

Original Article

Minimizing the cost of converting waste fat from fish-canning-factory wastewater treatment system to biofuel oil

Pheerawit Punyawansiri, Sininart Chongkhong, Songtham Photaworn, and Kulchanat Prasertsit*

*Department of Chemical Engineering, Faculty of Engineering,
Prince of Songkla University, Hat Yai, Songkhla, 90110 Thailand*

Received: 15 April 2020; Revised: 13 July 2020; Accepted: 22 September 2020

Abstract

A food factory constantly releases waste containing oil and fat into its wastewater treatment system. To obtain zero waste, the waste should be utilized as an energy source, such as biofuel oil (BFO). In this study, waste fat containing 86.13%wt. of free fatty acid (FFA) was converted to BFO through esterification. Effects of methanol-to-FFA molar ratio, amount of catalyst, reaction time and reaction temperature on the production were investigated and used to find model-based conditions that produced BFO at the desired 90% FFA conversion and 96% yield. The results showed that a molar ratio 5:1 with 6 %wt. H₂SO₄ and reaction temperature of 60°C for 30 minutes gave BFO that met the specifications of fuel oil no. 4. The production costs at these conditions were 423.89 US\$/ton BFO, which is below the combined costs of boiler fuel and waste disposal. Therefore, such conversion of waste fat to BFO is economic.

Keywords: biofuel oil, cost estimation, esterification, waste fat, wastewater

1. Introduction

Waste oil and fat (called “waste fat” in this work) are produced by food industries, food service establishments, domestic properties, and leather industries. Every day large quantities of waste fat are produced from a variety of sources and the disposal costs of such waste are high (Adewale, Dumont, & Ngadi, 2015; Wallace, Gibbons, O’Dwyer, & Curran, 2017). The metropolitan wastewater treatment plant at St. Paul, MN (Metro Plant) spent US\$100,000 per year for disposing waste fats in landfills (Bi *et al.*, 2015). If waste fat is disposed inappropriately, it will make deposits and block the sewage system. Waste fat deposits also release concentrated pathogens and solids to water, presenting risks to public health and the environment (Hasuntree, Toomthong, Yoschoch, & Thawornchaisit, 2011). To reduce disposal costs and potential risks in the disposal, waste to energy process concept should be considered. Since waste fat is composed of fatty acids, triglycerides, lipid hydrocarbons, soaps and other impurities, the transformation of waste fat into energy sources

such as biodiesel, biofuel oil (BFO) and biogas is an interesting proposition (Bi *et al.*, 2015; He *et al.*, 2013).

If waste fat contains high quantities of long-chain fatty acids, it is not suitable for producing biogas because the long-chain fatty acids inhibit biogas production (Martín-gonzález *et al.*, 2011). Also it is difficult to produce biodiesel that meets the standards from high impurity waste fat, because of its high viscosity and sulfate ash content. As a result, waste fat can be used to produce BFO, which is then used in boilers to produce steam and generate electricity in various industries, because BFO can meet the specifications of fuel oil (FO) or boiler fuel more easily than the biodiesel specifications.

BFO can be produced by many approaches such as fermentation, pyrolysis, transesterification and esterification. Bioethanol is an alcoholic BFO, which is produced by fermentation of renewable agricultural products such as corn, sugar and molasses. Although bioethanol is less toxic than FO, the gross heating value is lower than of other BFOs (Vohra, Manwar, Manmode, Padgilwar, & Patil, 2014). BFO produced by pyrolyzing organic materials has to be treated before use because of its low gross heating value, high water content, high acidity, and variable viscosity. The negative properties are a drawback in use as a FO. In addition, the process usually needs high temperatures (500-800°C) with a

*Corresponding author

Email address: kulchanat.k@psu.ac.th

high energy consumption (Nguyen, Zabeti, Lefferts, Brem, & Seshan, 2013). For biodiesel approach the BFO can be produced by both esterification and transesterification in the same way as biodiesel. The high gross heating value of BFO is similar to FO. This approach is also convenient and has a lower energy consumption.

Therefore, the aim of this research was to evaluate the feasibility of converting waste fat recovered from the wastewater system of a fish-canning factory to BFO, to use it in the factory instead of disposing it as waste.

2. Materials and Methods

2.1 Materials

The feedstock used in this study was sun-dried waste fat (SWF) from a wastewater treatment system, supplied by Siam International Food Company Limited (Thailand). The methanol (99.8%) was purchased from Boss Optical Limited Partnership. Sulfuric acid (98%), isopropyl alcohol (99.8%), sodium hydroxide (98%) and phenolphthalein pH indicator were purchased from S.M. Chemical Supplies Company Limited.

2.2 Waste fat preparation

The moisture content of SWF was measured according to ASTM D3173 before preparation. In the preparation, the SWF was mixed with water at 70°C. The SWF-water mixture was left to settle for 3 hours. The bottom layer contained water, soil, and impurities. The fatty acids and other components in the top layer were collected by using a cloth filter and dried in an oven at 105°C. The other components and impurities stayed in the filter cake while the prepared waste fat (PWF) was the filtrate. Each part was kept in the oven until the weight of the PWF was constant. Each part was weighed and calculated to a percentage.

The fatty acid composition of the PWF was determined using a GC-FID gas chromatograph (Agilent 6890, USA) with a capillary column length of 30 m, a film thickness of 0.25 μm and an internal diameter of 0.32 mm. Helium was used as the carrier gas and the split ratio was 50:1. The oven temperature was initially set at 210°C for 12 minutes and increased at a rate of 20°C/minute until 250°C, and maintained at this temperature for 8 minutes. The injector and detector temperatures were set at 290°C and 300°C, respectively. Heptadecanoic acid (C17:0) was used in the analysis as an internal standard because C17:0 is unnatural, and surely absent from any feedstock biodiesel.

2.3 Esterification reaction

The PWF was esterified with methanol and catalyst in a 500 mL-screwcap bottle. The sample was stirred at 500 rpm at the studied temperature and reaction time. After the reaction was completed, the mixture was transferred to settle in a separating funnel for 3 hours and the top layer containing alcohol was separated. The bottom layer was washed many times with warm water to neutralize it, and then the water was removed by centrifuging at 5,000 rpm for 10 minutes. After that, the top layer was dried in an oven at 105°C until constant weight. The method to determine the FFA content was

adapted from AOCS Ca 5a-40. The % FFA conversion and % yield were calculated from Equations (1)-(2).

$$\text{FFA conversion (\%)} = \frac{(\text{Initial FFA} - \text{residue FFA})}{\text{Initial FFA}} \times 100 \quad (1)$$

$$\text{Product yield (\%)} = \frac{\text{Weight of BFO produced}}{\text{Weight of PWF}} \times 100 \quad (2)$$

2.4 Multiple regression in Microsoft Excel and application

Effects of the studied parameters: molar ratio of methanol-to-FFA (8:1-12:1), sulfuric acid concentration (4-8 %wt./FFA), temperature (50-70°C) and time (30-90 minutes) on FFA conversion and product yield were investigated with a 2⁴ factorial design of experiments with 2 replicates at center points, and analyzed by multiple regression in Microsoft Excel 2016. The response model equation is shown as Equation (3).

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \sum_{j=i+1}^n \beta_{ij} X_i X_j + \sum_{i=1}^n \sum_{j=i+1}^n \sum_{k=j+1}^n \beta_{ijk} X_i X_j X_k + \epsilon \quad (3)$$

Where Y is the response, β_0 , β_i , β_{ij} and β_{ijk} are the constant coefficients, X_i , X_j and X_k are the parameters, n is the number of parameters studied in the experiment, and ϵ is the error between the model fit and the experimental values.

The regression model was then applied to optimize the conditions numerically with function "Solver" in Microsoft Excel 2016. Besides that, the regression model was used to determine the minimum operating cost conditions for the esterification step at the desired FFA conversion of 90% and 96 %yield, by imposing conditions on the cost of materials and energy equations.

2.5 Biofuel oil characterization

The BFO characteristics were determined according to the relevant ASTM standards. These were specific gravity at 15°C (ASTM D1298), flash point (ASTM D93), kinematic viscosity at 40°C (ASTM D445), copper corrosion (ASTM D130), sulfated ash (ASTM D874), ash content (ASTM D482), water content (ASTM D6304) and gross heating value (ASTM D240).

3. Results and Discussion

3.1 Characterization of waste fat

From Figure 1, the SWF was mainly composed of fatty acids, moisture, soil and other components. The last two items were from soil contamination during sun-drying of the waste from a wastewater treatment system.

SWF should not be directly used as FO because soil, metal and ash can block the nozzles of the boiler and damage the burners. The high moisture content also leads to the production of smoke due to incomplete combustion (Schobing *et al.*, 2018). Therefore, the SWF should be purified by

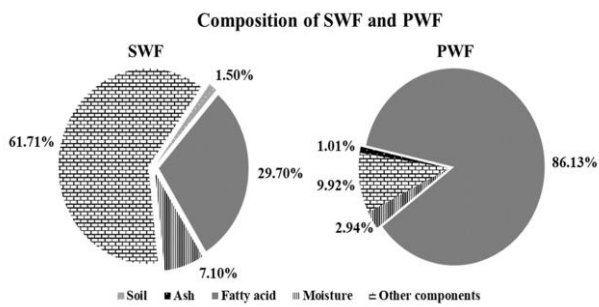


Figure 1. Compositions of SWF and PWF

removing impurities before use as FO.

After preparation, the PWF met the specifications of FO in terms of specific gravity and flash point. The gross heating value of PWF (34.59 MJ/kg) was higher than that of SWF (29.24 MJ/kg). However, the water and ash contents exceeded the specification limits for the lowest grade FO, as shown in Table 1. To upgrade the product to match the

specifications and the gross heating value of biodiesel produced by a similar method, PWF should be transformed into BFO rather than to biodiesel, because the high FFA content in feedstock makes it difficult to produce biodiesel that meets the standards.

The PWF had a high FFA content of 86.13 %wt. due to long retention time of the deposits in the grease trap of the wastewater system. This was consistent with the study of Husain *et al.* (2014) that found that grease-trap waste had an FFA content greater than 15%. The presence of detergents and sanitizers promotes the hydrolysis of triglycerides.

Fatty acid compositions of various oils and fats are shown in Table 2. The presence of long-chain fatty acids (LCFAs) indicated that the SWF used in this study was not suitable for biogas production. Mostly the fatty acids found in SWF were LCFAs including palmitic, stearic, and oleic acids that exhibit biogas formation (Martín-gonzález *et al.*, 2011). The approximate molecular weight of the PWF used in this work was 261.22 g/mol. The LCFAs in SWF were similar to those in brown grease because both brown grease and PWF had been deposited in the grease trap over a long time (Adewale *et al.*, 2015). Normally, fresh tuna muscle includes

Table 1. Fuel properties of SWF and PWF

Property	Method	Fuel Oil, ASTM D396		SWF	PWF
		No. 5 (Heavy)	No. 6		
Specific gravity at 60°C	D 1298	-	-	-	875*
Flash point (°C)	D93	Min. 55	Min. 60	192	188
Ash content (wt.%)	D482	Max 0.15	-	3.12**	1.01**
Water content (Vol.%)	D6304	Max. 1	Max. 2	7.10**	2.57**
Gross heating value (MJ/kg) (Engineering ToolBox, 2003)	D240	Min. 42.49 Max. 43.23	Min. 43.03 Max. 44.34	29.24	34.59

*The density of PWF at 60°C was measured according ASTM D5355.

**The ash content and water content of prepared waste fat were determined according ASTM D3174 and D3173, respectively.

Table 2. Fatty acid compositions of various oils and fats

Fatty acid	Structure	MW	Composition			
			PWF	Tuna	Brown grease	PFAD
Lauric acid	C12:0	200.3	0.04	-	-	-
Tridecanoic acid	C13:0	214.3	0.02	-	-	-
Myristic acid	C14:0	228.4	1.11	2.91	1.3	1.0
Pentadecanoic acid	C15:0	242.4	0.31	-	-	-
Palmitic acid	C16:0	256.4	75.35	19.37	38.3	45.6
Stearic acid	C18:0	284.5	6.55	6.7	7.2	3.8
Arachidic acid	C20:0	312.5	0.51	0.21	-	0.3
Behenic acid	C22:0	340.6	0.78	-	-	-
Lignoceric acid	C24:0	368.6	0.35	-	-	-
Palmitoleic acid	C16:1	254.4	0.16	3.62	1.2	0.2
Oleic acid	C18:1	282.5	4.65	26.14	36.9	33.3
Eicosenoic acid	C20:1	310.5	0.2	1.83	-	0.2
Erucic acid	C22:1	338.6	0.04	-	-	-
Selacholeic acid	C24:1	366.6	0.13	1.89	-	0.6
Linoleic acid	C18:2	280.5	0.11	1.37	15.1	7.7
Arachidonic acid	C20:4 n-6	304.5	-	1.3	-	-
Eicosapentaenoic acid	C20:5 n-3	302.5	-	4.65	-	-
Docosahexaenoic acid	C22:6 n-3	328.5	-	15.60	-	-
Saturated fatty acids			85.02	29.19	46.8	50.7
Unsaturated fatty acids			5.29	56.4	53.2	42
Total			90.31	85.59	100	92.7

unsaturated fatty acids (Roseiro *et al.*, 2017). However, the unsaturated fatty acids are oxidized to saturated fatty acids by exposure to oxygen and light (Arab-Tehrany *et al.*, 2012). He & Yan (2016) reported that LCFAs could be produced in a grease trap by microbial activity over a high hydraulic retention time. Since this work used SWF collected from a tuna (*Thunnus obesus*) fish-canning factory, the waste fat contained saturated fatty acids as mentioned before.

In addition, palm fatty acid distillate (PFAD) has been used as a biodiesel feedstock (Chongkhong, Tongurai, & Chetpattananondh, 2009). The main components in PFAD are palmitic, stearic and oleic acids. It was confirmed that BFO could be produced from PWF by acid esterification rather than by base transesterification, to prevent soap formation from the reaction between FFA and base catalyst that would lead to yield loss and difficulty in washing.

3.2 Esterification

The stoichiometry of esterification requires equimolar reactants. Nevertheless, the molar ratio of methanol-to-FFA used was 3:1, which is common because the reaction is reversible. The experimental designs and results are shown in Table 3. This work studied the molar ratio baseline set at 8:1 according to a previous study by Chongkhong *et al.* (2009). They studied biodiesel production from PFAD, which is very similar to PWF. Also, the study of potential of restaurant trap grease, with high content of impurities like in PWF, as biodiesel feedstock by Hasuntree, Toomthong, Yoschoch, & Thawornchaisit (2011), indicated that the esterification required 5:1 methanol-to-FFA ratio, and 5 %wt. H₂SO₄ at 60°C for 60 min to reduce the acid value from 60.38 to 11.60 mgKOH/g.

3.2.1 Statistical data and regression for esterification

The regressions for the %FFA conversion (R₁) and

%yield (R₂) of the esterification of PWF developed based on the actual parameters are shown in Equations (4)-(5). The related statistical and ANOVA results of the regression models are presented in Table 4.

$$R_1 = 5.721 + 5.827*A + 5.009*B + 1.209*C + 0.506*D - 0.238*A*B - 8.292e-2*A*C - 2.746e-2*A*D - 6.627e-2*B*C - 2.87e-3*B*D - 7.73e-3*C*D + 3.66e-3*A*B*C - 1.24e-4*A*B*D + 5.08e-4*A*C*D + 1.81e-4*B*C*D \tag{4}$$

$$R_2 = 18.63 + 6.194*A + 8.923*B + 1.470*C - 0.288*D - 0.680*A*B - 0.130*A*C + 3.503e-2*A*D - 0.172*B*C - 3.17e-4*B*D + 2.50e-3*C*D + 1.477e-2*A*B*C - 1.65e-3*A*B*D - 2.28e-4*A*C*D + 9.979e-5*B*C*D \tag{5}$$

where A is Molar ratio of methanol-to-FFA, B is Catalyst (%), C is Temperature (°C) and D is Time (min).

The high values of R² (0.990 for %FFA conversion and 0.971 for %yield) indicate excellent agreement between experimental data and model fit, while the R²_{adjusted} (0.945) supports high precision of the fitted model of %FFA conversion. The different values of R² and R²_{adjusted} for %yield reveal that the model was sensitive to the number of runs. Adding more experimental runs could reduce this sensitivity. However, this difference was acceptable because of the small difference and the low Standard Error (<1). The results show that MS_{regression} was larger than MS_{residual}, and the F-values of %FFA conversion and %yield were higher than F_{critical}. Thus, the results were statistically significant. The differences in the results depended on the different independent variables. The Standard Error of the regression model was small, so the observations were close to the fitted model outputs. Based on ANOVA results for the %FFA conversion, terms A and C and interaction AC were significant. Besides the results of %yield show that the main effect terms in C and the interaction terms in AC were significant at the *p-value* level 0.05.

Table 3. Experimental design and results from esterification experiments

Run	Parameter				Response	
	A=Molar ratio of methanol-to-FFA	B=Catalyst (%)	C=Temperature (°C)	D=Time (min)	FFA conversion (%)	Yield (%)
1	8	8	70	30	95.56	95.94
2	8	8	70	90	97.14	94.84
3	12	4	70	30	94.25	93.19
^o 4	8	4	50	30	87.30	92.79
5	12	8	50	30	95.44	96.89
[*] 6	12	8	70	90	97.28	96.88
7	8	8	50	30	91.78	94.75
8	8	4	70	90	95.21	98.49
9	12	4	70	90	96.61	94.96
10	10	6	60	60	94.23	95.65
11	12	4	50	30	92.20	94.21
12	10	6	60	60	95.52	94.18
13	12	8	50	90	96.81	96.53
14	8	8	50	90	96.25	92.46
15	12	4	50	90	95.88	95.96
16	8	4	50	90	92.45	91.98
17	8	4	70	30	93.37	97.44
18	12	8	70	30	95.92	95.99

Note: ^o = Minimal FFA conversion condition;
^{*} = Maximal FFA conversion condition

Table 4. R² of regression fits and ANOVA results for the response surface models for esterification

Summary	%FFA conversion	%Yield
R	0.995	0.985
R ²	0.990	0.971
R ² adjusted	0.945	0.833
Standard Error	0.585	0.795
MS _{regression}	7.420	4.465
MS _{residual}	0.342	0.632
F _{regression}	21.69	7.066
F _{critical}	8.72	4.64
F Signif	0.0137	0.0666
Model	<i>p</i> -value	<i>p</i> -value
Constant	0.775	0.509
A	0.04289	0.07710
B	0.143	0.08168
C	0.02570	0.03430
D	0.07627	0.345
AB	0.385	0.122
AC	0.05625	0.03936
AD	0.195	0.217
BC	0.197	0.05120
BD	0.891	0.991
CD	0.07507	0.570
ABC	0.390	0.05892
ABD	0.384	0.392
ACD	0.129	0.541
BCD	0.512	0.783

Here A is the molar ratio of methanol-to-FFA; B is the %H₂SO₄ to FFA; C is the reaction temperature (°C); and D is the reaction time (min); MS is Mean sum of Square

3.2.2 Response surface and contour plots of the effects of various parameters on esterification

The impacts of the parameters and their effects on FFA conversion and yield, along with interactions between any two of the parameters, were considered while the other parameters were held constant at their central values, using 3D response surfaces and contour plots of the esterification as shown in Figures 2 and 3.

3.2.2.1 Effects of various parameters on FFA conversion

Figure. 2 demonstrates that increasing the shown parameters increases FFA conversion. The interactions had a positive effect. Figures 2a, 2b, and 2c indicate that increasing the molar ratio of methanol increased the FFA conversion because of increased probability of molecular collisions. Theoretically, esterification of one mole requires one mole of alcohol. However, the reaction is reversible so there should be more moles of alcohol available (Khayoon, Olutoye, & Hameed, 2012) to bias the reaction balance.

Figures 2a, 2d, and 2e demonstrate that an increase in the %catalyst increased FFA conversion. The acid catalyst concentration improved the reaction rate and increased the FFA conversion because acid made protons available in the FFA in a sufficient quantity to catalyze the reaction. The

results are also similar to those reported for acid-catalyzed esterification Su (2013).

Figures 2b, 2d, and 2f show that the FFA conversion increased from 92% to 96% with temperature change from 50°C to 70°C. However, the maximal temperature is slightly above the boiling point of methanol (65°C) at atmospheric pressure. The results suggest that a rise in reaction temperature increases the internal energy of all the molecules, mass transfer between reactants and catalyst, and also successful collisions between the reactants according to the Arrhenius equation (Mueanmas, Nikhom, Petchkaew, Iewkittayakorn, & Prasertsit, 2018).

Figures 2c, 2e, and 2f indicate that the FFA conversion was affected by both parameters in each plot. Regarding the effect of reaction time, the conversion of FFA seemed to depend very little on it, indicating that the rate of esterification was fast, which agrees with the results of Kanjaikaew, Tongurai, Chongkhong, & Prasertsit (2018).

3.2.2.2 Effects of various parameters on yield

Figure 3 shows that the effects of molar ratio and catalyst were positive. The temperature had also a positive effect. Figure 3a indicates that at a smaller catalyst content, molar ratio is less significant, which can be attributed to the lower overall catalyst concentration at higher reaction mixture volumes. Figures 3b, 3d, and 3f indicate that the yield was strongly influenced by reaction temperature. However, at a low molar ratio and with a long reaction time, adding catalyst decreased the yield in Figures 3c and 3e, because the sulfuric acid acts as an emulsifier between the BFO and formed water. The high viscosity of BFO-water emulsion causes difficulties in the washing stage, leading to product losses (Costa, Almeida, Alvim-Ferraz, & Dias, 2013).

3.2.3 Application of esterification regression

Although using excess reactants and a higher temperature increase FFA conversion and yield, as in Figures 2 and 3, these also increase the operating costs. Hence, the regressions shown in Equations (4)-(5) were applied to optimize the conditions and minimize the operating costs in the esterification step. The operation cost for esterification step (Cost_{Esterification}: US\$/ton) is shown in Equation (6),

$$\text{Cost}_{\text{Esterification}} = \text{Cost}_{\text{Methanol}} + \text{Cost}_{\text{Sulfuric}} + \text{Cost}_{\text{Reaction}} \quad (6)$$

where Cost_{Methanol} is the cost of the methanol used in US\$/ton; Cost_{Sulfuric} is the cost of the sulfuric acid used in US\$/ton; and Cost_{Reaction} is the cost of heat used in the reaction in US\$/ton.

Equations (7)-(8) are the cost equations from multiplying the selling price of chemicals (methanol and sulfuric acid) and the actual quantity of each chemical used. Equation (9) is the cost from energy consumption based on standard heat of reaction at any temperature.

$$\text{Cost}_{\text{Methanol}} = [A * \text{MW}_{\text{MeOH}} * \% \text{FFA} * C_{\text{Methanol}} * 100] / [\text{MW}_{\text{FFA}} * \% \text{Yield}] \quad (7)$$

$$\text{Cost}_{\text{Sulfuric}} = [B * \% \text{FFA} * C_{\text{Sulfuric}}] / [\text{Conc.} * \% \text{Yield}] \quad (8)$$

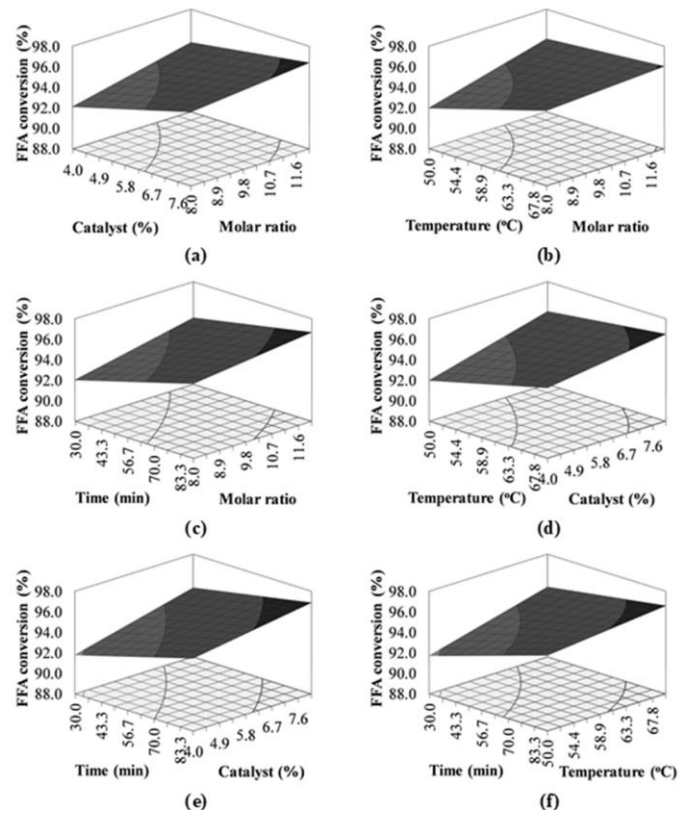


Figure 2. 3-D response surface and contour plots of effects of interactions on %FFA conversion

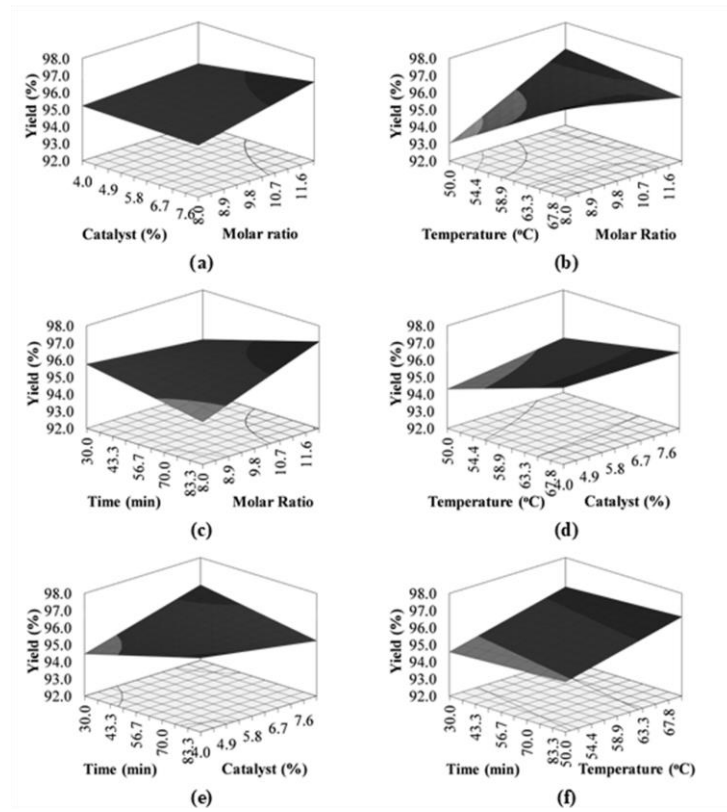


Figure 3. 3-D response surface and contour plots of effects of interactions on %yield

$$\begin{aligned} \text{Cost}_{\text{Reaction}} &= [\{\sum m_f C_p * (C - T_a)\}_{\text{Feed}} + \{(\sum m_r \Delta H_f^0)_{\text{Product}} - (\sum m_r \Delta H_f^0)_{\text{Reactant}}\} + \\ &\quad \{\sum m_r C_p * (C - T_r)\}_{\text{Product}} - \{\sum m_r C_p * (C - T_r)\}_{\text{reactant}}] * C_{\text{Electricity}} / [3,600,000] \end{aligned} \quad (9)$$

where Conc. is the concentration of sulfuric acid (98 %wt.),
 MW_{MeOH} and MW_{Ester} are the molecular weights of methanol (32.04 g/mol) and ester (275.2 g/mol),
 MW_{FFA} and MW_{water} are the molecular weights of FFA (261.22 g/mol) and water (18.02 g/mol),
 %FFA is the free fatty acid content at the beginning of the reaction expressed as a percentage (86.13%wt. for the PWF),
 m_f and m_r are the masses of chemicals in feed and in the reaction in g,
 T_r is the reference temperature (25°C),
 T_a is the ambient temperature (28°C),
 C_{Methanol} and C_{Sulfuric} are the prices of methanol and sulfuric acid in US\$/ton (El-Galad, El-Katib, & Zaher, 2015; Gebremariam & Marchetti, 2018),
 $C_{\text{Electricity}}$ is the electricity cost in US\$/kWh (El-Galad *et al.*, 2015),
 C_p is the heat capacity of chemicals in J/g K (Lide *et al.*, 2003; Pauly, Kouakou, Habrioux, & Le Mapihan, 2014),
 ΔH_f^0 is the heat of formation of chemicals in the reaction at 25°C in J/g (Lide *et al.*, 2003).

On applying the regression model, the %FFA conversion was fixed at 90% because this would produce BFO meeting the criteria of a FO. Moreover, the yield was fixed at 96% because commercial BFO production would require a high yield. While the manipulated variables would be set at decimal numbers, they are approximated with integer numbers here. Thus, the minimal cost condition based on regression model had about 5:1 molar ratio of methanol-to-FFA and 6

%wt. of H_2SO_4 at 60°C for 30 minutes. The desired %FFA conversion and %yield were also changed to 91.21% and 95.20%, respectively, which pass the specifications for biodiesel production.

The operating point for minimal cost based on a model was validated experimentally, and the %FFA conversion was 90.71 and %yield was 95.98. Hence, the relative model errors in these responses were 0.55% and 0.81%, respectively. This chosen molar ratio of 5:1 could be extrapolated from the lower limit of data used in regression fitting, with acceptable accuracy since the regression had no peaks and was quite linear. The low molar ratio of methanol-to-FFA could also reduce methanol and reaction costs.

Considering the production costs in esterification step, a ton of BFO required 0.549 tons of methanol, 0.054 tons of H_2SO_4 and 148.71 MJ of electricity. So, the minimum cost of materials and energy for the esterification step was 258.83 US\$/ton BFO, with the details shown in Table 5.

3.3 Characterization of BFO

The properties of the BFO produced are summarized in Table 6. The results indicate that the BFO at the minimum cost conditions met the specifications for biodiesel, except for the kinematic viscosity at 40°C and sulfated ash content. However, this BFO met the specifications of FO No.4. Evidently, it is easier to convert waste fat to BFO than to biodiesel.

3.4 Production cost estimation

Overall, 75% of the biodiesel production costs are the costs of raw materials and the washing process, which has a high energy consumption. The operating costs of BFO production are shown in Table 7.

Table 5. The operating costs of esterification step at minimum cost condition

Sensible heat				Unit Cost of chemical (US\$/ton)	Cost of chemical (US\$/ton BFO)
Reactant	Feed at 28 °C (ton)	C_p (J/gK)	Energy (MJ)		
PWF	1.040	1.93	64.23	0.00	0.00
Methanol	0.549	2.53	44.45	441.40	242.33
Sulfuric	0.054	1.38	2.38	275.00	14.85
Total = $\{\sum m_f C_p * (C - T_a)\}_{\text{Feed}}$			111.06 (a)		257.18
Heat of reaction					
Chemical	Reaction at 60 °C (ton)	H_f (kJ/g)	Energy (MJ)		
FFA	0.895	-3.18	-2846.10		
Methanol	0.092	-7.44	-684.48		
Ester	0.855	-2.94	-2513.70		
Water	0.062	-15.88	-984.56		
Total = $\{(\sum m_r \Delta H_f^0)_{\text{Product}} - (\sum m_r \Delta H_f^0)_{\text{Reactant}}\}$			32.32 (b)		
Chemical	Heat capacity at 60 °C (ton)	C_p (J/gK)	Energy (MJ)		
FFA	0.895	1.77	55.45		
Methanol	0.092	2.53	8.15		
Ester	0.855	2.00	59.85		
Water	0.062	4.18	9.07		
Total = $\{\sum_i m_r C_p * (C - T_r)\}_{\text{Product}} - \{\sum_i m_r C_p * (C - T_r)\}_{\text{reactant}}$			5.33 (c)		
Total Energy = (a) + (b) + (c) = 148.71 MJ					
Total energy cost US\$/ton BFO from sensible heat = 1.65 US\$/ton BFO					

Table 6. Fuel properties of BFO

Property	Unit	Biodiesel, ASTM D6751		Fuel oils, ASTM D396								BFO
				No.1	No.2	No.4 (Light)	No.4	No.5 (Light)	No.5 (Heavy)	No.6		
Specific gravity at 15 °C		Max.	D1298	0.9	0.850	0.876	-	-	-	-	-	0.882
		Min.		0.86	-	-	>0.876	-	-	-	-	
Flash point	°C	Min.	D93	130	38	38	38	55	55	55	60	167
Kinematic viscosity at 40 °C	mm ² /s	Min.	D445	1.9	1.3	1.9	-	5.5	>24.0	>58	-	7.655
		Max.		6	2.1	3.4	-	24	58	168	-	
Copper corrosion		Max.	D130	No.3	No.3	No.3	-	-	-	-	-	No.1
Sulfated ash	wt.%	Max.	D874	0.02	-	-	-	-	-	-	-	0.027
Ash content	wt.%	Max.	D482	-	-	-	0.05	0.1	0.15	0.15	-	0.083
Water content	vol.%	Max.	D6304	0.05	0.05	0.05	0.05	0.05	1	1	2	0.049
Gross heating value (Engineering ToolBox, 2003)	MJ/kg	Min.	D240	37.5	37.80	38.96	40.33	40.70	41.75	42.49	43.03	37.3
		Max.			38.96	40.33	40.70	42.12	42.66	43.23	44.34	

Table 7. Operating costs of BFO production and feasibility of converting waste fat to BFO when processing 50 tons (the daily amount) of fresh fish in a fish-canning factory

Item	Amount	Unit cost	Cost (US\$/ton BFO)
Chemicals			
Methanol	0.549 ton	441.4 US\$/ton (El-Galad <i>et al.</i> , 2015)	242.33
Sulfuric acid	0.054 ton	275 US\$/ton (Gebremariam and Marchetti, 2018)	14.85
Utilities			
Water	45.710 ton	0.007 US\$/ton (El-Galad <i>et al.</i> , 2015)	0.32
Electricity	4,159.8 kWh	0.04 US\$/kWh (El-Galad <i>et al.</i> , 2015)	166.39
Total Production cost in esterification			423.89
Feasibility study of producing BFO from 50 tons of fresh fish			
Item	Daily use/produced	Unitary cost (US\$/ton)	Daily cost (US\$/day)
Costs of boiler fuel and disposal			
Waste disposal	550.0 kg of waste fat	170	93.50
Energy consumption	20,242.8 MJ	418.6	201.2
Total expenditure			294.8
Produce and use BFO			
Desired BFO	542.7 kg of BFO	423.89	230.04

Water removal after washing was by sun-drying with a very low mixing rate (Reynold number 215) in an open pond. So, the electricity costs in this part can be ignored.

Table 7 shows the cost of utilizing BFO compared with the combined costs of waste disposal and FO. For 50 tons/day of fresh fish, the fish-canning factory produced 550.0 kg of waste fat/day (Chowdhury, Viraraghavan, & Srinivasan, 2010). The disposal cost of waste fat was 170 US\$/wet ton (Cristóvão *et al.*, 2014). So, the factory spent on waste disposal about 93.62 US\$/day. Additionally, for energy the factory consumed commercial FO equivalent to 20,242.8 MJ/day (Quijera, Alriols, & Labidi, 2014) that becomes 201.2 US\$/day at FO cost 418.6 US\$/ton (U.S. Department of Energy, 2020). Since this BFO had a heating value of 37.3 MJ/kg, the factory required 542.7 kg BFO/day to replace the FO, and the production cost of this BFO is 230.04 US\$/day.

Comparing to the daily expenditures on FO and waste disposal totaling 294.8 US\$/day, replacing FO with BFO from waste fat could therefore result in a cost savings of approximately 21.8% per day. Thus, the production of BFO is economically feasible in the fish-canning factory.

4. Conclusions

Application of regression model of the process with the costs of materials and energy in the esterification step enabled minimizing the costs of BFO production from waste fat that had a high free fatty acid content. Additionally, the water removal step could be conducted in an open pond that would not require electricity. Our BFO met the criteria of FO no. 4. When BFO would be used to replace FO in the fish-canning factory, the cost of producing BFO from SWF would

be lower than the combined costs of waste disposal and purchasing of commercial FO. Therefore, instead of disposing waste, the factory can economically convert waste fat to BFO and use the BFO to replace purchased FO.

Acknowledgements

Financial support for this research was obtained from the Graduate School, Prince of Songkla University (PSU). Technical support of Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University is recognized. Waste fat was supplied by the Siam International Food Company Limited (Thailand). The authors also thank Seppo Karrila, Michael Currie, and the Research and Development Office, Prince of Songkla University, for assistance with manuscript preparation.

References

- Adewale, P., Dumont, M. J., & Ngadi, M. (2015). Recent trends of biodiesel production from animal fat wastes and associated production techniques. *Renewable and Sustainable Energy Reviews*, *45*, 574–588. doi:10.1016/j.rser.2015.02.039
- Arab-Tehrany, E., Jacquot, M., Gaiani, C., Imran, M., Desobry, S., & Linder, M. (2012). Beneficial effects and oxidative stability of omega-3 long-chain polyunsaturated fatty acids. *Trends in Food Science and Technology*, *25*(1), 24–33. doi:10.1016/j.tifs.2011.12.002
- Bi, C., Min, M., Nie, Y., Xie, Q., Lu, Q., Deng, X., . . . Ruan, R. (2015). Process development for scum to biodiesel conversion. *Bioresource Technology*, *185*, 185–193. doi:10.1016/j.biortech.2015.01.081
- Chongkhong, S., Tongurai, C., & Chetpattananondh, P. (2009). Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. *Renewable Energy*, *34*(4), 1059–1063. doi:10.1016/j.renene.2008.07.008
- Chowdhury, P., Viraraghavan, T., & Srinivasan, A. (2010). Biological treatment processes for fish processing wastewater - A review. *Bioresource Technology*, *101*(2), 439–449. doi:10.1016/j.biortech.2009.08.065
- Costa, J., Almeida, M., Alvim-Ferraz, M., & Dias, J. (2013). Biodiesel production using oil from fish canning industry wastes. *Energy Conversion and Management*, *74*, 17–23. doi:10.1016/j.enconman.2013.04.032
- Cristóvão, R. O., Botelho, C. M., Martins, R. J. E., Loureiro, J. M., & Boaventura, R. A. R. (2014). Primary treatment optimization of a fish canning wastewater from a Portuguese plant. *Water Resources and Industry*, *6*, 51–63. doi:10.1016/j.wri.2014.07.002
- El-Galad, M. I., El-Katib, K., & Zaher, F. (2015). Economic feasibility study of biodiesel production by direct esterification of fatty acids from the oil and soap industrial sector. *Egyptian Journal of Petroleum*, *24*(4), 455–460. doi:10.1016/j.ejpe.2015.06.002
- Engineering ToolBox. (2003). *Fuel oil combustion values*. Retrieved from https://www.engineeringtoolbox.com/fuel-oil-combustion-values-d_509.html
- Gebremariam, S. N., & Marchetti, J. M. (2018). Biodiesel production through sulfuric acid catalyzed transesterification of acidic oil: Techno economic feasibility of different process alternatives. *Energy Conversion and Management*, *174*(3), 639–648. doi:10.1016/j.enconman.2018.08.078
- Hasuntree, P., Toomthong, V., Yoschoch, S., & Thawornchaisit, U. (2011). The potential of restaurant trap grease as biodiesel feedstock. *Songklanakarin Journal of Science and Technology*, *33*(5), 525–530.
- He, X., de los Reyes, F. L., Leming, M. L., Dean, L. O., Lappi, S. E., & Ducoste, J. J. (2013). Mechanisms of fat, oil and grease (FOG) deposit formation in sewer lines. *Water Research*, *47*(13), 4451–4459. doi:10.1016/j.watres.2013.05.002
- He, X., & Yan, T. (2016). Impact of microbial activities and hydraulic retention time on the production and profile of long chain fatty acids in grease interceptors: A laboratory study. *Environmental Science: Water Research and Technology*, *2*(3), 474–482. doi:10.1039/c6ew00013d
- Husain, I. A. F., Hoda, A., Mirghani, M. E. S., Zainudin, Z. Bin, Jammi, M. S., & Alkhatib, M. F. (2014). Problems, control, and treatment of fat, oil, and grease (FOG): A review. *Journal of Oleo Science*, *63*(8), 747–752. doi:10.5650/jos.ess13182
- Kanjaikaew U., Tongurai C., Chongkhong S., Prasertsit K. (2018). Two-step esterification of palm fatty acid distillate in ethyl ester production: Optimization and sensitivity analysis. *Renewable Energy*, *119*, 336–344. doi:10.1016/j.renene.2017.12.002
- Khayoon, M., Olutoye, M., & Hameed, B. (2012). Utilization of crude karanj (*Pongamia pinnata*) oil as a potential feedstock for the synthesis of fatty acid methyl esters. *Bioresource Technology*, *111*, 175–179. doi:10.1016/j.biortech.2012.01.177
- Lide, D. R., Data, S. R., Board, E. A., Baysinger, G., Chemistry, S., Library, C. E., Berger, . . . Zwillinger, D. (2003). *CRC handbook of chemistry and physics*. Boca Raton, FL: CRC Press.
- Martín-gonzález, L., Castro, R., Pereira, M. A., Alves, M. M., Font, X., & Vicent, T. (2011). Thermophilic co-digestion of organic fraction of municipal solid wastes with FOG wastes from a sewage treatment plant: Reactor performance and microbial community monitoring. *Bioresource Technology*, *102*, 4734–4741. doi:10.1016/j.biortech.2011.01.060
- Mueanmas, C., Nikhom, R., Petchkaew, A., Iewkittayakorn, J., & Prasertsit, K. (2018). Extraction and esterification of waste coffee grounds oil as non-edible feedstock for biodiesel production. *Renewable Energy*, *133*, 1414–1425. doi:10.1016/j.renene.2018.08.102
- Nguyen, T. S., Zabeti, M., Lefferts, L., Brem, G., & Seshan, K. (2013). Conversion of lignocellulosic biomass to green fuel oil over sodium based catalysts. *Bioresource Technology*, *142*, 353–360. doi:10.1016/j.biortech.2013.05.023
- Pauly, J., Kouakou, A. C., Habrioux, M., & Le Mapihan, K. (2014). Heat capacity measurements of pure fatty acid methyl esters and biodiesels from 250 to 390 K.

- Fuel*, 137, 21–27. doi:10.1016/j.fuel.2014.07.037
- Quijera, J. A., Alriols, M. G., & Labidi, J. (2014). Integration of a solar thermal system in canned fish factory. *Applied Thermal Engineering*, 70(2), 1062–1072. doi:10.1016/j.applthermaleng.2014.04.012
- Roseiro, L., Santos, C., Gonçalves, H., Serrano, C., Aleixo, C., Partidário, A., . . . da Ponte, D. J. B. (2017). Susceptibility of dry-cured tuna to oxidative deterioration and biogenic amines generation: I. Effect of NaCl content, antioxidant type and ageing. *Food Chemistry*, 228, 26–34. doi:10.1016/j.foodchem.2017.01.125
- Schobing, J., Tschamber, V., Brillard, A., Leyssens, G., Iojoiu, E., & Lauga, V. (2018). Impact of engine operating cycle, biodiesel blends and fuel impurities on soot production and soot characteristics. *Combustion and Flame*, 198, 1–13. doi:10.1016/j.combustflame.2018.08.025
- Su, C.-H. (2013). Kinetic study of free fatty acid esterification reaction catalyzed by recoverable and reusable hydrochloric acid. *Bioresource Technology*, 130, 522–528. doi:10.1016/j.biortech.2012.12.090
- U.S. Department of Energy. (2020). Refiner petroleum product prices by sales type. Retrieved from https://www.eia.gov/dnav/pet/pet_pri_refoth_dcu_us_m.htm
- Vohra, M., Manwar, J., Manmode, R., Padgilwar, S., & Patil, S. (2014). Bioethanol production: Feedstock and current technologies. *Journal of Environmental Chemical Engineering*, 2(1), 573–584. doi:10.1016/j.jece.2013.10.013
- Wallace, T., Gibbons, D., O'Dwyer, M., & Curran, T. P. (2017). International evolution of fat, oil and grease (FOG) waste management – A review. *Journal of Environmental Management*, 187, 424–435. doi:10.1016/j.jenvman.2016.11.003