Research Article

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Evaluation of Biodiesel Production Using Oil Feedstock from Contaminated Macro Algae in Shrimp Farming

Thawipon Wuttilerts and Suphang Chulalaksananukul*
Department of Chemical Engineering, Faculty of Engineering, Mahidol University, Salaya campus, Nakhon Pathom, Thailand

Peeriya Peerapongpipat
P.P Tutor House, Non buri, Nonthaburi, Thailand

Pongpan Suksommanat
Sun Genesis Industry, Teparak road Km24, Bangsaothong, Samut Prakan, Thailand

* Corresponding author. E-mail: suphang.chu@mahidol.ac.th DOI: 10.14416/j.ijast.2018.11.005
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Abstract
This research was aimed to manage and utilize 3 contaminated macro algae from shrimp farming, *Caulerpa lentillifera*, *Caulerpa racemosa* and *Acanthophora spicifera* as an alternative oil feedstock for biodiesel production. Oil extraction was performed and biodiesel production was conducted in further to get the maximum yield. The optimization of condition, such as the molar ratio of oil to methanol, effect of reaction time, reaction temperature, and percentage of catalyst were carried out. The results were discovered that the average amount of oil from these macro algae were approximately 3.3% from dried basis. The optimum condition for biodiesel production with these 3 macro algae was nearly the same. The reaction was completed within 8 h and the achievement of biodiesel yield was 55.58% from *Caulerpa lentillifera* with the suitable condition of oil to methanol molar ratio 1:15 using 1% of KOH at 60°C. *Caulerpa racemosa* can be produced 58.36% of biodiesel from the condition of oil to methanol ratio 1:15 with 1.5% of KOH at 60°C. As well, the optimum condition for biodiesel production from *Acanthophora spicifera* was using 1:12 of oil to methanol ratio with 1% of KOH and obtained 49.29% of biodiesel.

Keywords: Biodiesel, Greenhouse gas, Oil feedstock, Macro algae, Shrimp farming

1 Introduction

Biodiesel, an alternative energy produced from oil and alcohol, has been well-known as a carbon neutral fuel. Biodiesel production from non-edible oil sources is highly interesting due to non-interrupt to the food feedstock [1]. Recently, many researches have been focused on algae for much higher growth rate than terrestrial crops. The other advantages over another food crops for oil feedstock are that algae can grow in any water sources, even on sewage water. Their growth does not require any land use; moreover they do not need any hazardous chemical for pest control [2]. Consequently, they save an environmental performance.

Macro algae or seaweed are a potential alternative source for the conventional oil feed stocks [3]. Some reports were revealed the possibility to produce biodiesel from microalgae, *Chlorella protothecoides*, which

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was yielding of 98% of biodiesel from 55.2% of lipid in algal cell. The optimum condition was to produce by 1 : 56 oil to methanol ratio at 30°C for 4 h and the obtained biodiesel was in high quality [4], [5].

In this study, macro algae in the species of *Caulerpa lentillifera*, *Caulerpa racemosa* and *Acanthophora spicifera* have been found as contaminated species in shrimp farming, regarding of their growth reducing the productivity yields of farming. The huge amount of approximately 10 ton per day of these macro algae have been dumped into the environment resulting to cause a seriously uncontrollable greenhouse gases releasing to the atmosphere and further enhance global warming.

Particularly, to concern an environmental performance, this research was aimed to manage and utilize these solid wastes (macro algae biomass) as an alternative oil feedstock to produce biodiesel, a carbon neutral fuel via direct trans-esterification. The optimum condition for biodiesel production was evaluated in further.

2 Experimental Method

The main objective of this work was to exploit the potential of macro algae as an alternative oil feedstock for biodiesel production. The experiments were performed as the following procedures:

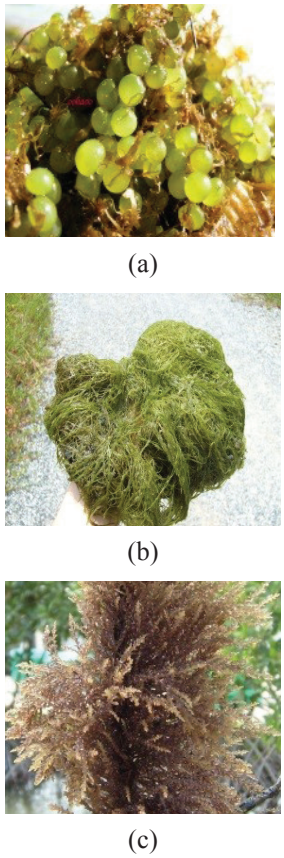
2.1 *Macro algae preparation and oil extraction*

Three species of macro algae (*Caulerpa lentillifera*, *Caulerpa racemosa* and *Acanthophora spicifera*) seen in Figure 1 were collected from shrimp farming located near Bangkok, Thailand. After being washed with many times of water, they were sun dried for a few days and were ground to be a small particle size before oil extraction process was preceded.

2.2 *Macro algae and its oil characteristic*

The moisture content of the dried and crushed algae was analyzed due to the water in the sample reduced the trans-esterification reaction resulting to lower biodiesel yield.

Oil extraction was performed by solvent (hexane) extraction in a soxhlet apparatus. Then, the properties of macro algae oil were analyzed followed the standard method for oil and lipid analysis. The saponification value was determined followed AOCs method TI Ia-64, Acid value by AOCs method Cd3a-63, and Iodine value by following Wijs method (AOCS Cd1-25).



(a) (b) (c)

Figure 1: Macro algae collected from shrimp farming (a) *Caulerpa lentillifera* (b) *Caulerpa racemosa* and (c) *Acanthophora spicifera*.

2.3 *Trans-esterification reaction to biodiesel production*

The obtained oil feed stocks were continuing to do trans-esterification reaction with methanol to become biodiesel. The variables affecting trans-esterification were carried on. The effect of oil to methanol molar ratios was conducted (1 : 3, 1 : 6, 1 : 9, 1 : 12, and 1 :1 5). The effect of retention time, as well as percentage of KOH as catalyst were applied at 0.5, 1.0, and 1.5% by weight of oil, the reaction temperature (40, 50, and 60°C) were controlled.

After the trans-esterification reaction to generate biodiesel was completed, glycerol-a byproduct, was needed to be separating out. After washing for several time of water to remove base catalyst. Biodiesel was drying and then the concentration of biodiesel (yield) was ready to analyze by gas chromatography (PERKIN ELMER N931-6079) using PE-5 capillary column (0.25mm I.D. × 60 m length, 0.25 μm film thicknesses) and equipped with flame ionization detector. Pure nitrogen was used as a carrier gas with a flow rate of 500 mL/min. The injector and detector temperature were at 240 and 250°C, respectively. The temperature program of oven was carried on from 110 to 240°C within 15 min at a heating rate of 10 degree/min.

The fatty acid composition in biodiesel was determined by using High Performance Liquid Chromatography (HPLC) equipped with C-18 column. The analytical conditions were as follows: column Vertisep UPS C18 column, 250 × 4.6 mm, 5 μm; liquid mobile phase acetone and acetonitrile (HPLC grade) was fed with the flow rate of 0.5 mL/min. The concentrations were compared to the standard fatty acid methyl ester (standard FAME).

2.4 *Analysis of biodiesel properties*

Biodiesel obtained by transesterification was determined for its physical and chemical properties including of fuel properties of biodiesel.The analysis methods were followed the American Standard Test Method for materials (ASTM) [6]. Density, viscosity, flash point and caloric heat value were analyzed.

3 Results and Discussion

3.1 *Macro algae oil extraction and composition*

Percentage of extracted oil from *Caulerpa lentillifera*, *Caulerpa racemosa*, and *Acanthophora spicifera* were obtained by 3.62, 3.46, and 2.80%, respectively as shown in Table 1.

Table 1: The percentage of algae oil obtained from the extraction process

Macro Algae Species	%Oil Obtained (Dried Basis)
Caulerpa Lentillifera	3.62
Caulerpa Racemosa	3.46
Acanthophora Spicifera	2.80

Noticeably, the extracted oils from algae in this study were obtained in low amount when compared to the other oil crop and other species of algae [4], [5]. Besides, the amount of oil content particularly depends on the species of algae. However, the nearly percentage of oil content obtained from some algae was observed in the same range of 2–8% by weight reported by Rohani-ghadikolaei and Abdulalian, 2012 [7].

The physical and chemical properties of macro algae oil were also investigated in order to predict further characteristic of produced biodiesel. The chemical properties of algae oil was showed in Table 2.

The saponification value and acid value of macro algae oil from this study was better value than that reported by Miao *et al*., 2006 [4] Miao *et al*. result showed both higher saponification and acid values (189.3 mg HCl/g oil of saponification value and acid value of 8.97 mg KOH/g oil). The high saponification value and acid value affected soap formation during biodiesel production process and decrease both quality and quantity of biodiesel and resulting to further induce system erosion.

Table 2: The chemical properties of studied macro algae oil

Macro Algae Oil from the Algae Species	*Caulerpa Lentillifera*	*Caulerpa Racemosa*	*Acanthophora Spicifera*
%Moisture Content	14.7	13.3	14.2
Saponification Value (mg HCl/g)	166.43	151.41	153.34
Acid Value (mg KOH/g)	6.73	7.41	5.16
Iodine Value (g Iodine/100g)	12.69	11.42	25.38

For instance, macro algae oil has been investigated as the possible alternative source for biodiesel production because it expressed an allowance saponification and acid values.

Also, iodine value of macro algae oils in this study was low. The higher iodine value affected the lower performance of biodiesel production by forming polymers which induced an odor and color in product; undesirable properties.

3.2 *Trans-esterification reaction to biodiesel production*

The variables affecting trans-esterification were preceded to find the optimum condition for biodiesel

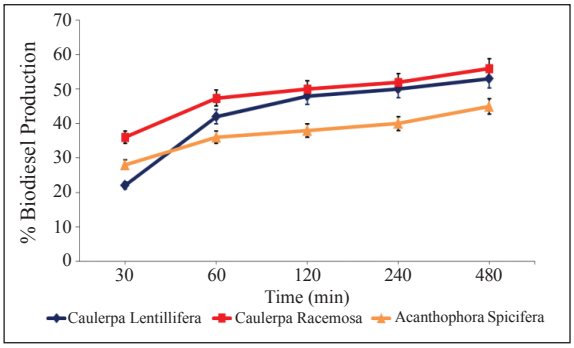


Figure 2: Effect of reaction time to biodiesel production using oil to methanol at 1 : 15 catalysed with 1%KOH at 60°C.

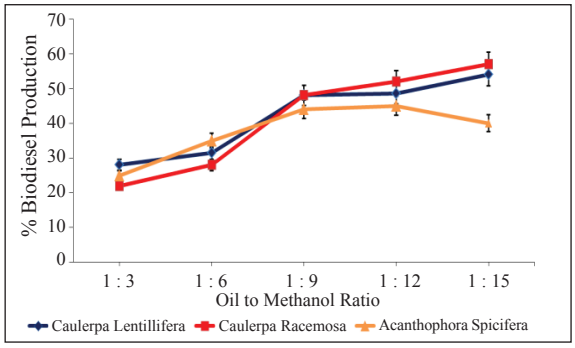


Figure 3: Effect of molar ratio of oil to methanol to biodiesel production at 480 min of reaction time using 1%KOH as catalyst at 60°C.

production. Oil to methanol molar ratio, reaction time, temperature, and %catalyst were studied in order to achieve higher conversion. The trans-esterification reaction was performed under the certain condition as mentioned before.

As the reaction time is the controlling factor for the yield of biodiesel, the reaction was started up with the molar ratio of oil to methanol at 1 : 15 catalyzed with 1% of KOH under 60°C. The %yield of biodiesel production from *Caulerpa lentillifera*, *Caulerpa racemosa* and *Acanthophora spicifera* were up to 55.58, 58.36, and 49.29% within 480 min , respectively as showed in Figure 2. Practically, this time was set as the optimum time for biodiesel production. After this time, the rate of reaction was slow lest it gone the appropriate yield to extend further reaction.

Another important variable affecting the yield of biodiesel is the molar ratio of oil to methanol. The percentage of biodiesel obtained at 480 min of reaction time at different molar ratio of oil to methanol was shown in Figure 3. Biodiesel yield produced from *Caulerpa lentillifera* and *Caulerpa racemosa* at molar ratio 1 : 9 was equaled and the ratio less than 1 : 12 was achieved lower yield of biodiesel indicated the reaction was incomplete.

While *Acanthophora spicifera* at molar ratio less than 1 : 9, the reaction was incomplete resulting from the separation of glycerol was difficult and the apparent yield of biodiesel production was low [8]. So, the optimum molar ratio of oil to methanol was suitable at 1 : 12 for *Acanthophora spicifera* and at 1 : 15 for 2 other species of algae; *Caulerpa lentillifera* and *Caulerpa racemosa*. Nonetheless, percentage of biodiesel obtained from 3 types of algae was nearly the same.

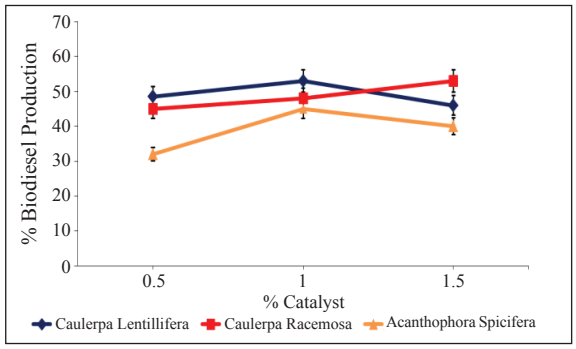


Figure 4: Effect of the amount of catalyst to biodiesel production using oil to methanol at 1 : 12 for *Aconthophora spicifera* and 1 : 15 for *Caulerpa lentillifera* and *Caulerpa racemosa*, time of 480 min and controlled at 60°C.

The study to find out the suitable percentage of catalyst applied as shown in Figure 4 was different in 3 macro algae species because oils of *Caulerpa lentillifera* and *Acanthophora spicifera* had the acid value lower than that of *Caulerpa racemosa* as mentioned previously in Table 2. The higher acid value was reduced the efficiency of production, because of base catalyst had reacted to acid in oil prior to catalyze the reaction. The reduction of the yield of biodiesel due to the formation of soap in the presence of high amount of catalysts applied [9].

By the way, the optimum amount of catalyst to produce biodiesel from *Caulerpa lentillifera* and *Acanthophora spicifera* was 1% KOH and 1.5% KOH for *Caulerpa racemosa*. Yield of 55.64, 55.75, and 48.93% of biodiesel from *Caulerpa lentillifera*, *Caulerpa racemosa* and *Acanthophora spicifera* were obtained, respectively.

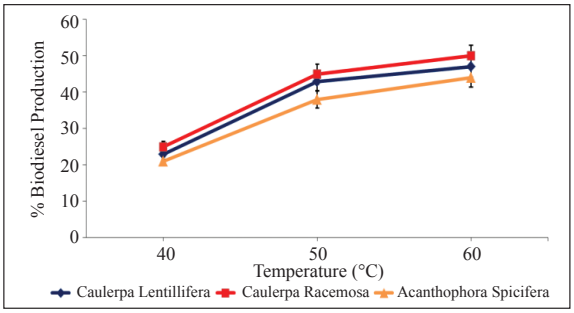


Figure 5: Effect of temperature to biodiesel production at 480 min using oil to methanol 1:12 for *Aconthophora spicifera* and 1 : 15 for *Caulerpa lentillifera* and *Caulerpa racemosa* and catalyzed with 1%KOH for *Caulerpa lentillifera* and *Aconthophora spicifera* and 1.5% KOH for *Caulerpa racemose*.

The result of suitable reaction temperature to generate biodiesel from 3 species of macro algae was shown in Figure 5.

The higher temperature, the higher yield of biodiesel were achieved. The optimum temperature to produce biodiesel was at 60°C for three types of algae. The optimum temperature for biodiesel production in this study was different result from obvious report [5] that the suitable temperature to produce biodiesel was at 30°C. This was probably from different in species of algae oil.

The optimum condition for biodiesel production with these three kinds of macro algae was nearly the same. *Caulerpa lentillifera* biodiesel was generated within the suitable condition of oil to methanol molar ratio 1 : 15 using 1% of KOH at 60°C. While *Caulerpa racemosa* was able to be produced to be biodiesel with the condition of oil to methanol ratio 1 : 15 using 1.5% of KOH at 60°C. As well as the optimum condition for biodiesel production from *Acanthophora spicifera* was using 1 : 12 of oil to methanol ratio with 1% of KOH as summarized in Table 3.

Table 3: The optimum condition of biodiesel production from 3 macro algae species at 480 min

Macro Algae Species	Molar Ratio Oil : MeOH	Temperature (°C)	%Catalyst
Caulerpa Lentillifera	1 : 15	60	1.0
Caulerpa Racemosa	1 : 15	60	1.5
Acanthophora Spicifera	1 : 12	60	1.0

The average of biodiesel achieved at 480 min was of 55.58, 58.36, and 49.29% from *Caulerpa lentillifera*, *Caulerpa racemosa*, and *Acanthophora spicifera*, respectively as expressed in Table 4.

Table 4: Yield achievement from trans-esterification reaction of three macro algae

Macro Algae Species	%Biodiesel Achieved
Caulerpa Lentillifera	55.58
Caulerpa Racemosa	58.36
Acanthophora Spicifera	49.29

Comparatively, the percentage of obtained biodiesel from these three kinds of macro algae was much higher than the report of Maceiras *et al*. [10] which obtained only 11.5% as a maximum methyl esters (biodiesel) content from 14 different macro algae.

Even though the moisture content of *Caulerpa racemosa*, *Caulerpa lentillifera* and *Acanthophora spicifera* as showed in Table 2 were not in different values (13.3–14.7%), this was not relatively concerned to the yield of biodiesel. So, this could be mentioned that it was not influenced the reaction of biodiesel production.

3.3 *Biodiesel properties*

The analyzed physical, chemical and fuel properties of biodiesel were elucidated as showed in Table 5.

Table 5: The physical, chemical and fuel properties of macro algae biodiesel

Biodiesel Properties	*Caulerpa Lentillifera*	*Caulerpa Racemosa*	*Acanthophora Spicifera*
Density (g/cm^3)	0.89	0.90	0.88
Viscosity (cSt, 40°C)	5.1	8.4	6.7
Flash point (°C)	129	140	135
Heating Value (MJ/kg)	34.5	38.8	36.6

Finally, Biodiesel composition was further analyzed the components by comparing with standard methyl ester of fatty acid. For *Caulerpa lentillifera* and *Acanthophora spicifera* consisted mainly of methyl linoleate, methyl oleate and methyl stearate. Also, *Caulerpa racemosa* comprised mainly methyl linoleate and methyl oleate.

Scenedesmus acutus, the microalgae species

was explored to have the same composition of polyunsaturated Fatty Acid Methyl Ester (FAMEs) which were methyl oleate, methyl linoleate and methyl linolenate [11]. In the other hand, the high fraction of polyunsaturated FAMEs was reported in a microalgae namely chlorella spp. which the extracted fraction mainly composted of linoleic and linolenic acid as different composition of this result [12].

Noteworthy was that all of these macro algae in this study contained much polyunsaturated fatty acid methyl ester (or biodiesel), especially linoleic acid which was not beneficial for biodiesel properties due to their lowered oxidation stability. Moreover, the polymerization reaction of polyunsaturated fatty acid chain was probably occurred to form a jelly biodiesel which diminished the quality of the products.

4 Conclusions

Oil extracted from macro algae were 2–4% obtained from dry weight. However, the production of biodiesel from macro algae oil of *Caulerpa lentillifera*, *Caulerpa racemosa*, and *Acanthophora spicifera* species were successful.

The optimum conditions for biodiesel production was conducted with 1.0–1.5% KOH, oil to methanol molar ratio was between 1 : 12 to 1 : 15. The reaction temperature was 60°C. The higher molar ratio of oil to methanol and higher temperature, the higher yield of biodiesel was achieved. Also, the reaction time was influencing the percentage of yields. Larger amount of catalyst was not enhancing production yield. The yield of biodiesel was achieved from 49.29–58.36% after 8 h of reaction.

The result of this research was the profit in not only reduced an environmental pollution, but also provided a solution for an alternative energy and the potential value of macro algae oil to be an alternative biodiesel feedstock.

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References

[1] Pacific Biodiesel. (Jun. 2017). *Pacific Biodiesel Technologies*. Pacific Biodiesel. Hawaii, USA [Online]. Available: http://www.biodiesel.com/biodiesel/

[2] A. B. Ross, J. M. Jones, M. L. Kubacki, and T. Bridgeman, "Classification of macroalgae as fuel and its thermochemical behaviour," *Bioresource Technology*, vol. 99, pp. 6494–6504, 2008.

[3] B. Bharathiraja, M. Chakravarthy, R. R. Kumar, D. Yogendran, D. Yuvaraj, J. Jayamuthunagai, R. P. Kumar, and S. Palani, "Aquatic biomass (algae) as a future feed stock for bio-refineries: A review on cultivation, processing and products," *Renewable & Sustainable Energy Reviews*, vol. 47, pp. 634–653, 2015.

[4] H. Xu, X. Miao, and Q. Wu, "High quality biodiesel production from a microalga *Chlorella protothecoides* by heterotrophic growth in fermenter," *Bioresource Technology*, vol. 126, pp. 499–507, 2006.

[5] X. Miao and Q. Wu, "Biodiesel production from heterotrophic microalgal oil," *Bioresource Technology*, vol. 97, pp. 841–846, 2006.

[6] ASTM International. (1991). Annual book of ASTM standards, Petroleum Products and Lubricants (I-III). Philadelphia, USA [Online]. Available: https://www.astm.org/BOOKSTORE/BOS/index.html

[7] K. Rohani-ghadikolaei and E. Abdulalian, "Evaluation of the proximate, fatty acid and mineral composition of representative green, brown and red seaweeds from the Persian Gulf of Iran as potential food and feed resources," *Journal of Food Science Technology*, vol. 49, pp. 774–780, 2012.

[8] J. M. Encian, J. F. Gonzaliz, J. J. Rodriguez, and A. Tajedor, "Biodiesels fuels from vegetable oils; Transesterification of *Cynara* cardunculus L. oils with ethanol," *Energy & Fuels*, vol. 16, pp. 443–450, 2002.

[9] M. P. Dorado, E. Ballesteros, J. A. Almeida, C. Schellet, H. P. Lohrlein, and R. Krause, "An alkali-catalysed transesterification process for

high free fatty acid oils," *Transactions of the American Society of Agricultural Engineers*, vol. 45, no. 3, pp. 525–529, 2002.

[10] R. Maceiras, M. Rodrı´guez, A. Cancela, S. Urréjola, and A. Sánchez, "Macroalgae: Raw material for biodiesel production," *Applied Energy*, vol. 88, no. 10, pp. 3318–3323, 2011.

[11] E. Santillan-Jimenez, R. Pace, S. Marques, T. Morgan, C. McKelphin, J. Mobley, and M. Crocker, "Extraction, characterization, purification and catalytic upgrading of algae lipids to fuel-like hydrocarbons," *Fuel*, vol. 180, pp. 668–678, 2016.

[12] C. V. Viegas, I. Hachemi, S. P. Freitas, P. Maki-Arvela, A. Aho, J. Hemming, A. Smeds, I. Heinnmaa, F. B. Fontes, D. C. da Silva Pereira, N. Kumar, G. A. G. Aranda, and D. Y. Murzin, "A route to produce renewable diesel from algae: Synthesis and characterization of biodiesel via in situ transesterification of *Chlorella* alga and its catalytic deoxygenation to renewable diesel," *Fuel*, vol. 155, pp. 144–154, 2015.