Tallow waste utilization from leather tanning industry for biodiesel production

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ABSTRACT

The propose of this research was to develop a two-step biodiesel production from tallow waste from leather tanning industry. With special attention to optimize the first step is acid catalyzed esterification to reduce acid value into low level that can further react in the second step. The second step is alkali catalyzed transesterification for converting triglyceride to biodiesel. tallow waste containing 78.80 mg KOH/g of high acid value was used as raw material. By using response surface methodology (RSM), a quadratic polynomial equation was obtained for acid value. The optimum esterification indicated at 1.10 (v/w) of methanol to tallow waste ratio, 2.40% sulfuric acid concentration in 1.00 h of reaction time and 60 °C of reaction temperature. After transesterificaiton, the methyl ester yield was 86.10% and the properties of the tallow waste biodiesel met biodiesel specification

Keywords: *Tallow waste, triglyceride, biodiesel, esterification, transesterification, RSM*

1. Introduction

Biodiesel is a renewable, non-toxic, environmentally friendly and biological origin alternative fuel for diesel engines. Biodiesel has many advantages compared to diesel fuel and it plays an important role in meeting future fuel requirements. It has higher cetane number than diesel fuel, and contains no aromatics, almost no sulfur and 10-12% oxygen by weight. Biodiesel fuelled engines produce less CO, HC and particulate emissions than petroleum diesel fuelled engines [1]. The major handicap is the high cost of biodiesel for its commercialization [2]. Using high quality virgin oil makes biodiesel more expensive than diesel fuel. Therefore, low cost feed stocks are needed. Animal fat is appealing feedstock to produce biodiesel. The price of tallow waste is about half time less than that of virgin vegetable oil. Therefore, the price of feedstock can be reducing about 50% with using low grade tallow waste. However, it often contain high amount of acid value (> 2 mg KOH/g) [3], that can not be converted to biodiesel using alkaline catalysts because free fatty acid react with an alkaline catalyst to produce soap that prevent the separation of ester and glycerin. This problem result diminished biodiesel yield. For solving, an acid catalyst can be use to esterify the free fatty acid to ester in esterification reaction. The pretreatment fat can be further transesterify with an alkaline catalyst to converse the triglyceride to ester in transesterification reaction [4].

Response surface methodology (RSM) is a useful statistical technique which has been applied in research into complex variable process [5]. It employs multiple regression and correlation analyses as tools to assess the effect of two or more independent factors on the dependent variables. Its principle advantage is the reduced number of experimental runs required to generate sufficient information for a statistically acceptable result. RSM has been successfully applied in the study and optimization of biodiesel production with different vegetable oils [6].

The objectives of this research are performed according to central composite design and response surface methodology to optimize the acid value level (below 2 mg KOH/g) of tallow waste in esterification step. After the optimum pretreatment parameters are determined, the transesterification

step is carried out with alkaline catalyst to produce biodiesel. The obtained biodiesel is characterized by determining its fuel properties according to standard test methods.

2. Methodology

2.1 Materials

Tallow waste of cattles obtained from tannery industry in Thailand. The tallow waste was subjected to a heating at 110°C for 1 h to remove water and then filtered to remove the insoluble materials. Table 1 showed the fatty acid composition of tallow waste. Reference standards of fatty acid methyl esters with > 99% purity were purchased from sigma chemical Co. Ltd. (ST.Louis, MO, USA). Methanol, Sulfuric acid, Potassium hydroxide, and all other chemicals were of analytical grade.

Table 1 Fatty acid compositions of tallow waste.

Fatty acid	Formula	Structure	wt %
Decanoic	$C_{10}H_{20}O_2$	10:0	0.07
Lauric	$C_{12}H_{24}O_2$	12:0	0.13
Myristic	$C_{14}H_{28}O_2$	14:0	3.51
Palmitic	$C_{16}H_{32}O_2$	16:0	26.50
Palmitoleic	$C_{16}H_{30}O_2$	16:1	7.77
Steric	$C_{18}H_{36}O_2$	18:0	19.24
Oleic	$C_{18}H_{34}O_2$	18:1	40.10
Linoleic	$C_{18}H_{32}O_2$	18:2	1.68
Linolenic	$C_{18}H_{30}O_2$	18:3	0.40
Arachidic	$C_{20}H_{40}O_2$	20:0	0.51
Behenic	$C_{22}H_{44}O_2$	22:0	0.10

2.2 Apparatus and reaction procedures

The reactions on esterification step were conducted in 50 ml three necked flask equipped with a reflux condenser, a thermometer. The flask was heated and stirred with magnetic stirrer on agitator heater. For esterification experiment, the flask was charged with 20 g of tallow waste and heated to the setting temperature with agitation. A certain quantity of sulfuric acid catalyst was dissolved in the required amount of methanol. After achieving the setting temperature of the reactant and catalyst, methanol catalyst was added to the flask. The reaction was timed immediately after the addition of catalyst and methanol. The reaction experiment parameters were designed as Table 2.

Table 2 Independent variables and their levels for central composite design in optimization of esterification step.

Independent variables	Symbols	Code levels[a]				
		-1.68 (-α)	-1	0	+1	+1.68 (+α)
Methanol to animal fat ratio	M	0.45	0.75	1.205	1.66	1.96
H_2SO_4 concentration (% w/w)	C	0.48	1.50	3.00	4.50	5.52
Reaction time (h)	T	0.32	1.00	2.00	3.00	3.68

[a] Transformation of variable levels from code (X) to uncoded could be obtained as: M= 1.205+0.455X ,C= 3+1.5X and T=2+X

For transesterification step, animal fat with low acid value less than 2 mg KOH/g that obtained from esterification step was further reacted with methanol and potassium hydroxide (KOH) which used as catalyst. The conditions of experiment followed Alptekin *et. al*. (2010) who produced methyl ester from chicken fat. This conditions were: molar ratio between alcohol and animal fat was 6:1, the catalyst amount was selected as 1% of the weight of fat. The experiment was carried out in laboratory scale with 1.5 h of reaction time and 60°C of reaction temperature. After the transesterification reaction, the glycerin layer was separated in a separating funnel. The methyl esters layer was washed with warm water. After washing, the methyl ester was subjected to a heating at 100°C to remove excess water. Methyl ester was further characterized for physical chemical properties and methyl ester yield.

2.3 Experimental design for esterification step

A five-level-three-factor central composite design was employed in this optimization study, requiring 20 experiments. Methanol-to-tallow waste ratio (M), acid catalyst concentration (C) and reaction time (T) were the independent variables to optimize the reduction of acid value (AV) of tallow waste. The coded and uncoded levels of the independent variables showed in Table 2. Each variable to be optimized was coded at five levels: –α (–1.68), –1, 0, +1, +α (+1.68). The central values (zero level) chosen for experimental design were 1.205 (v/w) of methanol-to- tallow waste ratio, 3.00% (w/w) of acid catalyst concentration and 2.00 h of reaction time. This gives a range of these variables of esterification step. Six replication runs at the center (0, 0, 0) of the design were performed to allow the estimation of the pure error.

2.4 Statistical analysis

The data obtained by carrying out the experiments according to central composite design were analyzed by SPSS package (version 12.0). The response surface was expressed as the following third–order polynomial equation.

Equation (1) :

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_{ii}^2 + \sum_{i=1}^{3} \beta_{iii} X_{iii}^3 + \sum_{i<j}^{2} \sum_{j=1}^{3} \beta_{ij} X_i X_j + \sum_{i<1}^{1} \sum_{i<k}^{2} \sum_{k=1}^{3} \beta_{ijk} X_i X_j X_k$$

Where Y = the response (AV; mg KOH/g), Xi, Xj, Xk = uncoded independent variables, β_0 = constant, β_i = linear term coefficients, β_{ii} = quadratic term coefficients, β_{iii} = cubic term coefficients, and β_{ij} and β_{ijk} are cross-product term coefficients. SPSS package was used for regression analysis of variance (ANOVA) and response surfaces methodology was performed using the SPSS software. Response surfaces plots was developed using the fitted quadratic polynomial equation obtain 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 [4].

2.5 Analytical methods

a. Acid value

The acid value was determined via ASTM D664. 10 g of sample was introduced into a 200 ml flask, after which 125 ml of propanol/tolulene (1:1, v/v) solution by solvent was added to the reactant. Add 2 ml of phenolphthalein (1 g of phenolphthalein in 100 ml of ethanol) solution into the flask and titration with 0.1 N potassium hydroxide solution.

The acid value in mg KOH/g was calculated in accordance with the following equation 2.

Equation (2) :

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

In which A was milliliter of potassium hydroxide solution titrated with sample, B was milliliter of potassium hydroxide solution titrated with blank, N was the concentration of potassium hydroxide in normality unit, W was the weight in gram of sample, and 56.1 was KOH molecular weight.

b. Fatty acid methyl ester content

The content of fatty acid methyl ester was measured via standard EN 14103. The analyses were conducted on a gas chromatography (Agilent Technologies GC-6890) using a fused silica capillary column (DB-WAX, Agilent Technologies, USA) and a flame-ionization detector with an injection temperature of 270°C, and a detector temperature of 270°C. The spit ratio was 30:1. The fatty acid methyl ester content was calculated via the following equation 3.

Equation (3) :

$$\%\,Methyl\ ester = \frac{\sum A - Ais}{Ais} \times \frac{Cis \times Vis}{W} \times 100$$

In which methyl ester content had unit in wt%, ΣA was the total peak area of methyl ester, Ais was the peak of methyl heptadecanoate which used as internal standard, Cis was the concentration of methyl heptadecanoate solution (mg/ml) Vis was the volume of methyl heptadecanoate solution (ml), and W was the weight in gram of sample.

2.6 Characterization of tallow waste methyl ester properties

The tallow waste methyl ester was characterized by determining its viscosity, density, flash point, acid value, total-free glycerin, mono-di-tri-glycerin and %methyl ester, the following test methods were used: density @ 15°C (ASTM D1293), Viscosity @ 40°C (ASTM D445), flash point (ASTM D93), acid value (ASTM D664), total glycerin content (EN 14105) and % methyl ester content (EN 14103).

Table 3 Physical and chemical properties of tallow waste.

Properties	Unit	Amount
Density at 15 °C	(g/cm^3)	0.8928
Kinematic viscosity at 40 °C	(cSt)	32.27
Acid value	(mg KOH/g)	78.80
Water content	(%wt.)	0.32
Average molecular weight	(g/mol)	851

3. Results and discussion

3.1 Properties of Tallow waste

The physical and chemical properties of the tallow waste showed in Table 3. It indicated that the tallow waste had high acid value (78.80 mg KOH/g) with it need to reduce to less than 2 mg KOH/g (or 1% free fatty acid) which was suggested by many researchers [7] before using the alkaline catalysis. High kinematic viscosity of tallow waste was due to high molecular weight of tallow waste. The average molecular weight (g/mole) of tallow waste was determined by a weight average method utilizing the fatty acid profiles (Table 1). Specifically, the molecular weight of each fatty acid found in tallow waste was multiplied by its corresponding weight percentage as determined by GC. The sum of these values (minus the acidic proton) was multiplied by three and the glycerol fragment (minus of hydroxyl groups) was added, result in average molecular weight of tallow waste. This average molecular weight was used to calculated the mole ratio of methanol to tallow waste in transesterification step.

Table 4 Central composite design arrangement and response for esterification step.

Run	M	C	T	M	C	T	Acid value (mg KOH/g)	
				(v/w)	(%w/w)	(h)	Experimental	Predicted
1	-1	-1	-1	0.75	1.50	1.00	2.59	2.54
2	-1	-1	1	0.75	1.50	3.00	2.12	2.06
3	-1	1	-1	0.75	4.50	1.00	13.61	13.56
4	-1	1	1	0.75	4.50	3.00	13.34	13.29
5	1	-1	-1	1.66	1.50	1.00	1.12	1.06
6	1	-1	1	1.66	1.50	3.00	5.11	5.05
7	1	1	-1	1.66	4.50	1.00	3.89	3.84
8	1	1	1	1.66	4.50	3.00	1.26	1.20
9	-1.68	0	0	0.441	3.00	2.00	10.65	10.73
10	+1.68	0	0	1.969	3.00	2.00	0.69	0.76
11	0	-1.68	0	1.205	0.48	2.00	1.12	1.19
12	0	+1.68	0	1.205	5.52	2.00	14.16	14.25
13	0	0	-1.68	1.205	3.00	0.32	1.77	1.85
14	0	0	+1.68	1.205	3.00	3.68	2.10	2.17
15	0	0	0	1.205	3.00	2.00	2.82	2.52
16	0	0	0	1.205	3.00	2.00	2.58	2.52
17	0	0	0	1.205	3.00	2.00	2.19	2.52
18	0	0	0	1.205	3.00	2.00	2.54	2.52
19	0	0	0	1.205	3.00	2.00	2.36	2.52
20	0	0	0	1.205	3.00	2.00	2.66	2.52

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

Model	Sum of Squares	df	Mean Square	F	Sig.
Regression	386.665	13	29.743	581.146	0.000[a]
Residual	0.307	6	0.051		
Total	386.972	19			

[a] Predictors: (Constant), MCT, MMM, TTT, CCC, T, C, M, CT, MT. MC, TT, CC, MM

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

Model	Unstandardized Coefficients		Standardized Coefficients	Sig.
	B	Std. Error	Beta	
1	9.865	1.610		0.001
M	-25.159	3.106	-2.149	0.000
C	5.033	0.596	1.418	0.000
T	-2.682	0.894	-0.504	0.024
MM	14.615	2.640	3.066	0.001
CC	-0.990	0.184	-1.729	0.002
TT	-0.248	0.414	-0.193	0.570
MC	-1.773	0.262	-0.774	0.001
MT	4.324	0.393	1.258	0.000
CT	0.970	0.151	0.801	0.001
MMM	-2.514	0.726	-1.078	0.013
CCC	0.201	0.020	1.925	0.000
TTT	0.011	0.068	0.032	0.873
MCT	-1.249	0.117	-1.445	0.000

3.2 Model development

The central composite design conditions, responses, and the statistical analysis of the ANOVA were given [8] in Table 4 and 5, respectively. The acid value of experiment were calculated with 20 experimental values for predicted model. The multiple regression coefficients were obtained by employing a least square technique to predict a quadratic polynomial model for acid value (Table 6). The model was tested for adequacy by analysis of variance. The regression model was found to by highly significant of R-squared (R^2) as shown in Figure 1.

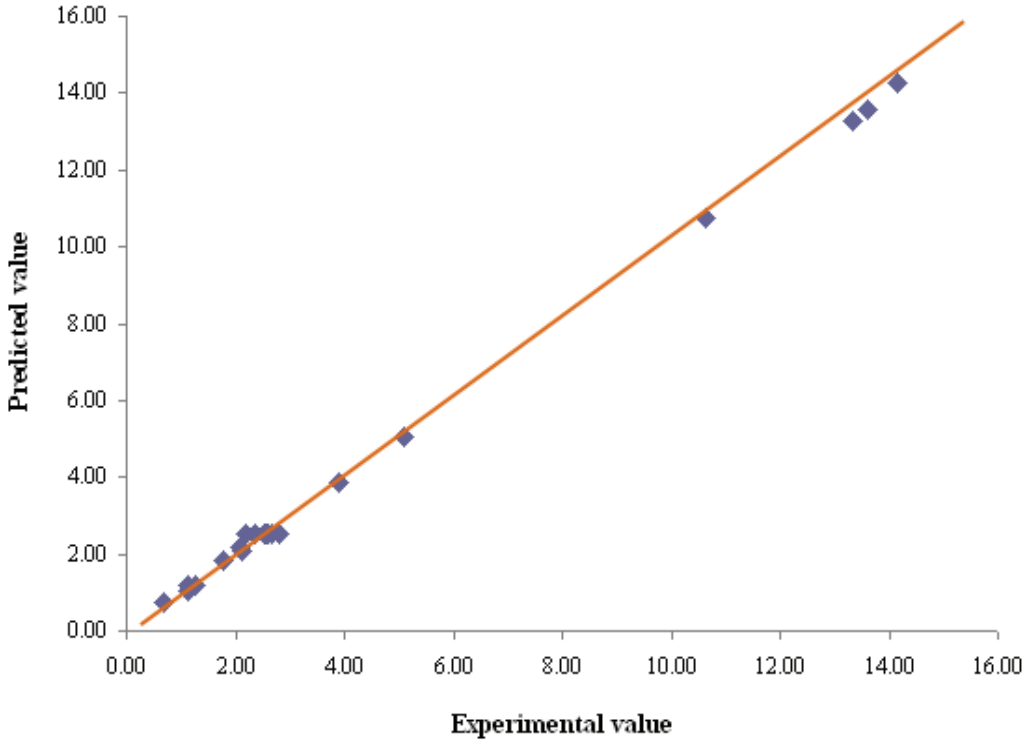

Figure 1 Correlation of experimental and predicted acid value (mg KOH/g)

The Fig. 1 indicated that the values of the response predicted from the empirical model were in agreement with the experimental values in the range of the operating variable ($R^2 = 0.9990$)

The predicted model for mg KOH/g of acid value (Y) in term of the coded factors was shown in equation 4.

Equation (4) :

$$Y = 9.865 - 25.159M + 5.033C - 2.682T + 14.615M^2 - 0.990C^2 - 0.248T^2 - 1.773MC + 4.324MT + 0.970CT - 2.514M^3 + 0.201C^3 + 0.011T^3 - 1.249MCT$$

In addition, the predicted model equation of acid value could calculated with the code value (-1, 0, 1, -1.68, +1.68) that the new predicted model as equation 5 was obtained.

Equation (5) :

$$Y = 2.52 - 2.299M + 1.967C + 0.066T + 1.143M^2 + 1.841C^2 - 0.18T^2 - 2.915MC + 0.262MT - 0.802CT - 0.236M^3 + 0.678C^3 + 0.011T^3 - 0.853MCT$$

When the code value M=0, C=0 and T=0 were replaced in this equation, the result of acid value(Y) was 2.52 that equal the predicted value from experiment run 15 to 20 in Table 4. It meaned that this predicted model equation was reasonable correlation. The regression model of equation 5 is the same high R^2 (0.9990) value as equation 4, so response surface plots and optimization of esterificaiton step can further study by using both predicted model equations. But in this further study, the predicted model equation 4 is selected because it is not need to transform the code value to experimental value. Also, the experimental value M=1.1, C=2.4, and T=1.0 were replaced in equation 4, the result of acid value (Y) was 1.87 that equals the predicted value from experiment 1 in Table 7. The result showed that the predicted model of equation 4 was reasonable correlation.

3.3 Response surface plots

The optimized levels of variables were determined by constructing three-dimensional surface plots according to equation 4. Two variables were plotted at any one time on the x_1 and x_2 axes, respectively, with the other remaining variables set at their centre point values(coded level: 0). Figure 2 (a) showed the effect of methanol-to-animal fat ratio (M), acid catalyst amount (C). Figure 2 (b) showed the effect of methanol-to- tallow waste ratio, reaction time (T), and Figure 2 (c) showed the effect of acid catalyst amount, reaction time and their mutual interaction on the acid value.

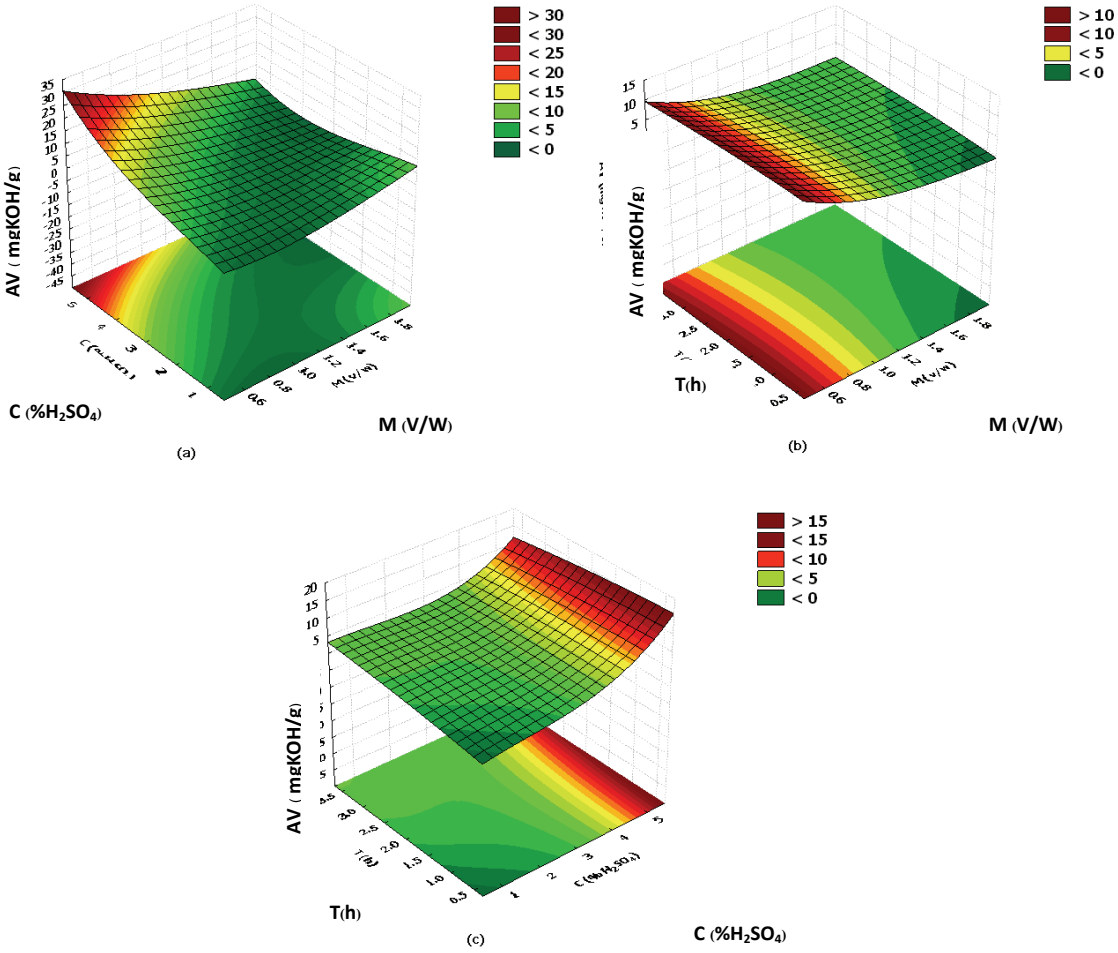

Figure 2 Response surface plots showing the effect of acid catalyst amount methanol-to-animal fat ratio, reaction time and their mutual effect on acid value predicted from the quadratic polynomial model.

The result from Fig. 2 (a), (b) and (c) indicated the optimum value of amount of acid catalyst methanol-to- tallow waste ratio, and reaction time in the range 2.40-3.3% were 1.1-1.4 (v/w) and 1-2.5 h respectively that reduced acid value below 2 mg KOH/g.

3.4 Optimization of esterification step

The optimal conditions for esterification step from tallow waste were predicted using the optimization function of the SPSS software [9]. These were presented in Table 7 along with their experimental and predicted values. Among the various optimum conditions, all experiments had acid value less than 2 mg KOH/g which could further reacted in transesterification step without problem. The reaction condition of 1 h, methanol-to- tallow waste ratio (v/w) 1.10:1 and 2.4% amount of acid catalyst (experiment 1) was chosen as the optimum condition because this condition used less amount of catalyst, methanol and shorter time in reducing acid value than other experiments.

Table 7 Solutions of Optimum Conditions.

Experiment	M (v/w)	C (% w/w)	T (h)	Acid value (mg KOH/g)	
				Experimental	Predicted
1	1.1	2.4	1.0	1.83	1.87
2	1.2	2.7	1.0	1.79	1.80
3	1.3	3.0	1.2	1.77	1.87
4	1.4	3.2	1.5	1.78	1.80
5	1.4	3.3	1.0	1.84	1.81

3.5 Transesterification step and biodiesel properties

After the esterification step with 2.40 % sulfuric acid and methanol-to- tallow waste ratio at 1.1 (v/w) for 1 h at 60°C, the transesterification reaction was run for 1.50 h at 60°C, methanol-to-tallow waste mole ratio was 6:1 base on the tallow waste. The potassium hydroxide catalyst was selected at 1 % on the weight of tallow waste.

The methyl ester yield was 86.10 % after transesterification. This result was nearly methyl ester yield with the two-step experiment of Alptekin (2010). The color of the product was light yellow after transesterification. The fuel properties of tallow waste methyl ester were given in Table 8. As seen in Table 8, the measured fuel properties were mostly suitable for the ASTM D 6751 and EN 14214 standards. This meaned that high fuel quality methyl ester was produced via two-step catalyzed process. The 5.06 cSt viscosity level was within 1.9-6.0 cSt of ASTM D 6751 standard, and the 170 °C Flash point has been highly more comparing with the accepted minimum level (120 °C) of ASTM D 6751 standard.

Table 8 Fuel properties of tallow waste methyl ester.

Properties	**Unit**	**Tallow waste biodiesel**	**ASTM D 6751**	**EN 14214**
Density at 15°C	g/cm^3	0.85	-	0.86-0.96
Viscosity at 40°C	cSt	5.06	1.9-6.0	3.50-5.00
Flash point	°C	170	120 min	130 min
Acid value	mg KOH/g	0.53	0.80 max	0.50 max
Total glycerin	%wt.	0.07	0.24 max	0.25 max
Free glycerin	%wt.	0.00	0.02 max	0.02 max
Monoglyceride	%wt.	0.11	-	0.80 max
Diglyceride	%wt.	0.09	-	0.20 max
Triglyceride	%wt.	0.02	-	0.20 max

4. Conclusion

The tallow waste with high acid value (78.80 mg KOH/g) could be used as raw material for biodiesel production. The high acid value could be reduced to less than 2 mg KOH/g by using the central composite design and response surface methodology in esterification step. The optimum condition of esterification reaction was obtained at 1.10 (v/w) of methanol to tallow waste ratio, 2.40% sulfuric acid concentration in 1 h of reaction time and 60 °C of reaction temperature. After the optimum conditions were determined, the process was continued for transesterification step. The high ester yield was obtained after transesterificaiton reaction with KOH. The methyl ester yield was 86.10% and the properties of tallow waste methyl ester met the ASTM D6751 and EN 14214 biodiesel standards.

5. Acknowledgement

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