

Optimization of biodiesel production from trap grease via acid catalysis

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Abstract—As a kind of waste collected from restaurants, trap grease is a chemically challenging feedstock for biodiesel production for its high free fatty acid (FFA) content. A central composite design was used to evaluate the effect of methanol quantity, acid concentration and reaction time on the synthesis of biodiesel from the trap grease with 50% free fatty acid, while the reaction temperature was selected at 95 °C. Using response surface methodology, a quadratic polynomial equation was obtained for ester content by multiple regression analysis. Verification experiments confirmed the validity of the predicted model. To achieve the highest ester content of crude biodiesel (89.67%), the critical values of the three variables were 35.00 (methanol-to-oil molar ratio), 11.27 wt% (catalyst concentration based on trap grease) and 4.59 h (reaction time). The crude biodiesel could be purified by a second distillation to meet the requirement of biodiesel specification of Korea.

Key words: Biodiesel, Trap Grease, Acid Catalysis, Central Composite Design, Response Surface Methodology

INTRODUCTION

As a kind of waste collected in grease traps of restaurants before it goes down the sewer, trap grease contains FFA from 40 to 100% [1]. In America, about 13 pounds/person of trap grease is produced annually [2]. But trap grease is unmarketable in America because it is simply a waste product, most typically disposed of at sewage treatment facilities. In China, the companies authorized by the local government are responsible to collect trap grease. For example, 20,000 tons water-free trap grease is produced annually in Guangzhou, the third biggest city in China. Recently, the Chinese government has banned using trap greases as animal feed. Therefore, development of an economical biodiesel production process from trap grease will provide an attractive option to handle this waste.

Trap grease is a chemically challenging feedstock for biodiesel production. The use of alkaline catalysts requires that the reactants are anhydrous and the oil contains less than 1% FFA [3]. Canakci and Van Gerpen [4] developed a two-step acid-catalyzed pretreatment process to reduce the FFA of the trap grease from 40% to less than 1%. Then the transesterification reaction was continued with 0.21% sodium methoxide as catalyst. This approach effectively solves the FFA problem, but the increased batch times make it too complicated for commercial biodiesel production.

A one-step acid catalyzed process was studied to make the biodiesel production from low grade feedstock easy to operate, where the FFA and TG in the feedstock can be simultaneously converted into mono-ester. Freedman et al. [5] and Zhang [6] stressed that acid catalyst will be much more effective than the alkaline if the vegetable has more than 1% free fatty acid. In an effort to increase utilization of fats and oils with high concentrations of FFA, Goff et al. [7] studied the acid catalyzed alcoholysis of soybean oil using sulfuric, hydrochloric, formic, acetic and nitric acids as catalyst at elevated tem-

peratures (100-120 °C), but only sulfuric acid was effective. Canakci and Van Gerpen [8] specified the reaction temperature at 60 °C and investigated the effect of other variables on acid catalyzed biodiesel production process. They concluded that the ester conversion efficiency was strongly affected by the molar ratio of alcohol to oil and a higher molar ratio is required than that of alkali-catalyzed. At the same time, the water formed by the esterification of FFA would inhibit a further reaction. Zheng et al. [9] provided a pseudo-first-order model of acid-catalyzed transesterification reaction of waste fryer oil in methanol when molar ratio of methanol to oil is close to 250 : 1 at 70 °C or in the range 74 : 1-250 : 1 at 80 °C.

This study optimized the biodiesel production from trap grease via acid catalysis at elevated temperature (95 °C). Trap grease from Guangzhou (China) contains 50 wt% FFA. Central composite design and response surface methodology (RSM) were used to complete this study because the central composite design has the advantage of predicting responses based on few sets of experimental data in which all factors are varied within a chosen range.

EXPERIMENTAL

1. Material

Trap grease was provided by Guangzhou environmental protection agency of China. Refined soybean oil was provided from CJ Co. in Korea. Comparison of the composite of the refined soybean oil and the trap grease is shown in Table 1. The acid value and water content of the trap grease are 100±0.02 mg KOH/g and 0.8%, respectively. Anhydrous methanol and sulfuric acid (96-99%) were purchased from Duksan Chemical (Korea). 1,2,4-Butanetriol and 1,2,3-tricaproylglycerol standards for the analysis of mono-, di- and triglycerides were purchased from Supel-Co (USA). N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) and methyl heptadecanoate were obtained from Sigma-Aldrich Co (Switzerland).

2. Apparatus and Experiment Procedure

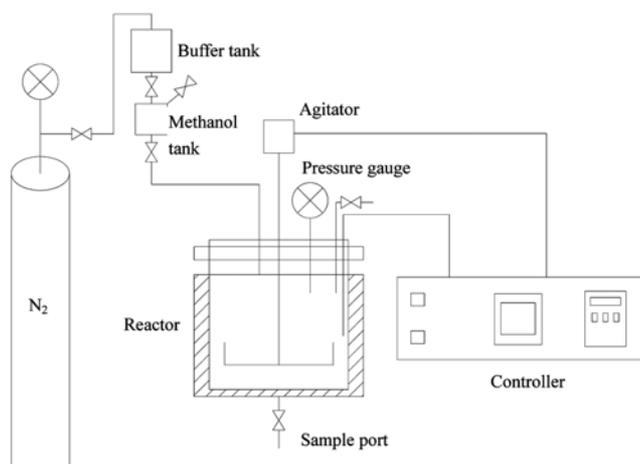
A 500 ml stainless reactor equipped with baffle tank and feed-

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Table 1. Comparison of fatty acid in trap grease and soybean oil

Fatty acid	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	Unidentified fatty acid
Soybean oil	0.07	10.95		4.31	23.12	53.27	6.77	0.27	1.24
Trap grease	1.16	30.38	1.42	6.02	38.39	18.83	1.31		2.49

**Fig. 1. Schematic diagram of experimental setup.**

ing tank was used for this study (Fig. 1). The trap grease was preheated to specified temperature in the 500 ml stainless reactor, and then the mixture of methanol and sulfuric acid pressured by nitrogen was introduced in the reactor from the feeding tank. Samples were taken from the sample port on the bottom of the reactor at intervals.

3. Experimental Design

Effect of the temperature on the purity of crude biodiesel was investigated by carrying out the experiments at three levels of temperature at 75 °C, 85 °C and 95 °C while the sulfuric acid and the molar ratio of methanol to trap grease was specified at 10 and 30 wt%, respectively. Because oleic acid is the main composite of fatty acid in trap grease, the molecular weight of oleic acid triglyceride was used as the molecular weight of trap grease in these experiments.

Based on the results of the above experiments, a five-level-three-factor central composite design was employed in this study, requiring 20 experiments. Methanol-to-oil ratio (M), catalyst concentration (C) and reaction time (T) were the independent variables selected to optimize the ester content of biodiesel from trap grease. To prevent scorching of the oil by the acid, the acid concentration in the methanol was almost kept in the range of 1.5-3.5 mol% of H₂SO₄ in the total reactants [9,12]. The coded and uncoded levels of the independent variables are given in Table 2. Two replications were carried out for all design points except the center point (0, 0, 0), and the experiments were carried out in randomized order. The central point was replicated in six times to study the reproducibility.

4. Statistical Analysis

The data obtained by carrying out the experiments according to central composite design were analyzed by SPSS package (version 12). The response surface was expressed as the following second-

Table 2. Independent variables and levels used for central composite rotatable design

Variables	Symbols	Levels				
		-1.68 -a	-1	0	1	1.68 a
Molar ratio of methanol to trap grease	M	13.2	20	30	40	46.8
Weight ratio of sulfuric acid (w/w)	C	1.6	5	10	15	18.4
Reaction time (h)	T	2.32	3	4	5	5.68

Transformation of variable levels from coded (X) to uncoded could be obtained as: Mr=30+10X, C=10+5X and T=4+X.

order polynomial equation:

$$y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i < j=1}^3 \beta_{ij} x_i x_j$$

Where y is the response (%); x_i and x_j are the uncoded independent variables and β₀, β_i, β_{ii} and β_{ij} are intercept, linear, quadratic and interaction constant coefficients, respectively. Response surfaces and contour plots were developed by 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.

5. Methanol Recovery and Purification of the Biodiesel

Calcium oxide was added to neutralize sulfuric acid in the reactants and methanol was recovered at 50 °C and 10 mmHg vacuum. After calcium sulfate was drained off by filtering and glycerol was decanted, crude biodiesel was left. A simple vacuum distillation system was used to purify the biodiesel. The vacuum was adjusted to be at 5±1 mmHg. The first distillate was collected at 120 °C, and most of the distillate was collected from 170 °C to 180 °C. Finally, the temperature was raised to 220 °C and the distillate was collected. The distillation was terminated when no more distillate was collected.

6. Analysis Methods

Acid values of the samples were determined according to KSTM-1051 by using KOH as a titrant. Water content was measured by Karl Fisher titrator (METTLER TOLEDO DL31, USA).

The composition of the methyl esters was analyzed by HP 6890 gas chromatograph system equipped with 7683 auto-injector, a split/splitless injection system. The INNOWAX GC column (60 mm×0.32 mm×0.5 μm, Agilent Inc, USA) was used for the analysis of FAME. The oven temperature was started at 150 °C for 1 min, in-

creased to 200 °C at a rate of 15 °C/min, held at the temperature for 9 min and again increased to 250 °C at a rate of 2 °C and then held at the temperature for 2 min. Methyl heptadecanoate was used as the internal standard.

Free and total glycerol and mono-, di-, triglycerides were determined by 6890N gas chromatograph equipped with on-column injector and FID. The DB-5HT column (15 m×0.32 mm×0.1 μm, Agilent Inc, USA) was used for the analytical work. The column temperature was held at 50 °C for 1 min, increased to 150 °C at a rate of 15 °C and increased to 230 °C at a rate of 7 °C and again increased to 370 °C at a rate of 10 °C and then held at the temperature for 5 min. 1,2,4-butanetriol and 1,2,3-tricaproylglycerol were used as the internal standards.

RESULTS AND DISCUSSION

1. Effect of the Reaction Temperature

Reaction temperature played an important role in this acid catalysis (Fig. 2). When the reaction temperature was 75 °C and 85 °C, after 6 h reaction, the ester content of crude BD was only 72.45% and 82.36%, respectively. But the ester content of crude BD was increased significantly to 87.95% within 4 h reaction when the reaction temperature was 95 °C. Then the ester content of crude BD remained almost on the same level for the following 2 h reaction. Considering the total fatty acid content of the trap grease, the purity of crude BD around 88% could be close to the maximum value. Hence, this reaction condition was selected as the central point for the RSM experiment design.

2. Optimization of the Biodiesel Production from Trap Grease

The ester content of crude BD obtained from the designed experiments is given in Table 3. These data were analyzed by SPSS package (12.0 version), and multiple regression coefficients indicated in Table 4 were obtained. All the three variables significantly affected the ester content of the product, methanol being the most

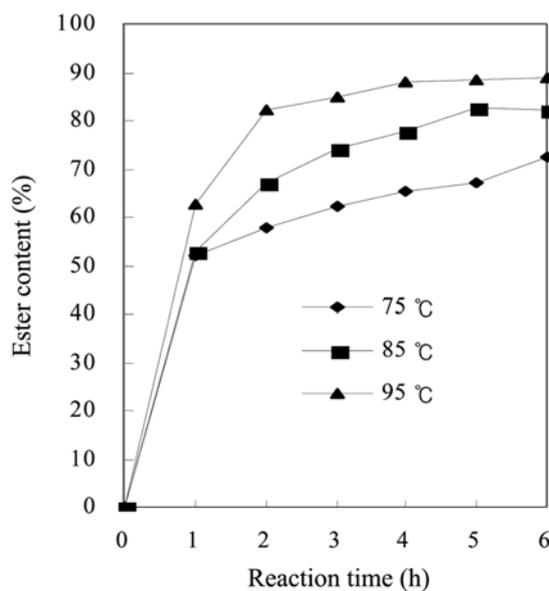


Fig. 2. Effect of temperature of ester content when the catalyst was 10 wt% and the molar ratio of methanol to trap grease was 30 : 1.

effective followed by reaction time and acid catalyst concentration. The model was tested for adequacy by analysis of variance. The regression model for data was found to be highly significant with a

Table 3. Central composite rotatable design arrangement and responses

Design points	Coded independent variable levels			Ester content (%)
	Methanol to TG molar ratio	H ₂ SO ₄ (w%)	Reaction time (h)	
	M	C	T	
1	-1	-1	-1	68.74
2	-1	-1	1	80.99
3	-1	1	-1	76.01
4	-1	1	1	81.99
5	1	-1	-1	80.75
6	1	-1	1	87.06
7	1	1	-1	87.36
8	1	1	1	89.63
9	-1.68	0	0	65.99
10	1.68	0	0	88.91
11	0	-1.68	0	79.41
12	0	1.68	0	86.47
13	0	0	-1.68	82.98
14	0	0	1.68	87.02
15	0	0	0	88.15
16	0	0	0	88.98
17	0	0	0	87.65
18	0	0	0	87.01
19	0	0	0	89.20
20	0	0	0	86.90

Table 4. Regression coefficients of predicted quadratic polynomial model

Terms	Coefficients ^a	Standard error
Linear		
B ₀	-29.941	16.734
B ₁	3.440**	0.498
B ₂	3.108*	0.917
B ₃	18.259*	5.479
Quadratic		
B ₁₁	-0.039**	0.006
B ₂₂	-0.076*	0.023
B ₃₃	-1.176	0.583
Interaction		
B ₁₂	-0.008	0.016
B ₁₃	-0.135	0.078
B ₂₃	-0.243	0.156
R ²	0.940	
F ratio	17.350	
P value	<0.0005	

^aCoefficients refer to the model given.

*Significant at 0.01 level.

**Significant at 0.0005 level.

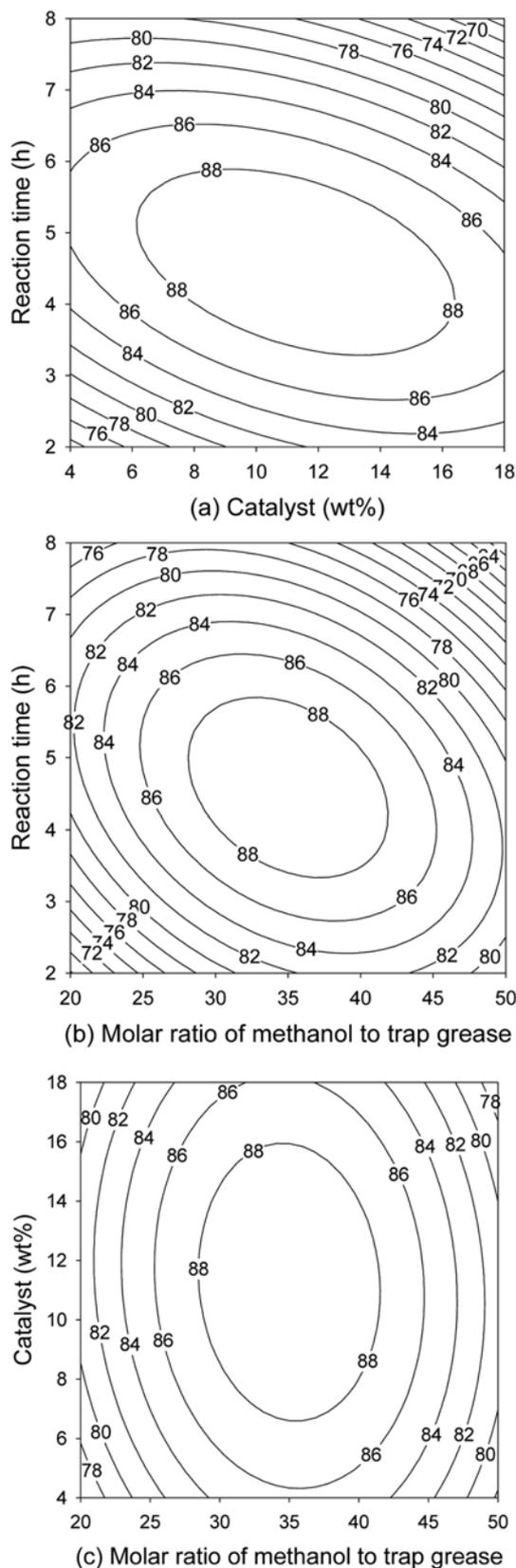


Fig. 3. Contour plots of ester content predicted from the quadratic model while one of the variables is at critical value.

- (a) Molar ratio of methanol to trap grease 35.00
 (b) Concentration of catalyst is 11.27 wt%
 (c) Reaction time is 4.59 h

very small P-value (<0.0005) and a satisfactory coefficient of determination ($R^2=0.940$). Using the coefficients determined, the predicted model for ester content is:

$$E = -29.941 + 3.440 M + 3.108 C + 18.259 T - 0.039 M^2 - 0.076 C^2 - 1.176 T^2 - 0.008 MC - 0.135 MT - 0.243 CT$$

The relationship between independent and dependent variables of the developed model is shown in Fig. 3(a)-3(c) in the form of contour plots. The critical values of three variables were found to be 35.00 (methanol-to-oil molar ratio), 11.27 wt% (catalyst concentration base on the trap grease) and 4.59 h (reaction time) locating the stationary point in the experimental region. The sulfuric acid consumed at the critical point was 2.6 mol% based on the total reactant; therefore, the scorching caused by sulfuric acid could be avoided. Verification experiments showed reasonably close value of $89.50 \pm 0.40\%$ to the predicted value for the stationary point (89.67%), thus confirming the adequacy of the predicted model. The total fatty acid content of trap grease was 86.67% (Table 5), and the yield of crude biodiesel with $89.50 \pm 0.40\%$ ester content was 91%. The conversion of total fatty acid to ester was 93.97%, calculated as follows:

$$y_c = x_c x_p / x_f = 89.50\% \times 91\% / 86.67\% = 93.97\%$$

Where y_c stands for the conversion of total fatty acid; x_c stands for the ester content of crude biodiesel; x_p stands for the yield of the crude biodiesel; x_f stands for the amount of total free fatty acid.

The contour plots indicate that more than 88% ester contents of crude BD can be achieved within a wide range. When one of the dependent variables is fixed at the critical value, the minimum value of the second dependent variable can be obtained by increasing the value of the third dependent variable. Hence, this regression model provides many feasible options of reaction conditions for biodiesel production from trap grease to obtain crude biodiesel from trap grease with close ester content of 88% to the critical value (89.67%).

3. Purification of the Crude Biodiesel

Distillation was applied to get high purity biodiesel. The yield of biodiesel obtained through simple distillation was $82 \pm 0.5\%$ (w/w) based on the crude biodiesel. The distilled biodiesel was clear and not smelly. Ester content of the distilled biodiesel was 95.5%, but could not meet the biodiesel specification of Korea (96.5%). Second distillation was done to further purify the biodiesel. The distillate obtained with 97.6% ester content qualified for the biodiesel specification of Korea (Table 5). The loss during the second distillation process was $5 \pm 0.5\%$ (w/w). A more economical distillation process should be developed to improve the purity and yield of biodiesel from trap grease.

SUMMARY

A second-order model was obtained by carrying out the central composite rotatable design to make biodiesel from trap grease. This model was found to describe adequately the experimental range studied through verification experiments. Trap grease with high FFA (50%) could be converted into crude biodiesel with an ester content of 89.33% at 95 °C while the three variables were at critical values: molar ratio of methanol to trap grease was 35.00, sulfuric acid concentration was 11.27 wt%, reaction time was 4.59 h. The contour plots of the second order model indicate that more than 88%

Table 5. Compositions of trap grease and biodiesel

	FFA	MG	DG	TG	Glycerol	Ester	Water	Other impurities
	50	0.6676	9.3954	26.6020				
Trap grease (%)	Total fatty acid 86.67				4.393	0	0.08	8.862
Crude BD (%)	0.6	0.0122	0.0114	0.0515	0.0171	89.50	0.02	9.7878
Purified BD (%)	0.2	0.0000	0.0012	0.0000	0.0120	97.6	0.01	2.1768
BD Specification of Korea	≤0.25	≤0.8	≤0.2	≤0.2	≤0.24	96.5≤	≤0.05	-

ester contents of crude BD can be achieved within a wide range of the three variables, and it provide many feasible options for biodiesel production from trap grease. The crude biodiesel could be purified by a second distillation to meet the requirement of biodiesel specification of Korea.

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