# การใช้ขยะน้ำมันปาล์มในบ่อน้ำเสียเพื่อผลิตไบโอดีเซลชุมชน
# Use of Waste Palm Oil in Wastewater Pond to Prepare Community Biodiesel

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## บทคัดย่อ

การผลิตไบโอดีเซลโดยกระบวนการใช้ด่างเป็นตัวเร่งปฏิกิริยาเพียงขั้นตอนเดียวไม่สามารถผลิตไบโอดีเซลจากขยะน้ำมันปาล์มจากบ่อบำบัดน้ำเสียของโรงงานสกัดน้ำมันปาล์มดิบที่มีปริมาณกรดไขมันอิสระเป็นส่วนประกอบอยู่สูงได้ เพราะกรดไขมันอิสระทำให้เกิดสบู่ซึ่งไปขัดขวางการแยกชั้นของไบโอดีเซลและกลีเซอรีน ดังนั้น กระบวนการใช้ตัวเร่งปฏิกิริยาแบบสองขั้นตอนจึงเป็นวิธีที่เหมาะสมสำหรับการผลิตไบโอดีเซลจากขยะน้ำมันปาล์ม โดยขั้นตอนแรกคือขั้นตอนเอสเทอริฟิเคชันใช้กรดเป็นตัวเร่งปฏิกิริยาเพื่อลดกรดไขมันอิสระในขยะน้ำมันปาล์มให้ลดต่ำกว่า 2 เปอร์เซ็นต์ ส่วนขั้นตอนที่สองคือขั้นตอนทรานส์เอสเทอริฟิเคชันใช้ด่างเป็นตัวเร่งปฏิกิริยาเพื่อเปลี่ยนไตรกลีเซอไรด์ในขยะน้ำมันปาล์มให้เป็นโมโน-เอสเทอร์หรือไบโอดีเซล งานวิจัยนี้มีจุดประสงค์เพื่อพัฒนาวิธีการผลิตไบโอดีเซลแบบสองขั้นตอนจากขยะน้ำมันปาล์มในบ่อบำบัดน้ำเสียของโรงงานสกัดน้ำมันปาล์มดิบโดยการใช้สถิติRSM (Response surface methodology) ในการศึกษาและออกแบบการทดลอง สำหรับการศึกษาสภาวะที่เหมาะสมของปฏิกิริยาเอสเทอริฟิเคชันสำหรับลดกรดไขมันอิสระในขยะน้ำมันปาล์มให้ลดต่ำกว่า 2 เปอร์เซ็นต์ ได้ทำการศึกษา 3 ตัวแปรคือ อัตราส่วนของเมทานอลต่อกรดไขมันอิสระของขยะน้ำมันปาล์ม, ปริมาณของกรดตัวเร่งปฏิกิริยา (ซัลฟุริก) และระยะเวลาในการทำปฏิกิริยา โดยศึกษาทั้งหมด 20 การทดลอง ส่วนการศึกษาหาสภาวะที่เหมาะสมของปฏิกิริยาทรานส์เอสเทอริฟิเคชันเพื่อเปลี่ยนไตรกลีเซอไรด์ให้เป็น fatty acid methyl ester (FAME) หรือไบโอดีเซล ศึกษา 3 ตัวแปรคือ อัตราส่วนของเมทานอลต่อน้ำมันของขยะน้ำมันปาล์ม (ขยะน้ำมันปาล์มที่มีความเป็นกรดต่ำได้จากขั้นตอนการทำปฏิกิริยาเอสเทอริฟิเคชัน), ปริมาณของด่างตัวเร่งปฏิกิริยา (โพแทสเซียมไฮดรอกไซด์) และระยะเวลาในการทำปฏิกิริยาทั้งหมด 20 การทดลอง ผลการศึกษาพบว่าขยะน้ำมันปาล์มมีปริมาณกรดไขมันอิสระสูงถึง 65.09 เปอร์เซ็นต์โดยน้ำหนัก มีน้ำหนักโมเลกุลเฉลี่ยของกรดไขมันเท่ากับ 271 กรัมต่อโมล น้ำหนักโมเลกุลเฉลี่ยของขยะน้ำมันปาล์มเท่ากับ 885 กรัมต่อโมล ซึ่งพบกรดปาลมิริกสูงที่สุด สภาวะที่เหมาะสมของปฏิกิริยาเอสเทอริฟิเคชันและทรานส์เอสเทอริฟิเคชันถูกศึกษาโดยใช้สถิติ RSM และคุณสมบัติของไบโอดีเซลจากขยะน้ำมันปาล์มที่ผลิตได้ในสภาวะที่เหมาะสมภายใต้กระบวนการใช้ตัวเร่งปฏิกิริยาสองขั้นตอนถูกศึกษาตามมาตรฐาน ASTM

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## Abstract

Waste palm oil (WPO) from wastewater treatment pond of palm oil mill plant has high free fatty acid (FFA) content which is not converted to biodiesel by one step (the alkaline catalyzed process). The FFA produces soap that prevents the separation of biodiesel from glycerin fraction. So, via two-step catalyzed processes are suitable for biodiesel production from WPO. The first step is esterification step that uses acid catalyze to reduce FFA in the WPO to less than 2%. The second step is transesterification step that uses alkaline catalyze to change the triglycerides that remained in WPO to mono-ester or biodiesel. The objective of this research was to develop a two-step technique of biodiesel production from WPO in wastewater treatment pond of palm oil mill plant by using the response surface methodology (RSM). The RSM was applied for investigating the experimental design. These were 20 experiments involving the three investigated variables of methanol to free fatty acids of WPO ratio, amount of sulfuric acid catalyst and reaction time that were studied on esterification to optimize the condition for decreasing FFA in WPO to less than 2%wt. The transesterifications were 20 experiments involving the three investigated variables of methanol to oil of WPO ratio (the WPO with low acid value from the esterification step), amount of potassium hydroxide catalyst and reaction time that were studied on transesterification to optimize the condition for converting triglycerides to fatty acid methyl ester (FAME) or biodiesel. The results showed the WPO containing 65.09%wt of high FFA and the average molecular weight of fatty acid and WPO are 271 g mol-1 and 885 g mol-1 with the highest palmitic acid content. The optimum conditions for the esterification and transesterification were investigated by using RSM. Waste palm oil biodiesel with optimized condition in two-step catalyzed process is further investigating the properties followed ASTM standard.


**Keywords :** Biodiesel; Palm Oil; Wastewater Pond; Esterification; Response Surface Methodology

## Introduction

Crude palm oil from all of palm oil mill plants in Thailand has been losed into wastewater treatment pond about 1-2% from the milling process of the fresh fruit bunches and washing the machines of factory. This palm oil or waste palm oil (WPO) was floated on the surface of wastewater in wastewater treatment pond and covered on the surface of wastewater. It caused problem in wastewater treatment system. The WPO is waste that must be treated before discharge from the mill plant. So, changing it to be raw material for making biodiesel fuels will be a green technology for a treatment of WPO. In addition, it can diminish the environmental problems, too.

Response surface methodology (RSM) is a useful statistical technique which has been applied in research into complex variable process. It employs multiple regression and correlation analyses as tools to assess the effect of three independent factors on the dependent variables. RSM has been successfully applied in the study and optimization of biodiesel production in fat and oil feed stock (Bhatti *et al*., 2008)

In the present work, the esterification and transesterification steps are studied to optimize condition by RSM. The free fatty acid (FFA) in WPO was reduced to less than 2%wt in the esterification step and the fatty acid methyl ester (FAME) was produced in the transesterification step. After that FAME was analyzed for properties of biodiesel quality by ASTM and EN standard methods.

## Materials and Methods

### Materials

Waste palm oil is palm oil in wastewater treatment pond. The WPO was collected from wastewater treatment pond of the palm oil mill plant in the southern part of Thailand. The chemicals for this research are methanol, sulfuric acid, sodium hydroxide, potassium hydroxide, sodium chloride, N- heptanes ($C_7H_{16}$), methyl heptadecanoate, etc. 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

The solid particles contained in WPO was separated by mixing the WPO with methanol 1:2 by volume at 60°C for 5 min, after that the mixture product was filtrated on filter paper under vacuum filtration immediately to separate the solid particles from the mixture product. The methanol solution in filtrate was evaporated by using the rotary evaporator. The water in filtrate was removed by heating operated at 500 rpm at 105°C for 4 hrs. The final product was investigated to find the fatty acid composition of WPO by using GC and it was used as the feed stock for making biodiesel in the esterification and transesterification steps.

### Apparatus and reaction procedures

*Esterification step:* The reactions were conducted in 50 ml three-necked flask equipped with a reflux condenser and a thermometer. The flask was heated and stirred with magnetic stirrer on agitator heater, fixed stirred at 700 rpm and temperature reaction at 60°C. For esterification experiment, the flask was charged with 10 g of WPO and heated to the setting temperature with agitation. A certain quantity of sulfuric acid catalyst was dissolved in the required amount of methanol. After achieving the setting temperature of the reactant and catalyst, methanol and catalyst were added to the flask. The reaction was timed immediately. When the reaction completed to separate the oil from excess methanol, acid catalyst and water, the oil was washed with water and heated at 105°C. This final product was the feed stock for transesterification step.

*Transesterification step:* Esterified oil (the WPO with less than 2%wt of FFA contents) obtained from esterification step was further reacted with methanol and potassium hydroxide (KOH) that was used as catalyst. The operation condition was 700 rpm of stirring rate and 60°C of temperature reaction. When the reaction completed, methyl ester was separated from glycerol. The methyl ester layer was washed with warm 1%NaCl and warm water. After washing, the methyl ester was subjected to heat at 105°C for removing excess water. Methyl ester was further characterized for physical and chemical properties followed ASTM and EN methods.

**Experimental design**

*Esterification Step:* A five-level and three-factor central composite design (CCD) with 20 experiments was employed in this study. Methanol to FFA in waste palm oil molar ratio (M), acid catalyst concentration (C) and reaction time (T) were the independent variables to optimize the reduction of FFA in WPO. The coded and uncoded levels of the independent variables, independent factor, levels, experimental design and predicted FFA showed in Table 1. The central values (zero level) chosen for experimental design were 20:1(wt/wt) of methanol to FFA in waste palm oil molar ratio, 5.00% (wt/wt) of acid catalyst concentration and 120 min of reaction time.

*Transesterification step:* A five-level and three-factor CCD with 20 experiments was employed in this study. Methanol to esterified oil molar ratio (M), alkaline catalyst concentration (C) and reaction time (T) were the independent variables to optimize the conversion of triglycerides to FAME or biodiesel from the WPO. The coded and uncoded levels of the independent variables, independent factor, levels, experimental design and predicted FAME showed in Table2. The central values (zero level) chosen for experimental design were 10 (wt/wt) of methanol to esterified oil molar ratio, 1.50% (wt/wt) of alkaline catalyst concentration and 30 min of reaction time.

The experimental data were analyzed by the RSM regression procedure using a second-order polynomial as showed in Equation 1.

$$Y = \beta_0 + \sum_{i=1}^{3}\beta_i X_i + \sum_{i=1}^{3}\beta_{ii} X_i^2 + \sum_{i=1}^{2}\sum_{i=j+1}^{2}\beta_{ij} X_i X_j \qquad (1)$$

Where $Y$ is the response (%FFA or %FAME), $\beta_0$, $\beta_i$, $\beta_{ii}$ and $\beta_{ij}$ are intercept, linear, quadratic and interaction constant coefficients, respectively. ANOVA and RSM were performed using the SPSS software (Jeong *et al*., 2009)

## Results and Discussion

**Properties of waste palm oil**

The WPO had FFA contents of 65.09%. The average molecular weight (g/mole) of WPO was determined by a weight average method utilizing the fatty acid profiles (Table 3). The molecular weight of each fatty acid found in WPO was multiplied by its corresponding weight percentage as determined by GC. This average molecular weight was used to calculate the mole ratio of methanol to WPO in transesterification step.

**Optimization of esterification step**

The FFA contents for esterification step at the design points were given in Table 4. The statistical analysis

*Table 1* Independent variables and levels used for central composite design (CCD) for esterification step.

| Variables | Symbols (uncoded) | Code levels[a] | | | | |
|---|---|---|---|---|---|---|
| | | -1.68 (-α) | -1 | 0 | +1 | +1.68 (+α) |
| Methanol to FFA in waste palm oil molar ratio | M | 11.6:1 | 15:1 | 20:1 | 25:1 | 28.4:1 |
| $H_2SO_4$ concentration (% wt/wt) | C | 3.32 | 4.00 | 5.00 | 6.00 | 6.68 |
| Reaction time (min) | T | 69.6 | 90 | 120 | 150 | 170.4 |

[a] Transformation of variable levels from code (X) to uncoded could be obtained as: M= 20+5X ,C= 5+1X and T=120+30X

*Table 2* Independent variables and levels used for central composite design (CCD) for transesterification step.

| Variables | Symbols (uncoded) | Code levels[a] | | | | |
|---|---|---|---|---|---|---|
| | | -1.68 ($-\alpha$) | -1 | 0 | +1 | +1.68 ($+\alpha$) |
| Methanol to esterified waste palm oil molar ratio | M | 5.80 | 7.50 | 10.00 | 12.50 | 14.20 |
| KOH concentration (% wt/wt) | C | 0.66 | 1.00 | 1.50 | 2.00 | 2.34 |
| Reaction time (min) | T | 4.80 | 15.00 | 30.00 | 45.00 | 55.20 |

[a] Transformation of variable levels from code (X) to uncoded could be obtained as: M= 10+2.5X ,C= 1.5+0.5X and T=30+15X

*Table 3* Fatty acid composition of waste palm oil.

| Fatty acid | Formula | Structure | %wt |
|---|---|---|---|
| Myristic | $C_{14}H_{28}O_2$ | 14:0 | 0.87 |
| Palmitic | $C_{16}H_{32}O_2$ | 16:0 | 47.40 |
| Palmitoleic | $C_{16}H_{30}O_2$ | 16:1 | 1.12 |
| Steric | $C_{18}H_{36}O_2$ | 18:0 | 4.29 |
| Oleic | $C_{18}H_{34}O_2$ | 18:1 | 36.30 |
| Linoleic | $C_{18}H_{32}O_2$ | 18:2 | 6.95 |
| Erucic | $C_{20}H_{40}O_2$ | 20:0 | 3.06 |

model was performed to determine the variance (ANOVA). The linear regression coefficients were obtained by employing a least square technique to predict quadratic polynomial model for FFA. The models characteristics and the coefficients were indicated that the predictability of the model is at 95% confidence level.

The analysis of variance (ANOVA) showed that the model F-values of 13.166 with significance was 0.000 which less than 0.05 for the models, implied the model was significant. The high correlation coefficient ($R^2$=0.922) indicates that the model is suitable for represent the real relationships among the parameters studied.

The model to predict the FFA content in esterification step is presented in Equation 2.

$$Y = 30.171 + 0.143M - 10.384C + 0.002T - 0.002M^2 + 0.958C^2 + 0.00001513T^2 - 0.023MC + 0.001CT + 0.000MT \quad (2)$$

**Response surface plots of esterification step**

The optimized levels of variables were determined by constructing three-dimensional surface plots according to Equation 2. Fig. 1(a) shows the effect of methanol to FFA in waste palm oil molar ratio (M), acid catalyst amount (C) on the FFA of WPO. Fig. 1(b) shows the effect of methanol to FFA in waste palm oil molar ratio, reaction time (T), on the FFA and Fig. 1(c) shows the effects of acid catalyst amount and reaction time on the FFA.

Fig. 1(a), 1(b) and 1(c) indicates that the optimum values in reducing FFA to lower than 2%wt were 4.5-5.6% (wt/wt) of acid catalyst amount and 80-120 min of reaction time. Methanol should be used between 23 to 28 moles of methanol to FFA in WPO molar ratio which is obtained from the RSM. The optimized condition was predicted by using optimization function of the SPSS software at 28 moles methanol to FFA in waste palm oil molar ratio,

*Table 4* Central composite design (CCD) arrangement and response for esterification and transesterification step.

| Treatment | M | C | T | Free Fatty Acid (%FFA) | | Fatty Acid Methyl Ester (%FAME) | |
|---|---|---|---|---|---|---|---|
| | | | | Experimental | Predicted | Experimental | Predicted |
| 1 | -1 | -1 | -1 | 4.51 | 4.94 | 70.04 | 67.86 |
| 2 | -1 | -1 | 1 | 4.53 | 5.52 | 66.74 | 66.36 |
| 3 | -1 | 1 | -1 | 4.35 | 4.65 | 71.04 | 70.32 |
| 4 | -1 | 1 | 1 | 3.79 | 5.23 | 71.41 | 68.82 |
| 5 | 1 | -1 | -1 | 2.56 | 2.82 | 78.05 | 80.21 |
| 6 | 1 | -1 | 1 | 2.42 | 3.52 | 80.60 | 80.78 |
| 7 | 1 | 1 | -1 | 1.60 | 2.07 | 84.65 | 84.49 |
| 8 | 1 | 1 | 1 | 1.55 | 2.77 | 83.30 | 85.06 |
| 9 | -1.68 | 0 | 0 | 6.76 | 7.64 | 53.19 | 56.51 |
| 10 | +1.68 | 0 | 0 | 3.27 | 3.80 | 83.05 | 80.53 |
| 11 | 0 | -1.68 | 0 | 3.45 | 3.31 | 75.83 | 75.48 |
| 12 | 0 | +1.68 | 0 | 0.88 | 2.44 | 79.97 | 81.14 |
| 13 | 0 | 0 | -1.68 | 1.57 | 2.52 | 79.47 | 80.09 |
| 14 | 0 | 0 | +1.68 | 3.13 | 3.59 | 79.45 | 79.31 |
| 15 | 0 | 0 | 0 | 2.82 | 3.02 | 72.48 | 75.89 |
| 16 | 0 | 0 | 0 | 2.18 | 3.02 | 76.01 | 75.89 |
| 17 | 0 | 0 | 0 | 2.82 | 3.02 | 80.03 | 75.89 |
| 18 | 0 | 0 | 0 | 2.13 | 3.02 | 70.26 | 75.89 |
| 19 | 0 | 0 | 0 | 1.57 | 3.02 | 78.43 | 75.89 |
| 20 | 0 | 0 | 0 | 2.10 | 3.02 | 77.93 | 75.89 |

5.5% $H_2SO_4$ for 90 min of reaction time. This condition can reduce FFA to 1.76%wt.

**Optimization of transesterification step**

The methyl ester contents for transesterification step at the design points are given in Table 4. The predictability of the model is at 95% confidence level. The analysis of variance (ANOVA) showed that the model F-values was 8.966 (FAME) with significance of 0.001 that less than 0.05 for the models. It implied the model was significant. The high correlation coefficient ($R^2$=0.890) indicates that the model is suitable to represent the real relationships among the parameters studied.

The model to predict the FAME is presented in Equation 3.

$$Y = 52.317 - 2.661M + 39.939C - 0.479T + 0.137M^2 - 10.446C^2 + 0.006T^2 + 0.363MC + 0.069CT \quad (3)$$

**Response surface plots of transesterification step**

The optimized levels of variables were determined by constructing three-dimensional surface plots according to Equation be consistent in format used. Fig. 1(d) shows the effect of methanol to esterified oil molar ratio (M), alkaline catalyst amount (C) on the FAME. Fig. 1(e) shows the effect of methanol to esterified oil molar ratio, reaction time (T), on the FAME and Fig. 1(f) shows the effects

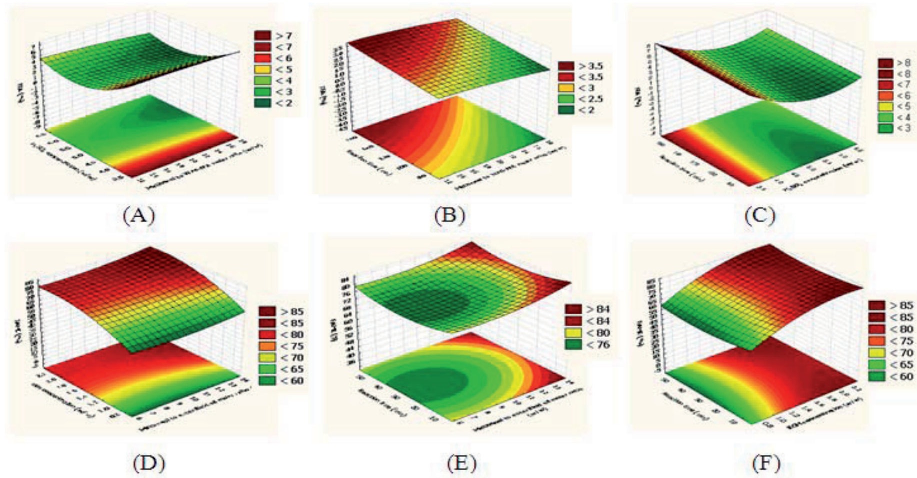


***Figure 1*** Response surface plots representing the effect of factors on FFA (A, B, C) and FAME (D, E, F) predicted from the quadratic polynomial model.

of alkaline catalyst amount and reaction time on the FAME.

Fig. 1(d), 1(e) and 1(f) indicates the optimum values of amount of alkaline catalyst and the reaction time from RSM was 1.4-2.2% of KOH and 30-55 min of reaction time. Mole ratio of methanol to esterified waste palm oil was 10 to 14 moles which is obtained from the RSM. The optimized condition was predicted using optimization function of the SPSS software at 14 moles methanol to esterified oil molar ratio, 1.5% KOH for 55 min of reaction time. This condition can convert triglycerides to 84.05% of FAME.

## Conclusion

The WPO with high FFA (65.09% of FFA) could be used as raw material to produce biodiesel. The FFA in WPO can be reduced to less than 2% by optimizing the CCD and RSM in esterification step. The optimum conditions of esterification reaction were obtained at 28 moles of methanol to FFA in WPO molar ratio, 5.5% sulfuric acid concentration in 90 min of reaction time and 60$^{o}$C of reaction temperature. In transesterification step, the optimum conditions were 14 moles methanol to esterified oil molar ratio, 1.5% KOH for 55 min of reaction time which can convert triglycerides to FAME. The result gave methyl ester content at 84.05% according to EN 14103 method. The properties of waste palm oil methyl ester met the standards for community biodiesel of Thailand.

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