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Original Article

The potential of restaurant trap grease as biodiesel feedstock

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Abstract

The possibility of using restaurant trap grease as feedstock in the production of biodiesel via acid catalyzed esterification is explored in this study. Sulfuric acid was used as a catalyst for the esterification reaction of free fatty acid (FFA) and methanol. The FFA levels of restaurant trap greases were reduced from 60.38±2.22 mg KOH/g to 11.60±1.60 mgKOH/g when conditions for biodiesel production are as follow: methanol-to-FFA ratio of 5:1, 5 wt.% H_2SO_4, and a reaction temperature at 60°C with a reaction time of 60 min. During the acid-catalyzed esterification, the percentage of methyl esters resulting from conversion of FFA in the obtained product was 83.59±1.51% based on the result of ^{1}H NMR analysis. Data obtained from the 2^3 full factorial designs revealed that methanol-to-FFA ratio term had the most significant effect on the percentage of methyl esters, followed by the H_2SO_4 concentration. Conversely, reaction time between 1 and 3 hours had no significant effect on the esterification of trap greases.

Keywords: waste greases, brown grease, methyl ester, factorial design, esterification

1. Introduction

Biodiesel is the name that has given to the mono-alkyl ester based oxygenated fuel chemically derived from renewable lipid feedstocks, such as vegetable oils (both edible and non-edible) or animal fats. It is the similarities in the constitution of the vegetable oils/animal fats and petroleum derived diesel that makes the vegetable oils/animal fats suitable for conversion to biodiesel (Nigam and Singh, 2011). The resulting biodiesel with quite similar characteristics to conventional diesel can then be used directly or blended in any proportion with petroleum diesel to create a stable biodiesel blend (Agarwal, 2007; Enweremadu and Mbarawa, 2009). With several merits, such as cleaner combustion emission profile, biodegradable, and superior lubricating property, in comparison with diesel fuel (Donovan Associates Inc., 1998; Nelson and Schrock, 2005), biodiesel is then seen as a promising alternative fuel for diesel engines.

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While many oil seed crops, such as soy beans, sunflowers, palms, coconut, canola and rapeseed, can be used as feedstock for biodiesel production, oil palm is by far the most prospective biodiesel feedstock in Thailand. It is widely grown in the country especially in the southern part (Siangjaeo *et al.*, 2011). In addition, palm plantations have the highest oil yields in terms of oil production per hectare of plantation compared to plantations of other oil crops (Chisti, 2007). Furthermore, oil palm is a low-energy input crop offering fruitlets annually from a tree for up to 30 years. With oil palm as a major feedstock for edible oil mill industry, the growth in the biodiesel industry raises one major concern about increasing feedstock competition between the two industries as discussed by Fargione *et al.* (2008) and Demirbas (2009). Furthermore, changes in agricultural land-use, for example, from food crop into energy crop plantation, require a good management plan to prevent any future problems with food scarcity and with increasing costs of food items (Enweremadu and Mbarawa, 2009; Escobar *et al.*, 2009). In order to lessen competition with food products, the search for less expensive, but still renewable potential feedstocks for the production of biodiesel, such as non-edible oils and

restaurant waste greases, have been investigated (Canakci, 2007; Wang *et al.*, 2008; Diaz-Felix *et al.*, 2009; Montefrio *et al.*, 2010; Kumar and Sharma, 2011).

With technology and process improvements, restaurant waste greases have a definite potential as a feedstock for lower cost biodiesel production. The greases are classified in two categories, *yellow grease* and *brown grease*, based on the presence of fatty acid contents (Canakci, 2007). Restaurant trap grease, which is sometimes called "brown grease", refers to a group of fats, oils, and greases with free fatty acid content over 15% w/w (Canakci, 2007). As the name stated, it is typically recovered from waste grease traps used in the food service industry. The installment of grease traps between wastewater effluent points and the sewer system is very encouraging for restaurants and other commercial food handling establishments to minimize fouling of sewer lines (North Carolina Department of Environment and Natural Resources, 2002). Subsequently, huge volumes of restaurant trap grease are generated and the requirement for treatment and disposal then becomes a major concern. While trap grease contains sufficient heating value for combustion and should be considered as alternative fuels for the future (Al-Shudeifat and Donaldson, 2010), rather than being considered for its utilization, restaurant trap greases are commonly collected manually after separation in grease traps and open dumped with municipal solid waste in Thailand (Stoll and Gupta, 1997). Therefore, investigation on possible utilization schemes of trap grease in energy industry shall be beneficial not only in terms of reduction of solid waste being discharged into the environment and value-added utilization of the waste, but also offer an option to reduce the cost of biodiesel as well as extending the supply of biodiesel feedstocks.

One major challenge of using restaurant trap greases as feedstocks for the production of biodiesel is the elevated levels of free fatty acids (FFA), which hinders the conversion of this low cost feedstocks by transesterification due to soap forming with alkaline catalysts and the deleterious effect of soap on glycerine separation (Canakci and Van Gerpen, 1999; Canakci and Van Gerpen, 2001; Lotero *et al.*, 2005; Diaz-Felix *et al.*, 2009). In order to solve this problem, a two-step acid and alkali catalyzed process has developed and shown to be an effective and efficient method (Issariyakul *et al.*, 2007; Ngo *et al.*, 2007; Charoenchaitrakool and Thienmethangkoon, 2011), however the increased batch times make it too complicated for commercial biodiesel production (Wang *et al.*, 2008). Alternatively, a one-step acid catalyzed process where the FFA and triglyceride in the feedstock can be simultaneously converted into mono-ester was studied in an effort to increase utilization of waste greases with high FFA (Wang *et al.*, 2008). An important advantage that the homogenous acid-catalyzed reaction holds over the base-catalyzed method is that the performance of acid catalyst is not adversely influenced by the presence of FFA (Moser, 2009).

Trap grease from different collection sources vary widely in FFA levels depending on the type of material and the time of year. Furthermore, each feedstock has a unique chemical composition; biodiesel produced from different feedstocks will in turn have different fuel properties (Moser, 2009). Moreover, nature of cooking and eating habits would influence chemical characteristic of trap grease. While much literature has addressed the potential of trap greases as feedstocks for the production of biodiesel, a limited number of works on utilization of trap grease from restaurants in Thailand has been reported. The objective of this research is to investigate the potential use of restaurant trap greases in Thailand as feedstock for the production of biodiesel via acid catalysis. In order to understand the simultaneous effects of various parameters including the effects of reaction time, catalyst concentration, methanol-to-oil (based on the FFA contents) on the percentage of methyl ester and the interaction among parameters, a 2^3 full factorial experimental design is applied.

2. Experimental

2.1 Materials

The following reagents, all in AR grade, were used for the experiments: anhydrous methanol (Apex Co. Ltd, >99.8%) for the esterification reaction, sulfuric acid (Labsystem, 98% purity) as catalyst. The mixing scum (fats, oil and grease, FOG) was collected from in-ground grease trap tanks that are installed between wastewater effluent points and the sewer system. Major source of wastewater entering grease traps came from commercial restaurants that are located in the PTT gas service station and retail business, a rest area of Thailand's First Stage Expressway System (PTT Park, inbound and outbound route of Bang Na-Bangkok Port Expressway). Before using the trap grease for biodiesel production, it was filtered with the muslin and then air-dried to get rid of water.

2.2 Acid catalyzed esterification of the trap grease

Synthesis of biodiesel via acid catalyzed reaction using trap grease as feedstock was carried out using the experimental setup as shown in Figure 1. The experimental

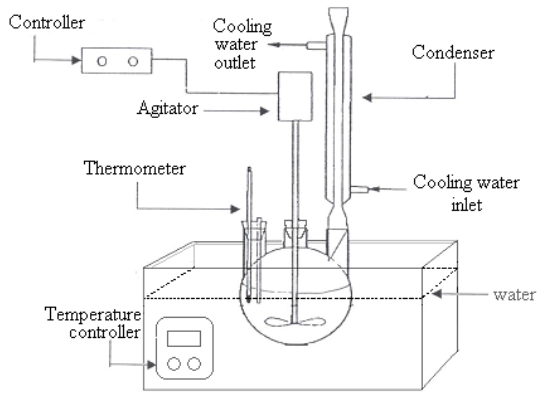

Figure 1. Experimental setup for the biodiesel production using acid-catalyzed method.

procedure as described by Zhang and Jiang (2008) was employed with a slight modification in the phase separation technique. The 100 g air-dried trap grease was poured into a three-neck round bottom flask and pre-heated to 60°C using a water bath with temperature controller (Fisher Scientific, Model ISOTEMP 228). The solution of H_2SO_4 in methanol was also preheated and added to the flask. The mixture was stirred at the same speed of 600 rpm for all test runs using a Sted fast™ stirrer (Fisher Scientific, Model SL2400). Heating and stirring were stopped after the reaction has reached the preset reaction time. After the reaction, the solution and solid phase of remaining trap grease was separated by centrifugation with a centrifuge (Sanyo, Model Centaur2) operated at 3,000 g for 10 min. The recovered solid phase was then analyzed for its acid value. The supernatant was decanted into a separating funnel and was washed four times using hot water (80°C) to remove the remaining catalyst. Excess methanol and water were removed by evaporation at 110°C. The percentage of purified ester phase was determined using ^{1}H Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR).

2.3 Analysis method

Free fatty acid in the samples was analyzed by titrimetry using 0.25 N NaOH and phenolphthalein as a titrant and indicator, respectively. The titration process was stopped when the solution turned into pink color. The percentage of free fatty acid was calculated using Equation 1 by assuming that oleic acid is the main composite of fatty acid in trap grease according to a report by Wang *et al.* (2008). Based on the results of the titration, the acid value was also calculated using Equation 2. Heating values in the original trap grease were determined according to ASTM D240-92. ^{1}H NMR analyses were performed on a Bruker DPX 300 MHz spectrometer (Bruker, Germany) with XWIN NMR 3.5 software using deuterated chloroform (CDC_{l3}) as the solvent.

$$\%\ Free\ fatty\ acid = \frac{volume\ of\ NaOH\ used, L \times 282 \times 0.25}{weight\ of\ sample, g} \times 100 \quad (1)$$

$$Acid\ value\left(\frac{mgKOH}{g}\right) = \frac{volume\ of\ NaOH\ used, mL \times 56.1 \times 0.25}{weight\ of\ sample, g} \quad (2)$$

2.4 Experimental design

In this study, a two-level three-factor full factorial design was employed to determine the influence of operational conditions on the methyl ester contents of biodiesel from trap grease. Reaction time (t), catalyst concentration (C), and methanol-to-free fatty acid content in trap grease ratio (M) were the independent variables selected to determine its effect on the percentage of methyl ester. The coded and uncoded levels of the independent variables are given in Table 1. Two replications were carried out for experimental error estimation and the experiments were carried out in randomized order to minimize errors due to possible systematic trends in the variables.

2.5 Statistical analysis

The SPSS version 14.0 (SPSS, USA) was used for statistical analysis of the data obtained by carrying out the experiments according to a 2^3 full factorial design.

3. Results and Discussion

3.1 Physical and chemical properties of trap grease

Crude trap grease was grey in color, very smelly and contains thick texture characteristic like porridge (Figure 2a). After filtering and air-drying prior to its use in the study, the pre-treated trap grease turn into the dry form as shown in Figure 2b.

Selected chemical properties of the pre-treated trap greases are shown in Table 2. The pre-treated trap grease

(a) (b)

Figure 2. Trap grease used in the study; (a) before pre-treatment and (b) after pre-treatment.

Table 1. Independent variables and levels used in this study.

Variables	Symbol coded	Range and Levels	
		-1	+1
Reaction time (hrs)	*T*	1	3
Weight ratio of sulfuric acid (%w/w)	*C*	2	5
methanol-to-free fatty acid content in trap grease ratio (w/w)	*M*	3:1	5:1

Table 2. Selected chemical properties of the pre-treated trap grease.

Property	Value (n=3)
Heating value	4,664±91 kcal/kg
Free fatty acid (FFA)	31.06±2.21%
Acid value	60.38±2.22 mg KOH/g

contains very high heating value to be considered as possible fuel substitute; however, it consists of high free fatty acids (31.06% FFA, 60.38 mg KOH/g), which made biodiesel production via alkaline catalyzed method impractical.

3.2 Effect of independent variables on reduction of acid value of trap grease

Esterification of the trap grease resulted in the reduction of acid value in all experiment runs as shown in Figure 3. The acid value of trap grease was reduced to about 15.59± 5.10 mg KOH/g from 60.38 mg KOH/g by acid catalyzed esterification with methanol to FFA ratio of 3:1 using H_2SO_4 catalysts. When the weight ratio of methanol increased to 5:1, acid value was reduced to 11.60±1.60 mgKOH/g suggesting that higher methanol-to-FFA ratio could further improve the reduction of acid value of trap grease. Similarly, Zhang and Jiang (2008) reported that acid value of *Zanthoxylum bungeanum* seed oil with initially high free fatty acid could not go below 10 mg KOH/g after 60 min of reaction time at 60°C with a 4:1 methanol-to-oil molar ratio, but a further increase of the methanol ratio to 24:1 reduced the acid value to less than 2 mg KOH/g. Figure 3 also showed that catalyst concentration has an influence on the ester content but in different ways compared to the methanol ratio. It was found that as the catalyst concentration increased from 2% to 5% wt. H_2SO_4, the acid value in the final product was increased from 10.79±1.08 to 16.39±4.14 mg KOH/g. Furthermore, increasing reaction time did not promote any reduction of acid value (Figure 3) corresponding to the results reported by Zhang and Jiang (2008) who observed that increasing reaction time beyond 80 min did not have much effect on reducing the acid value of *Zanthoxylum bungeanum* seed oil with an initial acid value of 45.51 mg KOH/g.

3.3 Effect of independent variables on percentage of purified ester phase

The methyl ester contents of biodiesel obtained from the designed experiment are given in Table 3. As two variables were kept constant, the %-methyl ester increased when the values of either the methanol to FFA weight ratio or the catalyst concentration increased suggesting a positive influence of these two factors. No such trend was observed with changing the reaction time when the catalyst concentration and the methanol to FFA weight ratio was kept constant.

The response was fitted to the factors through a general linear model (GLM). The ANOVA for the response surface linear model is provided in Table 4. While reaction time between 1 and 3 hours did not significantly affected the percentage of methyl ester in biodiesel from trap grease, the most significant factor was the methanol-to-FFA ratio (p-value 0.004<0.05) followed by the catalyst concentration (p-value 0.035<0.05) at 95% confidence level. The p-value of all the interaction terms was found to be more than 0.05,

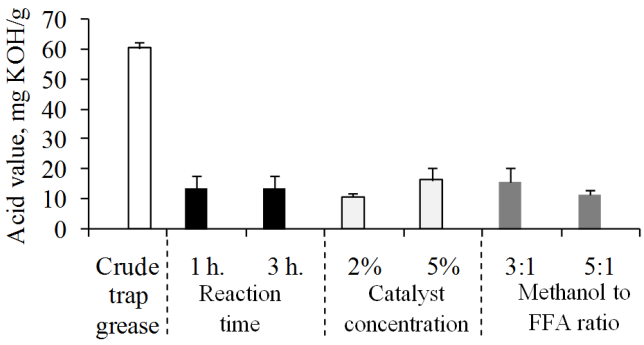

Figure 3. Acid values of crude trap grease and the pretreated trap grease after acid catalyzed esterification process as a function of reaction time, catalyst concentration, and methanol to FFA ratio.

Table 3. Experimental matrix and % methyl ester of the final product.

Experiment number	Reaction time (h)	H_2SO_4 concentration (wt %)	methanol -to-FFA ratio	% methyl ester
1	1	2	3:1	66.63±1.61
2	1	2	5:1	75.80±1.56
3	1	5	3:1	70.99±4.68
4	1	5	5:1	83.59±1.51
5	3	2	3:1	62.32±8.63
6	3	2	5:1	73.59±6.96
7	3	5	3:1	69.88±9.93
8	3	5	5:1	82.78±3.08

Table 4. ANOVA for general linear model.

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Corrected model	767.955	7	109.714	3.373	0.055
Reaction time (x_1)	17.830	1	17.830	0.548	0.480
Catalyst concentration (x_2)	208.730	1	208.730	6.417	0.035
Methanol-to-FFA ratio (x_3)	527.506	1	527.506	16.216	0.004
x_1*x_2	5.256	1	5.256	0.162	0.698
x_1*x_3	1.446	1	1.446	0.044	0.838
x_2*x_3	6.414	1	6.414	0.197	0.669
$x_1*x_2*x_3$	0.815	1	0.815	0.025	0.878
Error	260.239	8	32.530		
Corrected total	1028.234	15			

showing that interaction terms had no significant effect on the percentage of methyl ester.

4. Conclusions

The acid-catalyzed esterification using H_2SO_4 as catalyst reduces the acid value of trap grease with high FFA. The combination of methanol-to-FFA weight ratio 5:1, sulfuric acid 5%, temperature 60°C and reaction time 60 min reduced the acid value from 60.38 mg KOH/g to about 12 mg KOH/g. The highest methyl ester content obtained from this condition was found to be 83.59±1.51%. Methanol-to-FFA ratio was a major factor on the esterification followed by catalyst concentration. However, further research on increasing methanol ratio and fuel properties of the biodiesel is still necessary.

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