Biodiesel Production from Palm Oil in Wastewater Pond of Palm Oil Mill Plant Via Two-step Catalyzed Process

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Abstract

The objective of this research was to produce biodiesel from palm oil in wastewater pond of palm oil mill plant for adding value to waste palm oil and thereby reducing the load to the wastewater treatment system and minimizing environmental impact. Since the high free fatty acid content in waste palm oil, so biodiesel was produced by via two-step process reaction. The first step was esterification using sulfuric acid as catalyst in the reaction between free fatty acids and methanol to reduce free fatty acids from 48.62% to lower than 2%. In the second step, transesterification using potassium hydroxide as catalyst in the reaction between the product from the first step and methanol for converting triglycerides to mono-esters or biodiesel. The results showed that the optimum condition for the esterification step was 20:1 molar ratio of methanol to free fatty acids, 5% by weight of sulfuric acid based on free fatty acids and 120 minutes of reaction time. The optimum condition for transesterification step was found to be 12:1 molar ratio of methanol to oil, 1.5% by weight of potassium hydroxide based on oil weight and 30 minutes of reaction time. The final results showed that the maximum purity of biodiesel was about 80-87% and the quality of biodiesel met the community biodiesel standard of Thailand following ASTM standard.

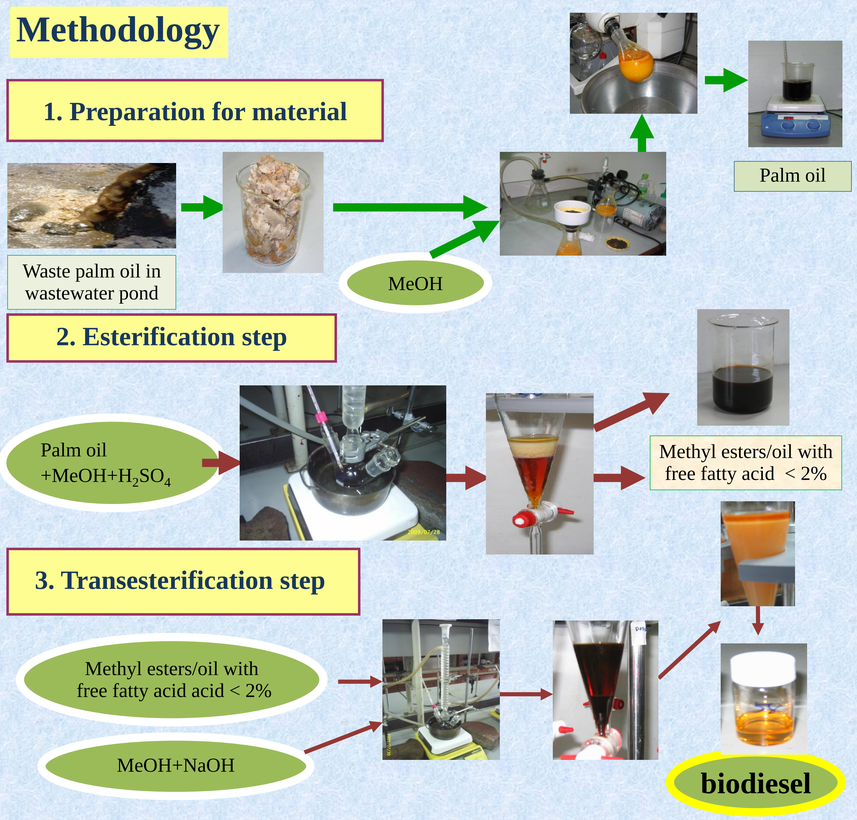
Introduction

Oil palms can be used to produce palm oil (Crude Palm Oil: CPO) by industries. Some of palm oil has been drained into wastewater pond of palm oil mill plant. It can be collected from wastewater pond by mixing palm oil with methanol and then filter it to separate the impurity out of palm oil. After evaporating methanol out of palm oil, the palm oil can be used to produce biodiesel that has as good quality as biodiesel that is produced from purity palm oil.

In Thailand, there are several palm oil mill plants that are produced the palm oil for foods and vehicles. Palm oil or CPO from all of palm oil mill plants in Thailand has been drained into wastewater pond about 1-2% from the milling process. This palm oil is floated on the surface of wastewater pond and covers on the surface of wastewater and smell pollution. If we leave it in the garbage, it will also cause the smell pollution which affects people in the area so using it as a raw material for making biodiesel fuels for treatment of waste palm oil. In addition, it can reduce the environment problem from global warming by consuming biodiesel that is produced from waste palm oil in wastewater pond of palm oil mill plant.

Palm oil had high free fatty acid from impurity of wastewater pond that is not converted to biodiesel product by one step (the alkaline catalyzed process) because it causes to produce soap that prevent the separation of biodiesel from glycerin fraction. So, via two-step catalyzed processes are suitable for biodiesel production from waste palm oils. The first step is esterification step that uses acid catalyze to reduce FFA in the waste palm oils to less than 2%. The second step is transesterification step that uses alkaline catalyze to change the triglycerides that remain in waste palm oil to mono-ester or biodiesel.

Methodology



Materials and methods

Materials

Waste palm oil from wastewater pond of the palm mill plant, Thailand. The chemicals are MeOH, H_2SO_4, NaOH, KOH,NaOH, N- heptanes (C_7H_{16}), methyl heptadecanoate, etc. that they are analytical grade. The reference standards of fatty acid methyl esters are more than 99% purity (FAME Mix. C8-C24; Supelco Analytical USA).

Preparation for material

Mixing the waste palm oil with methanol 1:2 by volume , heated at 60ºC , 5 min, after that the mixture solution was filtrated under vacuum filtration immediately. The methanol in filtrate was removed by using the rotary evaporator. The water in filtrate was removed by heating at 105ºC for 4 hr. The final product was the feed stock for making biodiesel.

Apparatus and reaction procedures

Esterification step used 10 g of waste palm oil, fixed stirred speed at 700 rpm , at 60°C. A certain quantity of sulfuric acid catalyst was dissolved in the requited amount of methanol. After achieving, separated the oil from excess methanol, acid catalyst and water, the oil was heated at 100°C for removing of impurities which remained in the oil. This final product was the feed stock for transesterification step.

Transesterification step, the oil (FFA<2%) was further react with methanol and used KOH of catalyst. The condition was maintained to molar ratio of methanol to the oil 12:1, 30 min of reaction time, 1.5 % by weight of KOH, stirred speed at 700 rpm , at 60°C. When the reaction completed to separate methyl ester from glycerol, washed methyl ester with warm 1%NaCl after washed with warm water until waste water was neutralize, removed water from methyl ester by heater at 100°C. In addition, analyzed quality of methyl esters followed ASTM and EN methods.

Results and Discussion

Table 1 Fatty acid composition of waste palm oil

Fatty acids name	structure	Fatty acids (%wt.)
Myristic acid	C14:0	0.87
Palmitic acid	C16:0	47.40
Palmitoleic acid	C16:1	1.12
Stearic acid	C18:0	4.29
Oleic acid	C18:1	36.30
Linoleic acid	C18:2	6.95
Erucic acid	C20:0	3.06

Table 2 Three factors effect on amount of acid catalyze, molar ratio of methanol to FFA in waste palm oil and reaction time that base on FFA content.

Amount of H_2SO_4 (% wt)	FFA (% wt)	Molar ratio of Methanol : FFA	FFA (% wt)	Reaction time (min)	FFA (% wt)
0	48.62	10:1	3.18	30	5.42
1	43.95	15:1	2.27	60	3.14
2	31.71	20:1	1.62	90	2.29
3	18.07	25:1	1.33	120	1.63
4	2.61	30:1	1.20	150	1.64
5	1.62	35:1	1.21		
6	1.44	40:1	1.50		
7	1.31				

Table 3 Three factors effect on amount of alkaline catalyze, olar ratio of methanol to oil and reaction time that base on oil content.

Amount of KOH (% wt)	%FAME	Molar ratio of Methanol : Oil	%FAME	Reaction time (min)	%FAME
0.5	59.427	6:1	66.917	30	86.47
1.0	81.577	8:1	68.929	60	86.26
1.5	83.992	10:1	77.104	90	85.91
2.0	84.881	12:1	80.963	120	85.81
2.5	84.391	14:1	79.113	150	84.78
3.0	84.614				

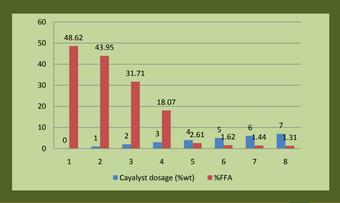


Figure1. Influence of catalyst dosage during acid esterfication on FFA (%) of waste palm oil. The reaction was controlled at a constant stirring speed of 700 rpm, a constant temperature of 60 ºC and a reaction time of 150 min.

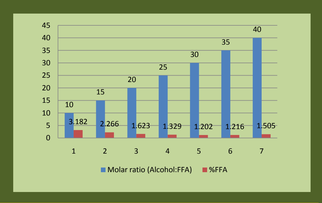


Figure2. Influence of molar ratio of alcohol to fatty acids during acid esterfication on FFA (%) of waste palm oil. The reaction was controlled at a constant stirring speed of 700 rpm, a constant temperature of 60 ºC, a reaction time of 150 min and catalyst dosage of 5% by weigh of FFA.

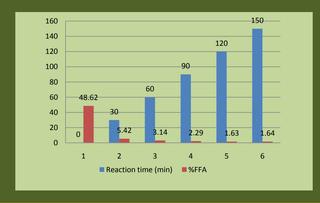


Figure3. Influence of reaction time during acid esterfication on FFA (%) of waste palm oil. The reaction was controlled at a constant stirring speed of 700 rpm, a constant temperature of 60 ºC, a reaction time of 150 min, catalyst dosage of 5% by weigh of FFA and molar ratio of methanol to the FFA of 20:1

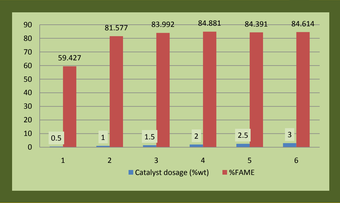


Figure4. Influence of catalyst dosage during alkaline transesterfication on FAME (%) of waste palm oil. The reaction was controlled at a constant stirring speed of 700 rpm, a constant temperature of 60 ºC, molar ratio of methanol to product from esterification step of 10:1 and a reaction time of 150 min.

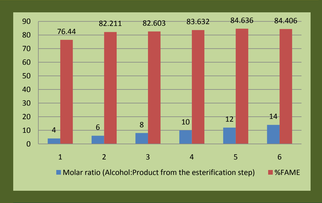


Figure5. Influence of molar ratio of alcohol to fatty acids during alkaline transesterfication on FFA (%) of waste palm oil. The reaction was controlled at a constant stirring speed of 700 rpm, a constant temperature of 60 ºC, a reaction time of 150 min and catalyst dosage 1.5%

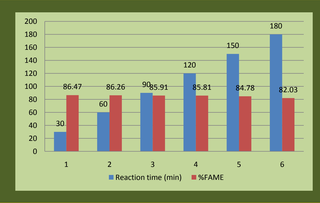


Figure6. Influence of reaction time during alkaline transesterfication on FFA (%) of waste palm oil. The reaction was controlled at a constant stirring speed of 700 rpm, a constant temperature of 60 ºC, catalyst dosage 1.5% and molar ratio of methanol to product from esterification step of 12:1

The properties of waste palm oil as raw material: The fatty acid compositions of waste palm oil are very important to identify the carbon chains and its properties. Palmitic acid (C16:0) is major of fatty acid composition in raw material that see in table 1. Saturated and unsaturated fatty acids are 55.62% and 44.37%, respectively. The average molecular weight of fatty acid and waste palm oil are 271 g mol^{-1} and 885 g mol^{-1}, respectively.

Acid catalyzed esterification step: Esterification step was used in order to pretreatment of waste palm oil by converting to high FFA content to FAMEs. The initial FFA content of waste palm oil was 48.62% that high FFA for biodiesel process by one step. Therefore, the maximum limit of FFA was 2% which esterification step can reduce it. The important factors of esterification step were amount of acid catalyze, molar ratio of methanol to FFA in waste palm oil and reaction time.

Effect of H_2SO_4 amount effect: The optimum of H_2SO_4 amount was 2% FFA. The H_2SO_4 catalyst was varied in the range of 1-7 % wt. The results showed in table 2, 5-7% of H_2SO_4 amount were less than 2% FFA but 5% of H_2SO_4 amount was selected, because it had low amount of catalyst to give an acceptable FFA content (table 2).

Molar ratio of methanol to FFA effect: It was one of the important factors effecting to reduce FFA content from the waste palm oil. The esterification step needs more value of methanol than transesterification step, in order to drive the reaction towards completion. This research studied molar ratio of methanol to FFA, it was varied the ratio in between 10:1 - 40:1. The results showed that, the optimum ratio was 20:1 (table 2).

Reaction time effect: In order to complete the esterification step, sufficient contact time must be provided. The reaction time at 120 min was selected the optimum condition because it used the less time to reduce FFA in less than 2% (table 2).

Alkaline catalyzed transesterification step: The transesterification into biodiesel (methyl esters) used KOH for alkaline catalyst. The condition was 12:1 molar ratio of methanol to oil, 1.5% KOH, 30 min of reaction time at 60°C and 700 rpm of stirring rate. The properties of biodiesel product were about 87% of methyl esters content, 4.57 cSt of viscosity@40°C, 171 °C of flash point and 0.78 mg KOH/g of acid value.

Conclusion

The optimum condition of esterification step was 20:1 ratio of methanol to FFA, 5% H_2SO_4 amount and 120 min of reaction time which it reduced FFA into less than 2%. The optimum condition of transesterification step was 12:1 molar ratio of methanol to oil, 1.5% KOH amount and 30 min of reaction time. The quality of biodiesel met the community biodiesel standard that can be used as fuel in agricultural machine.

References

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Acknowledgements

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