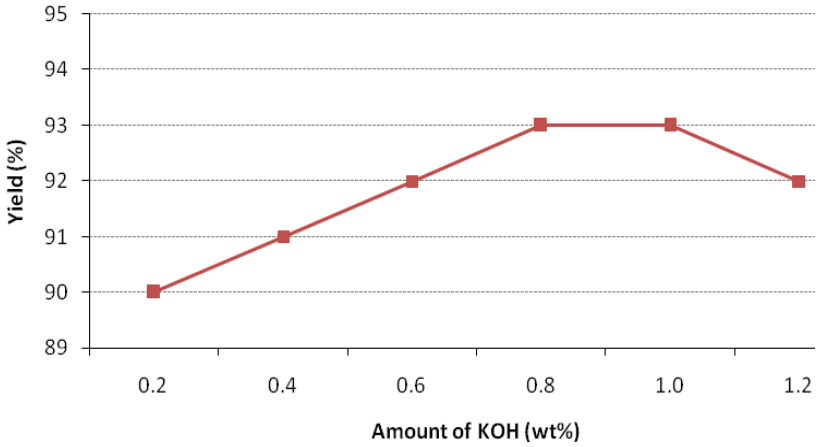

Figure 4 Effect of KOH percentages on the production yield

In Table 3 and Figure 5 showed the biodiesel production in orbital shaker, hot plate and auto clave. In experiment it was shown that hot plate had the highest yield of 92% due to temperature and continuous stirring. Whereas in auto clave had the lowest yield of 46% due to the evaporation of methanol at 120^{0}C.

Table 3 Data of different production process

Process	Oil (ml)	Methanol (ml)	KOH (gm)	Time (min)	RPM	Temperature (^{0}C)	Pressure (bar)	Biodiesel (ml)	%
Shaker	20	80	0.2	30	150	20	1.0	16.2	81
Hot Plate	20	80	0.2	30	150	50~60	1.0	18.4	92
Auto Clave	20	80	0.2	30	-	120	1.2	9.2	46

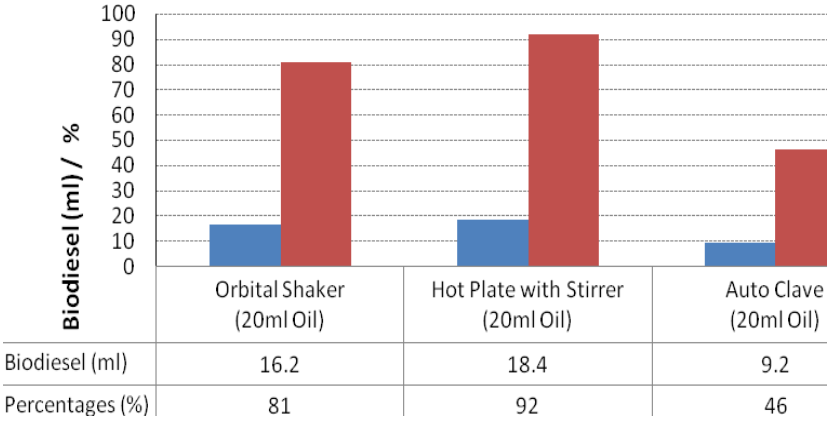

Figure 5 Biodiesel production yield of different process

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

In order to investigate the chemical composites of biodiesel product, FTIR test was performed and results are shown in Figure 6. The FTIR spectrum of both diesel (i.e. conventional and biodiesel) clearly shows the similar absorption band in the region of 2850~3000 cm^{-1} and 1350~1480 cm^{-1} due to C- H stretching vibration, which indicates the identical functional group of alkane in their molecular structural [12].

However, the FTIR spectrum of biodiesel shows new two absorption bands in the region of 1670~1820 cm^{-1} and 1000~1300 cm^{-1}. These absorption bands are due to the C=O and C-O stretching vibration in ester which led to prove the presence of oxygen in biodiesel [13]. However, there was no absorption peaks appeared at these regions for petroleum diesel. This result gave further evidence of oxygen molecule in the biodiesel product [12].

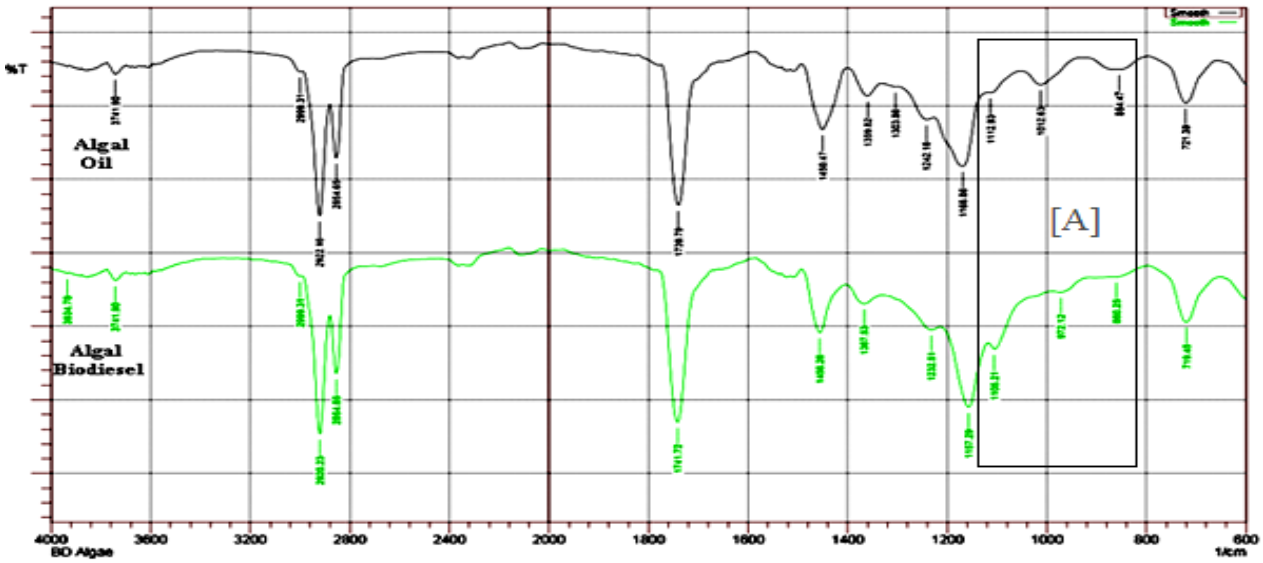

Figure 6 FTIR spectrum of algae oil and algae biodiesel

3.3 Heating Value and Fuel Properties

The heating value of biodiesel was measured and shown in Table 4. From table, it can be seen the heating value of biodiesel blend was decreases with the increase of biodiesel percentages. This result may be due to the methods such as apparatus, procedure and measurement. However, the TAN, Viscosity and specific gravity were compatible to petroleum diesel. The higher cetane will increase the fuel combustion efficiency. The Sulphur content was zero that is good for environment. The higher flash point 145^{0}C is safe uses of biodiesel [14].

Table 4 Measurement of heating value of fuel

Sample No.	Biodiesel Blend	Weight of Oil (gm)	Initial Temp. (^{0}C)	Temperature Rise (^{0}C)	Gross Heating Value (MJ/kg)
01.	B0 (Diesel)	1.012	29.63	11.44	44.56
02.	B100 (Biodiesel)	1.007	29.76	10.22	40.23
03.	B5	1.028	29.81	11.06	44.17
04.	B10	1.012	29.74	10.97	43.84
05.	B15	1.016	29.81	10.88	43.68
06.	B20	1.021	29.84	10.52	43.25
07.	B25	1.018	29.88	10.34	42.97
08.	B30	1.026	29.86	10.26	42.44

3.4 Burning Test

The burning test was carried out to observe the combustion criteria of biodiesel blend B100, B20 and B0. From table 5 it was shown that the burning rate of B100 was much lower compare to conventional diesel and B20. The conventional diesel burned vigorously because the energy density of conventional diesel is higher than the biodiesel. It can also be found the burning rate for B20 was higher than B100 due to the large percentage of conventional diesel. The conventional diesel produces more smoke in black color, whereas B100 emitted small amount of smoke in white color. There was a noticeable reduction in odour and smoke was observed for B20. All the above results suggested that the biodiesel contains more O_2, so that biodiesel blend undergoes more complete combustion compared to the conventional diesel and it produced less black smoke. Therefore, biodiesel blend improve the efficiency of combustion and it produced less pollutant.

Table 5 Comparison of fuel properties of algal biodiesel and conventional diesel

Fuel property	Biodiesel	Diesel
Heating Value (MJ/Kg)	39.68	43.37
TAN (mg/gm KOH)	0.20	0.12
Specific density, gm/cm^3	0.83	0.88
Viscosity (cSt)	4.38	~4.0
Flash point ^{0}C	145	60~80
Sulphur content, wt %	0.0	0.05 Max
Cetane Number	68	40~55

4. CONCLUSIONS

From the present study it can be calculated that the maximum (85%) biodiesel could be produced from extracted alage oil through transesterification process. The calorific value, FTIR spectrum and fuel properties of biodiesel were compared to conventional petroleum diesel and seemed to be similar or improved. In addition, a smoke free clear flam and slow burn was observed for B50 biodiesel blend. Therefore, the author proposed that different types of tropical Macroalgae could be utilized for green fuel/biodiesel production as they are considered renewable energy source for biodiesel production. Thus algae can be used as a feedstock of renewable source of energy to replace the existing energy sources of fossil fuel and also to reduce pollution.

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