

Optimization of Biodiesel Production from Trap Grease via Two-Step Catalyzed Process

S. Karnasuta^{1,*}, V. Punsuvon², C. Chiemchaisri³
and K. Chunkao⁴

¹ College of Environment, Karsetsart University, Bangkok 10900, Thailand

² Department of Chemistry, Faculty of Science, Karsetsart University,
Bangkok 10900, Thailand

³ Department of Environmental Engineering, Faculty of Engineering,
Karsetsart University, Bangkok 10900, Thailand

⁴ College of Environment, Karsetsart University, Bangkok 10900, Thailand

*Corresponding autho:sujinna@gmail.com, Tel: +(662)-9428981 ext 767

Abstract: The main purpose of this research was to develop a two-step biodiesel production technique from trap grease as a raw material. The developed process consists of esterification and transesterification steps. With special attention to optimize the first step is the acid catalyzed esterification to reduce the free fatty acid (FFA) content and the second step is the alkali catalyzed transesterification for converting to fatty acid methyl ester (FAME). Trap grease containing 26.2% of high free fatty acid and molecular weight of 846 g/mol with the highest oleic acid, could be reduced to less than 2% by using the response surface methodology (RSM) in acidic catalyzed esterification and alkali catalyzed transesterification of the two step catalyze process. Optimum condition for the esterification

was found to be 0.43 v/v of methanol-to-oil ratio, 2.5% v/v sulfuric acid concentration in 4 hours of reaction time. This optimum value gave an acid value of 2.66 mgKOH/g or 1.30% of FFA. The optimum conditions for the transesterification were 0.26 v/v of methanol-to-oil ratio, 1% w/v potassium hydroxide concentration in 1 hour of reaction time. The maximum fatty acid methyl ester content under the optimum conditions of the variables was 95.49%. Trap grease biodiesel with optimum condition in two-step catalized process has properties satisfying both the biodiesel standard of ASTM D 6751 and EN 14214. This developed production technique could be used for trap grease from cafeteria and restaurant wastewater while solving water pollution. Furthermore, the technique for the two step catalyzed process could be used in pilot plant.

Keywords: Biodiesel, Trap grease, optimization, wastewater, RSM, esterification, transesterification.

1. Introduction

Currently, an increase of waste grease and oils from households and restaurants in the city, is a growing environmental problem in Thailand and worldwide. This residue is regularly poured down sanitary sewer systems where it could cause blockages, resulting in problems for wastewater treatment plants and energy loss. Trap grease is waste fats and oils that are collected by the special traps before they are poured down the drain. Trap grease has high free fatty acids (FFA) and high moisture levels which affect the transesterification reaction in converting these feedstocks into biodiesel [1].

Biodiesel can be prepared from the high FFA fats and oils by the two step process (esterification and transesterification reactions). This is better than the one step process (transesterification reaction) in terms of lower reaction temperature, reduced catalyst and alcohol used and high yields obtained [2-4]. The main factors affecting transesterification are the amount of alcohol and catalyst, reaction temperature, pressure and time, the contents of free fatty acid (FFAs) and water in oils. Conversion is complicated if oil contains large amounts of FFA (>2% w/w) that will form soap with alkaline catalyst. The soap can prevent separation of the biodiesel from the glycerin fraction and contributes to emulsion formation during the water washing step. Acid catalyst such as sulfuric acid can esterify the free fatty acid to methyl ester in esterification reaction [5].

Response surface methodology (RSM) is a useful statistical technique which has been applied in research to complex variable processes. The multiple regression and correlation analyses are used as tools to assess the effects of two or more independent factors on the dependent variables. Furthermore, the central composite design (CCD) of response surface methodology has been applied in the optimization of several biotechnological and chemical processes. Its main advantage is the reduced number of experimental runs required to generate sufficient information for statistically acceptable results. Response surface methodology has been successfully applied for optimization of biodiesel production in fats and oil feedstocks - for instance mahua oil (*Madhuca indica*) [6], jatropha oil (*Jatropha curcas*) [7], waste rapeseed oil [8] and animal fat [9].

This study concentrated on developing a two-step biodiesel production technique from trap grease as a raw material. The developed process consists of esterification and transesterification steps. With special attention to optimize the first step is the acid catalyzed process (esterification) to reduce the free fatty acid (FFA) content and the second step is the alkali catalyzed process (transesterification) to produce fatty acid methyl ester (FAME) and to determine the fuel properties of trap grease biodiesel for vehicle use. The optimized biodiesel production technique from trap grease with the two step catalyzed process could be evaluated for the utilization of biodiesel plant.

2. Materials and Methods

Trap greases were collected from the grease trap tank in local cafeterias and restaurants. Food remaining in trap grease used in this study was removed by physical separation using filtration. Methanol, potassium hydroxide (KOH) in pellet and sulfuric acid, methyl heptadecanoate were analytical reagent (AR) grade. The reference standards of fatty acid methyl ester were obtained from Supelco.

2.1 Experimental design

The objective of this study was to develop a process for producing biodiesel from a low-cost feedstock like trap grease. The process consists of two step processes: acid esterification and alkali tranesterification. Acid esterification: the firsts step reduces the FFA value of trap grease to about less than 2% using acid catalyzed esterification. After removing the impurities of the product during

the first step, it is transesterified to mono-esters of fatty acids using alkali transesterification. The parameters affected the process are factors such as alcohol to oil ratio, catalyst amount and reaction temperature.

The wastewater separated trap grease had contained wastewater, solid particles, high FFA and many other chemicals. Hence the water and FFA were a problem during transesterification. Trap grease was treated before an experiment of two step catalyzed process. A solid portion of trap grease was removed using filtration. Water was removed by boiling at 105°C.

The treated trap grease was investigated for % free fatty acid (FFA). Kinematic viscosity of trap grease was determined using an Ubbelohde glass capillary viscometer. The trap grease was investigated for water content and fatty acid compositions of trap grease were determined by GC. Identification of fatty acids contained in trap grease was performed by comparison of retention times with fatty acids standard to determine the molecular weight of trap grease for calculating the molar ratio of methanol to oil in the experiment.

2.2 Acid catalyzed esterification

A five-level-three-factor central composite design (CCD) was employed in this optimization study, requiring 23 experiments [6]. Methanol-to-oil ratio (M), catalyst concentration (C) and reaction time (T) were the independent variables selected to optimize the reduction of acid value (AV) of trap grease after sulfuric acid catalyzed esterification. The coded and uncoded levels of the independent variables were given in Table 1. Two replications were carried out for all design points.

The central values (zero level) chosen for experimental design were methanol:oil ratio of 0.43 (v/v), catalyst concentration of 2.5% (v/v) and reaction time of 4 hours.

Table 1. Independent variables and levels used for central composite design for acid catalyzed esterification of two-step catalyzed process.

| Variables | Symbols | Levels ^a | | | | |
|-----------------------------------|---------|---------------------|------|------|------|---------------|
| | | -1.68 (-α) | -1 | 0 | +1 | +1.68 (+α) |
| Methanol-to-oil ratio (v/v) | M | 0.28 | 0.34 | 0.43 | 0.51 | 0.58 |
| Catalyst concentration (% v/v) | C | 0.02 | 1 | 2.5 | 4 | 5.02 |
| Reaction time (hr) | T | 0.64 | 2 | 4 | 6 | 7.36 |

^a Transformation of variable levels from coded (X) to uncoded could be obtained as: $M = 0.43 + 0.09X$, $C = 2.5 + 1.5X$ and $T = 4 + 2X$

2.3 Quantitative analysis of Acid value

Acid value was determined by the acid–base titration technique. Potassium hydroxide (KOH) was used as a standard alkali solution. Free fatty acid of oil (%) was calculated as percent oleic, lauric or palmitic. The acid value was divided by 1.99, 2.81 or 2.19 respectively. The Acid value was calculated by the following Equation 1.

$$\text{Acid value} = \frac{(A-B) \times N \times 56.1}{W} \quad (1)$$

A = mL of standard alkali used in the titration

B = mL of standard alkali used in the titrating the blank

N = normality of standard alkali

W = grams of sample

2.4 Alkali catalyzed transesterification

A five-level-three-factor central composite design (CCD) was also used. Methanol-to-oil ratio (M'), catalyst concentration (C') and reaction time (T') were the independent variables selected to optimize condition for % fatty acid methyl ester (% FAME) production after potassium hydroxide catalyzed transesterification.

The coded and uncoded levels of the independent variables in this step were given in Table 2. Two replications were carried out for all design points. The central values (zero level) chosen for experimental design were methanol:oil molar ratio of 0.26 (v/v), catalyst concentration of 1% (w/v), reaction time of 1 hour.

2.5 Quantitative analysis of fatty acid methyl ester content

The content of fatty acid methyl ester was measured by gas chromatography. Chromatographic analysis was performed on a Agilent Technologies GC-6890 gas chromatograph equipped with a DB-WAX 127-7012 column (30 m x 0.32 mm x 0.25 μm ; Agilent Technologies, USA) and a flame ionization detector (FID). The operating conditions were the following: The temperatures of injector and detector were set at 250°C. The split ratio was 1:50. Helium was used as carrier gas. The analysis of biodiesel for each sample was performed by dissolving 0.05 g of biodiesel sample and 1 ml of Methyl hepadecanoate (internal standard) and injecting 1 μl of this solution in the gas chromatograph (GC). Fatty acid methyl ester content was calculated by the following Equation 2.

$$C = \frac{\Sigma A - A_{SI}}{A_{SI}} \times \frac{C_{SI}}{m} \times \frac{V_{SI}}{m} \times 100 \quad (2)$$

C = the fatty acid methyl ester content (wt%)

ΣA = the total peak area from the methyl ester

A_{SI} = the peak area of methyl heptadecanoate

C_{SI} = the concentration of methyl heptadecanoate solution (mg/ml) used

V_{SI} = the volume of methyl heptadecanoate solution (ml) used

m = the weight of the sample (g)

Table 2. Independent variables and levels used for central composite design for alkali catalyzed transesterification of two-step catalyzed process.

| Variables | Symbols | Levels ^a | | | | |
|-----------------------------------|---------|------------------------|------|------|------|------------------------|
| | | -1.68 (- α) | -1 | 0 | +1 | +1.68 (+ α) |
| Methanol-to-oil ratio (v/v) | M' | 0.19 | 0.22 | 0.26 | 0.30 | 0.33 |
| Catalyst concentration (% w/v) | C' | 0.16 | 0.5 | 1 | 1.5 | 1.84 |
| Reaction time (hr) | T' | 0.45 | 0.67 | 1 | 1.33 | 1.55 |

^a Transformation of variable levels from coded (X) to uncoded could be obtained as: $M' = 0.26 + 0.04X$, $C' = 1 + 0.5X$ and $T' = 1 + 0.33X$

2.6 Statistical analysis

The experimental data were analyzed by the response surface regression procedure using the following second-order polynomial as shown in Equation 3.

$$Y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ij} X_i^2 + \sum_{i>j}^k \sum_j^k b_{ij} X_i X_j \quad (3)$$

Where y is the response, x_i and x_j are the uncoded independent variables and β_0 , β_i , β_{ii} and β_{ij} are intercept, linear, quadratic and interaction constant coefficients respectively, k is the number of factors studied and optimized in the experiment. SPSS package was used for regression analysis and analysis of variance (ANOVA). Response surfaces and contour plots were developed using the fitted quadratic polynomial equation obtained from regression analysis, holding one of the independent variables at a constant value corresponding to the stationary point and changing the other two variables. Confirmatory experiments were carried out to validate the equation, using combinations of independent variables, which were not part of the original experimental design but within the experimental region [6].

2.7 Biodiesel properties analysis

The analysis of biodiesel quality contained density (at 15°C), viscosity (at 40°C), flash point, acid value, iodine value, cloud point, and was carried out using the methods developed by Center of Excellence-oil palm, Kasetsart University and compared with some ASTM D6751 and EN 14214 biodiesel standards.

3. Results and Discussion

3.1 Properties of trap grease

The trap grease separated from cafeteria wastewater was originally contaminated with water, solid particles. Hence, a solid portion of trap grease was removed by filtering through filter paper.

Water was removed by boiling at 105°C. Next, the treated trap grease was investigated for free fatty acid (FFA) percentage, kinematic viscosity and fatty acid compositions of trap grease. The initial free fatty acid (FFA) in trap grease contains 26.197% corresponding to an acid value of 52.13 mg KOH/g, 29.8 cSt of kinematic viscosity at 40°C. Water content of trap grease was 1.156%. The result of major fatty acid profile of trap grease was octanoic acid (C8:0), decanoic acid (C10:0), lauric acid (C12:0), myristic acid (C14:0), palmitic acid (C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), arachidic acid (C20:0), behenic acid (C22:0), lignoceric acid (C24:0). The mean molecular weight of trap grease was 846 g/mol. Properties of trap grease were shown in Table 3.

3.2 Acid catalyzed esterification

Experimental values obtained for acid value responses at the design points are given in Table 4. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA) in Table 5 and multiple regression coefficients indicated that were obtained by employing a least square technique to predict quadratic polynomial model for the acid value (Table 6). The regression model for data was found to be highly significant with a correlation coefficient of determination, R^2 was 0.842. This implies that the full quadratic regression model can be used to explain acid catalyzed esterification. From the determined coefficients, the predicted model for acid value was shown in Equation 4.

$$Y = 78.215 - 217.419M - 9.392C - 4.680T + 237.241M^2 + 2.129C^2 + 2.544E - 03T^2 - 11.979MC + 6.441MT + 0.446CT \quad (4)$$

Table 3. Physical and chemical properties of the treated trap grease.

| Property | amount |
|-----------------------------------|--------|
| Acid value (mg KOH/g) | 52.1 |
| Kinematic viscosity at 40°C (cSt) | 29.8 |
| Water content (%wt) | 1.156 |
| Fatty acid composition (%wt) | |
| octanoic acid (C8:0) | 0.4 |
| decanoic acid (C10:0) | 0.4 |
| lauric acid (C12:0) | 3.0 |
| myristic acid (C14:0) | 1.9 |
| palmitic acid (C16:0) | 25.7 |
| palmitoleic acid (C16:1) | 2.0 |
| stearic acid (C18:0) | 5.5 |
| oleic acid (C18:1) | 39.4 |
| linoleic acid (C18:2) | 19.8 |
| linolenic acid (C18:3) | 1.0 |
| arachidic acid (C20:0) | 0.2 |
| behenic acid (C22:0) | 0.08 |
| lignoceric acid (C24:0) | 0.09 |
| average molecular weight (g/mol) | 846 |

The relationship between independent and dependent variables of the developed model indicated that with low methanol to oil ratio, there was reducing of acid value with increasing in catalyst concentration (Fig. 1a) and reaction time (Fig. 1b). For low catalyst concentration, acid value decreased with increasing reaction time (Fig. 1c). The response surface plots were generally the graphical representations of the regression equation. Each surface curve represented an infinite number of combinations of two test variables with the other two maintained at their respective zero level. The plots made it easy to understand the interactions between two variables and locate their optimum levels

of three variables. This were found to be 0.43 v/v methanol-to-oil ratio, 2.5% v/v catalyst concentration and 4 hour reaction time locating the stationary point in the experimental region. The model predicted that the minimum acid value of 2.661 mg KOH/g was obtained by putting the optimum levels of X_i in the regression equation 2 under the above optimum conditions of the variables.

Table 4. Central composite design arrangement and response for acid catalyzed esterification.

| Treatment t | M | C | T | Methanol/oil ratio(v/v) | H ₂ SO ₄ concentration (%v/v) | Reaction time (hr) | Acid value (mgKOH/g) | |
|----------------|-------|-------|-------|----------------------------|---|-----------------------|-------------------------|-----------|
| | | | | | | | Experimental | Predicted |
| 1 | -1 | -1 | -1 | 0.34 | 1.00 | 2.00 | 14.77 | 16.30 |
| 2 | -1 | -1 | 1 | 0.34 | 1.00 | 6.00 | 4.92 | 8.21 |
| 3 | -1 | 1 | -1 | 0.34 | 4.00 | 2.00 | 5.35 | 10.52 |
| 4 | -1 | 1 | 1 | 0.34 | 4.00 | 6.00 | 3.74 | 7.78 |
| 5 | 1 | -1 | -1 | 0.51 | 1.00 | 2.00 | 14.69 | 13.78 |
| 6 | 1 | -1 | 1 | 0.51 | 1.00 | 6.00 | 12.14 | 10.06 |
| 7 | 1 | 1 | -1 | 0.51 | 4.00 | 2.00 | 2.29 | 1.88 |
| 8 | 1 | 1 | 1 | 0.51 | 4.00 | 6.00 | 2.21 | 3.52 |
| 9 | -1.68 | 0 | 0 | 0.28 | 2.50 | 4.00 | 17.11 | 10.37 |
| 10 | +1.68 | 0 | 0 | 0.58 | 2.50 | 4.00 | 2.81 | 5.10 |
| 11 | 0 | -1.68 | 0 | 0.42 | 0.02 | 4.00 | 20.28 | 20.64 |
| 12 | 0 | +1.68 | 0 | 0.42 | 5.02 | 4.00 | 15.7 | 11.09 |
| 13 | 0 | 0 | -1.68 | 0.42 | 2.50 | 0.64 | 7.22 | 5.45 |
| 14 | 0 | 0 | +1.68 | 0.42 | 2.50 | 7.36 | 2.29 | -0.19 |
| 15 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.47 | 2.60 |
| 16 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.55 | 2.60 |
| 17 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.55 | 2.60 |
| 18 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.49 | 2.60 |
| 19 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.51 | 2.60 |
| 20 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.47 | 2.60 |
| 21 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.51 | 2.60 |
| 22 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.45 | 2.60 |
| 23 | 0 | 0 | 0 | 0.42 | 2.50 | 4.00 | 2.49 | 2.60 |

Many published papers suggested that alkaline catalysts could be applied when FFA content in the oils or fats is less than 2%. The optimum combinations for reducing the acid level of mahua oil to less than 2% after pretreatment was 0.32 v/v methanol-to-oil ratio,

1.24% v/v H₂SO₄ catalyst and 1.26 hr reaction time at 60°C [6]. Moreover the optimum combination for reducing the FFA of *Jatropha curcas* oil from 14% to less than 1% was found to be 1.43% v/v H₂SO₄ acid catalyst, 0.28 v/v methanol-to-oil ratio and 88-min reaction time at a reaction temperature of 60°C [7]. It was reported in the literature that a two step catalyzed process was adopted to prepare biodiesel from waste fats and oils whose acid value was 75.92±0.036 mgKOH/g [3].

Table 5. Analysis of variance (ANOVA) for the quadratic polynomial model for esterification.

| Model | Sum of Squares | df | Mean Square | F | Sig. |
|------------|----------------|----|-------------|-------|-------------------|
| Regression | 633.165 | 9 | 70.352 | 6.324 | .002 ^a |
| Residual | 144.630 | 13 | 11.125 | | |
| Total | 777.796 | 22 | | | |

^aPredictors: (Constant), X23, X1, X33, X22, X12, X13, X2, X3, X11

Table 6. Regression coefficients of predicted quadratic polynomial model for the regression equation for esterification.

| Model | Unstandardized Coefficients | | Standardized Coefficients | t | Sig. |
|--------------|-----------------------------|------------|---------------------------|--------|-------|
| | B | Std. Error | Beta | | |
| 1 (Constant) | 78.215 | 25.762 | | 3.036 | 0.010 |
| X1 | -217.419 | 99.601 | -2.503 | -2.183 | 0.048 |
| X2 | -9.392 | 4.660 | -1.860 | -2.015 | 0.065 |
| X3 | -4.680 | 3.546 | -1.240 | -1.320 | 0.210 |
| X11 | 237.241 | 107.397 | 2.360 | 2.209 | 0.046 |
| X22 | 2.129 | 0.377 | 2.223 | 5.643 | 0.000 |
| X33 | 2.544E-03 | 0.210 | 0.006 | 0.012 | 0.991 |
| X12 | -11.979 | 9.243 | -1.072 | -1.296 | 0.217 |
| X13 | 6.441 | 6.932 | 0.788 | 0.929 | 0.370 |
| X23 | 0.446 | 0.393 | 0.480 | 1.135 | 0.277 |

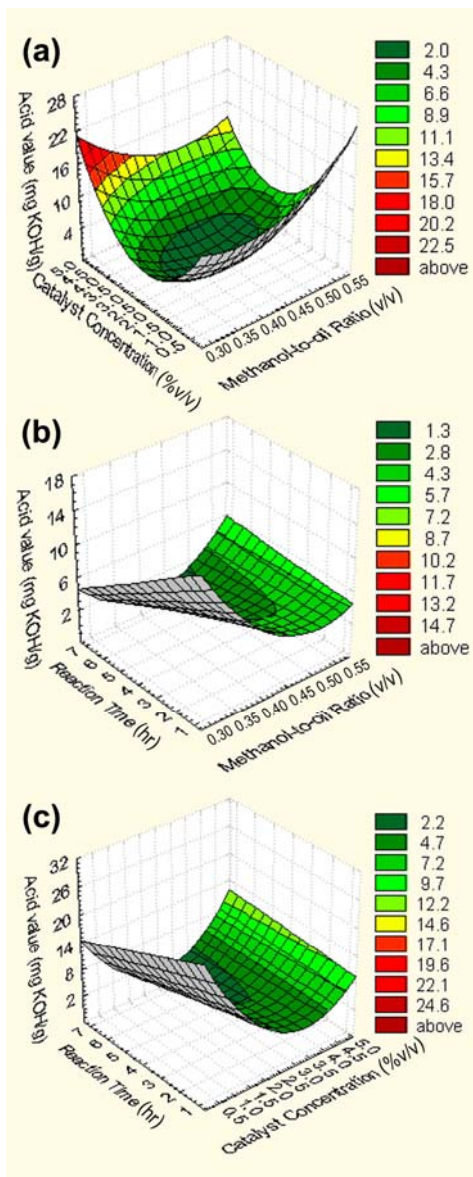


Figure 1. Response surface and contour plots representing the effect of factors on acid value predicted from the quadratic polynomial model.

3.3 Alkali catalyzed transesterification

Experimental values obtained for acid value responses at the design points are given in Table 7. Statistical analysis of the model was performed to evaluate the analysis of variance or ANOVA (Table 8) and multiple regression coefficients indicated were obtained by employing a least square technique to predict quadratic polynomial model for the fatty acid methyl ester content (Table 9). The model was tested for adequacy by analysis of variance. The regression model for data was found to be highly significant with a correlation coefficient of determination, (R^2) of 0.844. Using the coefficients determine, the predicted model for percentage of fatty acid methyl ester (FAME) in Equation 5.

$$Y' = -17.471 + 815.371 M' + 20.985 C' - 8.678 T' - 1636.963 M'^2 - 12.884 C'^2 - 10.563 T'^2 - 14.375 M' C' + 52.083 M' T' + 12.955 C' T' \quad (5)$$

The relationship between independent and dependent variables of the developed model in the response surface plots at the stationary value of 1 hour reaction time, 1% w/v catalyst concentration and 0.26 v/v methanol to oil ratio, respectively, is shown in Fig 2. At low methanol to oil ratio, %FAME increased with increasing catalyst concentration (Fig 2a). At low reaction time it was shown that %FAME raised with increasing methanol to oil ratio (Fig 2b). For high catalyst concentration, %FAME increased with increasing reaction time (Fig 2c).

From the response surface and contour plots, the optimum levels of three variables were found to be 0.26 v/v methanol-to-oil ratio, 1% w/v catalyst concentration and 1 hour reaction time. The model predicted the maximum percentage of fatty acid methyl ester content of 95.49%. In the literature, Model predicts that the maximum conversion to

biodiesel for alkali transesterification of waste rapeseed, under the optimum conditions of the variables, was 83.34 wt% [8].

Table 7. Central composite design arrangement and response for alkali catalyzed transesterification.

| Treatment | M' | C' | T' | Methanol/oil ratio (v/v) | KOH Concentration (%w/v) | Reaction time (hr) | Free fatty acid methyl ester (%) | |
|-----------|-------|-------|-------|--------------------------------|--------------------------------|-----------------------|----------------------------------|-----------|
| | | | | | | | Experimental | Predicted |
| 1 | -1 | -1 | -1 | 0.22 | 0.50 | 0.67 | 90.30 | 89.83 |
| 2 | -1 | -1 | 1 | 0.22 | 0.50 | 1.33 | 84.30 | 82.00 |
| 3 | -1 | 1 | -1 | 0.22 | 1.50 | 0.67 | 92.30 | 90.57 |
| 4 | -1 | 1 | 1 | 0.22 | 1.50 | 1.33 | 87.40 | 91.28 |
| 5 | 1 | -1 | -1 | 0.30 | 0.50 | 0.67 | 92.70 | 89.18 |
| 6 | 1 | -1 | 1 | 0.30 | 0.50 | 1.33 | 82.00 | 84.10 |
| 7 | 1 | 1 | -1 | 0.30 | 1.50 | 0.67 | 86.10 | 88.77 |
| 8 | 1 | 1 | 1 | 0.30 | 1.50 | 1.33 | 91.40 | 92.23 |
| 9 | -1.68 | 0 | 0 | 0.19 | 1.00 | 1.00 | 86.80 | 87.33 |
| 10 | +1.68 | 0 | 0 | 0.33 | 1.00 | 1.00 | 88.60 | 87.59 |
| 11 | 0 | -1.68 | 0 | 0.26 | 0.16 | 1.00 | 80.00 | 82.67 |
| 12 | 0 | +1.68 | 0 | 0.26 | 1.84 | 1.00 | 93.30 | 90.12 |
| 13 | 0 | 0 | -1.68 | 0.26 | 1.00 | 0.45 | 92.10 | 94.11 |
| 14 | 0 | 0 | +1.68 | 0.26 | 1.00 | 1.55 | 93.00 | 90.47 |
| 15 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 95.90 | 95.49 |
| 16 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 96.10 | 95.49 |
| 17 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 95.00 | 95.49 |
| 18 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 95.40 | 95.49 |
| 19 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 95.70 | 95.49 |
| 20 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 95.50 | 95.49 |
| 21 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 95.10 | 95.49 |
| 22 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 95.10 | 95.49 |
| 23 | 0 | 0 | 0 | 0.26 | 1.00 | 1.00 | 95.50 | 95.49 |

The response surface methodology (RSM) was used to optimize the conditions for the maximum conversion to biodiesel and understand the significance and interaction of the factors affecting the biodiesel production. The results showed that catalyst concentration and reaction time were the limiting conditions and little variation in their value would alter the conversion. At the same time, there was a significant mutual interaction between catalyst concentration and reaction time. The result of our study was similar to Jeong et al. [9] that studied response surface methodology, and the effects of five-level-three-

factors for optimizing the reaction conditions of animal fat biodiesel production. The referred study contained 20 individual experiments, which were designed to study reaction temperature, catalyst amount, and oil-to-methanol molar ratio. A statistical model predicted that the highest conversion yield of animal fat biodiesel would be 98.6%, at the following optimized reaction conditions: a reaction temperature of 65°C, a catalyst amount of 1.26%, and an oil-to-methanol molar ratio of 7.5:1, and 20-min reaction time. Using these optimal factor values under experimental conditions in three independent replicates, when fatty acid methyl ester content was $97.8 \pm 0.6\%$, it was found that the value was well within the range predicted by the mode.

Table 8. Analysis of variance (ANOVA) for the quadratic polynomial model from the transesterification.

| Model | Sum of Squares | df | Mean Square | F | Sig. |
|------------|----------------|----|-------------|-------|-------------------|
| Regression | 424.395 | 9 | 47.155 | 7.830 | .001 ^a |
| Residual | 78.291 | 13 | 6.022 | | |
| Total | 502.686 | 22 | | | |

^aPredictors: (Constant), X23, X11, X33, X22, X12, X13, X2, X3, X1

Table 9. Regression coefficients of predicted quadratic polynomial model for alkali catalyzed transesterification.

| Model | Unstandardized Coefficients | | Standardized Coefficients | t | Sig. |
|--------------|-----------------------------|------------|---------------------------|-------|------|
| | B | Std. Error | Beta | | |
| 1 (Constant) | -17.471 | 33.008 | | -0.53 | .606 |
| X1 | 815.371 | 204.150 | 5.47 | 3.99 | .002 |
| X2 | 20.985 | 13.453 | 1.73 | 1.56 | .143 |
| X3 | -8.678 | 21.340 | -0.47 | -0.41 | .691 |
| X11 | -1636.963 | 360.843 | -5.73 | -4.54 | .001 |
| X22 | -12.884 | 2.467 | -2.20 | -5.22 | .000 |
| X33 | -10.563 | 5.736 | -1.16 | -1.84 | .088 |
| X12 | -14.375 | 43.382 | -0.33 | -0.33 | .746 |
| X13 | 52.083 | 65.730 | 0.82 | 0.79 | .442 |
| X23 | 12.955 | 5.258 | 1.31 | 2.46 | .028 |

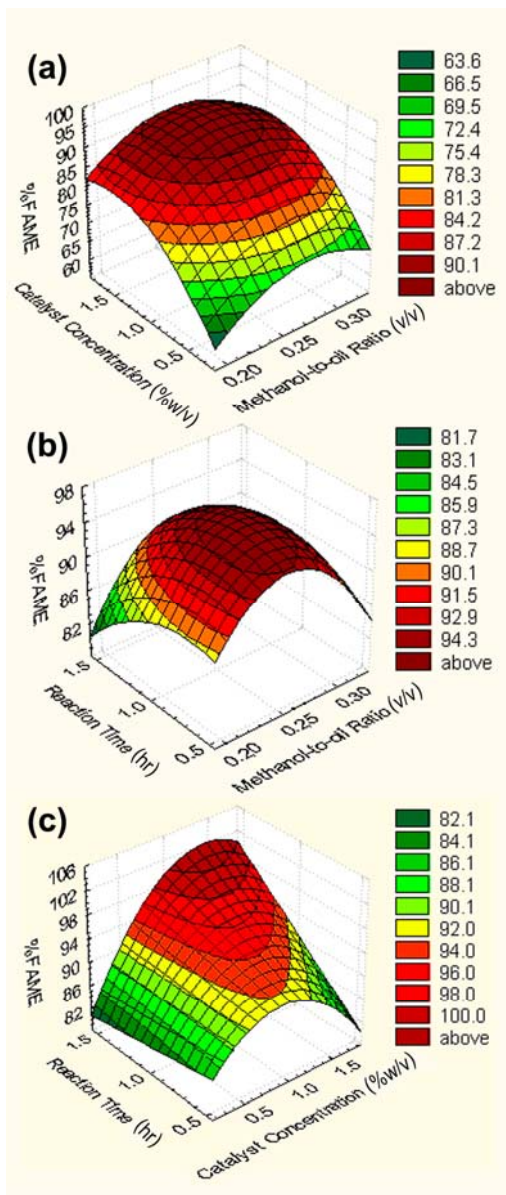


Figure 2. Response surface and contour plots representing the effect of factors on %FAME predicted from the quadratic polynomial model.

3.4 GC Analysis of the FAME from trap grease

The chromatogram of trap grease methyl ester was shown in Fig 3. The fatty acid methyl ester consisted of the major fatty acid esters including palmitic acid (C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1) and linoleic (C18:2), which was the requirement of biodiesel standard and oleic acid. This is the predominant compound in the fatty acid methyl ester. In contrast, The GC analysis of waste rapeseed biodiesel indicated that the biodiesel contains large amount of C19 and the amount of 9,12-octadecadienoic acid methyl ester was the highest in the biodiesel. The produced biodiesel in the literature, was analyzed by gas chromatography/mass spectrometry (GC/MS), which showed that it mainly contained six fatty acid methyl esters. The biodiesel diesel analysis showed that most of the fuel properties were in reasonable agreement with the diesel standard of China (GB252-2000) and the biodiesel standard of America (ASTM D6751) [8].

The literature discussed that Conversion is complicated if oil contains large amounts of FFA (>1% w/w) that will form soap with alkaline catalyst. The soap can prevent separation of the biodiesel from the glycerin fraction and contributes to emulsion formation during the water wash. In these cases, an acid catalyst, such as sulfuric acid, can be used to esterify the free fatty acid to methyl ester [5]. Previous studies [6-9] and our study indicated that more than 90% ester was obtained when two-step process was used compared to 50% ester in one step alkali catalyzed process.

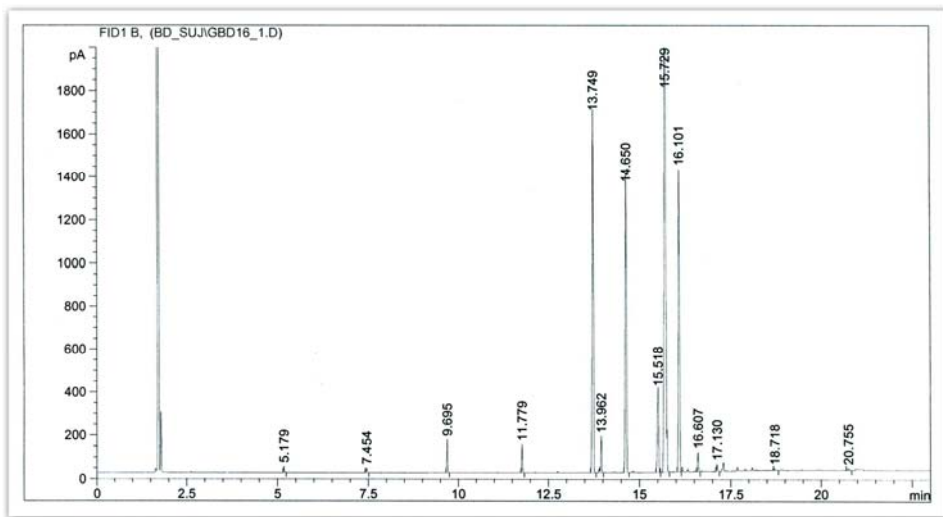


Figure 3. GC chromatogram of fatty acid methyl ester from trap grease in optimum condition of transesterification.

3.5 Properties of trap grease biodiesel

The properties of the biodiesel produced from cafeteria trap grease at the optimum reaction conditions were compared with ASTM D6751 and EN 14214 biodiesel standards as shown in Table 10. Acid value is defined as milligrams of potassium hydroxide necessary to neutralize fatty acids in 1 g of sample. Acid value of trap grease was very high but by using two step process, the acid value could be reduced to 0.54 mg KOH g⁻¹, which was like previous studies which show that acid value of esters were within the limit of the ASTM standard (0.8 mg KOH g⁻¹) [4,6-8,10-12]. Kinematic viscosity at 40°C of trap grease was very high at 29.8 mm²/s. Higher viscosity of trap grease was due to the higher molecular weight molecules such as triglycerides, polymerized

triglycerides and many other unknown heavier compounds formed during frying. After the two step process, trap grease methyl ester reduced to 4.84 mm²/s, while several oils showed reduction of viscosity in the range of 3.98–5.81 mm²/s. They were within the limit of the ASTM D6751 standard of 1.9–6.0 mm²/s [4,6-7,9-12]. Most of the biodiesel properties from trap grease were found to be in reasonable agreement with ASTM D6751 and EN 14214 standards.

Table 10. Fuel properties of trap grease biodiesel.

| Properties | Unit | Trap grease | Biodiesel standards | |
|---------------------|--------------------|-------------|---------------------|----------|
| | | | ASTM D6751-02 | EN 14214 |
| Density (at 15 °C) | Kg/m ³ | 880.13 | - | 860-900 |
| Viscosity (at 40°C) | mm ² /s | 4.835 | 1.9-6.0 | 3.5-5.0 |
| Flash point | °C | 165 | >130 | >120 |
| Acid value | mg KOH/g | 0.54 | <0.8 | <0.5 |
| Iodine value | g iodine/100g | 73.45 | - | <120 |
| Cloud point | °C | 7.2 | - | - |
| Heating value | Cal/g | 9187.9 | - | - |

The quality of trap grease biodiesel employed a production technique which was designed to obtain methyl ester from trap grease. The process consists of a filter process, reaction processes (two step catalyzed process) using optimized conditions from this study, separation process, washing process, recovery process and dehydration process. The temperature was maintained at 60°C and stir of 400 rpm. On the condition that the biodiesel standard values were met, biodiesel could be produced either from high-quality vegetable oils or from inexpensive poor quality feedstocks [1]. Moreover in the literature [10], waste frying oil biodiesel's emission values are decreased as 17.14% CO, 1.45% NO_x. Smoke intensity is increased at average

22.46% for the utilization of the waste frying oil biodiesel compared to diesel fuel and exhaust temperatures was decreased on average 6.5% more than diesel fuel. Therefore, Trap grease biodiesel was friendly alternative diesel fuel.

4. Conclusion

The trap grease with high free fatty acid (FFA) could be used to produce biodiesel. The high FFA (26.2%) level of trap grease could be reduced to less than 2% by using the central composite design and response surface methodology in acidic catalyzed esterification and alkali catalyzed transesterification. The two step catalyze process, optimum condition for the acid catalyzed esterification was found to be 0.43 v/v of methanol-to-oil ratio, 2.5% v/v sulfuric acid concentration in 4 hours of reaction time. This optimum value gave an acid value of 2.66 mg KOH/g or 1.30% of FFA. The optimum condition for the alkali catalyzed transesterification was 0.26 v/v of methanol-to-oil ratio, 1% w/v potassium hydroxide concentration and 1 hour of reaction time. The maximum percentage of fatty acid methyl ester content under the optimum conditions of the variables was 95.49%. Trap grease biodiesel with optimum condition in two-step catalyzed process had properties satisfying both the biodiesel standard of ASTM D6751 and EN 14214. In addition, biodiesel production from trap grease could be expected to benefit from a raw material cost advantage and it would help to reduce overall biodiesel cost.

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