Biodiesel Production and Optimization from Soapstock of Edible Oil Plants

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Abstract — **Up-to-date the predominant feed stocks for the production of biodiesel are semi-refined and refined vegetable oils. However, their relatively high costs render the resulting fuels unable to compete with petroleum derived fuel. In this study, the production of fatty acid methyl esters (FAME; biodiesel) from soapstock, a byproduct of edible oil refining that is substantially less expensive than edible grade refined oils, have been analyzed. A hydrolysis approach was taken in search of a route to the production of biodiesel from cottonseed soapstock. The method involved the complete saponification of the soapstock followed by drying and making as a pulverized powder form in a size of 5mm. Esterification of saponified, dried and pulverized soapstock with methanol was held in the presence of sulfuric acid as a catalyst. Design expert® v.7 software was used to optimization reaction conditions for acid catalyzed preparation of biodiesel from soapstock. Biodiesel yield of 59.9% (wt.) was obtained under optimum conditions of soapstock to methanol molar ratio of 1:25, reaction time of 3 hours and reaction temperature of 35oC. Validation experiments verified the availability and the accuracy of the model. The predicted value was in agreement with the experimental value, 59.6% (wt.).**

Key words - **Biodiesel, Soapstock, Esterification, Hydrolysis routine, Optimization**

I. INTRODUCTION

The world's energy demand has been steadily increasing since the beginning of industrialization in the 19th Century. Growth rates were particularly strong in western industrialized countries during the economic boom that followed the Second World War [1]. The 20th Century saw the rise of liquid fuels based on petroleum (petrol, diesel, kerosene, etc.). These fuels are especially important in the transportation sector. Their high energy content and ease of storage in tanks are to their advantage. Depending on the definitions and methods of calculation used, fossil fuels, i.e., coal, oil and gas, account for 80 to 90% of global primary energy supply. Nuclear energy, hydropower and mostly in developing countries non-commercial biomass fuels are further sources of energy worth of note. In most regions, oil continues the most important source of energy [1].

The world is facing severe energy crisis attributed to global oil reserve depletion, increasing consumption rate, incessant oil price hike and above all environmental concerns (air pollution and emission of greenhouse gases) dictate that the world community must hunt for alternative and sustainable energy sources. One of the mitigation efforts considered in response to the crisis is finding substitute for petroleum oil. Biofuels are becoming the most reliable energy sources, among which, biodiesel attracted attention to substitute for the ever-increasing petro-diesel demand and consumptions for every activity of human beings [2].Biodiesel is the monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats [3].

Biodiesel is the best candidate for diesel fuels in diesel engines. It burns like petroleum diesel as it involves regulated pollutants. On the other hand biodiesel probably has better efficiency than gasoline. Biodiesel also exhibits great potential for compression-ignition engines. Biodiesel is now mainly being produced from soybean, rapeseed, and palm oils. The higher heating values (HHVs) of biodiesels are relatively high. The HHVs of biodiesels (39 to 41 MJ/kg) are slightly lower than those of gasoline (46 MJ/kg), petro-diesel (43 MJ/kg), or petroleum (42 MJ/kg), but higher than coal (32 to 37 MJ/kg) [3]-[4].
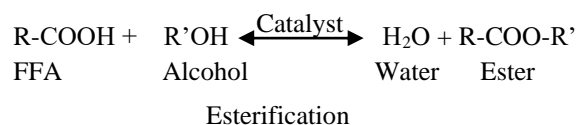
Biodiesel can be used in pure form or may be blended with petroleum diesel at any concentration for use in most modern diesel

engines [5]. The standardization of this product, and its industrial production, renders its use much more diverse than pure plant oil. Biodiesel is used in diesel engines and diesel vehicles [6].

In Ethiopia, currently there are over 50 developers registered for the cultivation of energy crops for biodiesel production of which 14 of them have started operations. So far, over 300,000 ha of land have already been allocated for investors. Jatropha, castor and oil palm are crop types suggested for production of biodiesel [7]. This envisages the establishment of a plant for the production of biodiesel with a capacity of 300 m3 per annum. The present demand for the proposed product is estimated at 44.138 million litters per annum. The demand is expected to reach at 79.26 million litters by the year 2022 [7].

Refined triglyceride oils have been the predominant feedstocks for the synthesis of biodiesel to date. However, such triglycerides are relatively high in cost and result in a product that cannot compete economically with petroleum-derived diesel fuel, fostering investigation of the use of lower value lipids, primarily animal fats and waste greases, as feed stocks. Soapstock, a lipid-rich by-product of vegetable oil refining, is another relatively inexpensive source of fatty acids. It contains substantial amounts of glycerides, phosphoglycerides, and free fatty acids (FFA), the latter as their sodium or, less commonly, potassium salts [8].

Biodiesel is generally produced by transesterification of triglyceride [9], but it might also be generated by direct esterification of free fatty acid; the esterification reaction could be summarized as follows where R, and R' denotes any hydrocarbon chain.

$$\text{R-COOH} + \text{R'OH} \xrightleftharpoons{\text{Catalyst}} \text{H}_2\text{O} + \text{R-COO-R'}$$

| FFA | Alcohol | Water | Ester |

Esterification

A wide variety of high FFA oils and by-products such as soapstock are available in large quantities. But these are unsuitable for human consumption. These are mainly used for making low-cost soap. It is difficult to transesterify these high FFA vegetable oils using the commercially available alkaline catalyst process due to soap formation. Esterification of the low cost high FFA oils and by-products using an acid catalyst

would substantially reduce the production cost of biodiesel [10].

In designing methods for the production of biodiesel from soapstock, it is necessary to consider its chemical composition, characterized by the high content of water (up to 50%) and soaps (up to 28% as FFA), and the presence of acylglycerols, gums, and lecithin. There is a general trend to pre-treat the soapstock before converting it to FAME either by (1) acidulation, in order to generate acid oil (soap-splitting route) or (2) by hydrolysis of neutral oil (hydrolysis route). However, some authors reported, (3) direct conversion of soapstock to FAME after drying, filtration or transesterification or (4) esterification with glycerol to acylglycerols prior transesterification [11]-[12].

In this study soapstock is considered as a potential alternative low cost feedstock for biodiesel production. The results of using inexpensive reagents and simple technologies to produce fatty acid esters from soapstock, both to address the economic challenges facing biodiesel and to provide alternative routes for soapstock utilization are reported.

II. METHODS AND MATERIALS

A. Sample preparation

Soapstock sample was collected from Addis-Modjo edible oil factory located in Addis Ababa, Ethiopia. The water content, pH, saponification value, density and viscosity of the raw soapstock were determined prior to saponification.

Saponification value, which is expressed by potassium hydroxide in milligrams required to saponify one gram of fat, depends on the kind of fatty acid contained in the fat. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. Measurement of saponification value was performed according to JIS K 0070, ASTM D5558, ISO 3657 standard procedures. The Reagents were 0.5mol/L Hydrochloric acid and 0.5mol/L Potassium hydroxide·ethanol.

After determining the saponification value, sodium hydroxide solution (50 wt %) was prepared and added to the soapstock on to the glass reactor mounted with a digital stirrer. At incubation temperature of 100ºC and atmospheric pressure the mixtures (soapstock

and caustic soda) were saponified with agitation. Samples were removed periodically, and their contents of residual fatty matter (glycerides and phosphoglycerides) were analyzed by titration using the same method as initially taken.

Prior to esterification, water content of the saponified soapstock was removed to less than 10% using tray drier followed by sun dry. This was necessary for not to favor the backward reaction (soap formation) later in the esterification process. The saponified, dried soapstock were passed through a disc mill of sieve size 0.5 mm.

B. Esterification

A full factorial design was employed to coordinately investigate the effects and interactions of methanol to free fatty acid ratio, temperature, and reaction time on the efficiency of esterification. Each reaction contained 100g (dry weight equivalents) of saponified and powder soapstock (size of 5mm). Reaction was held for 3 or 4 hour at 35 or 45°C and methanol to soapstock molar ratio of 1:25 or 1:35 mol/mol in a glass reactor mounted with digital stirrer at a speed of 250 rpm. A solution of methanol and sulfuric acid as per their molar ratios (5:1) were prepared early and mixed with the saponified, dried and meshed soapstock. After optimization of the esterification reaction, for the validation of the model three FAME production experiments were run at optimum temperature, soapstock to methanol molar and reaction duration combinations.

C. Product Purification

Following the esterification incubation, the reaction mixture was centrifuged for 30 min at 4,200rpm. The resulting upper liquid layer (FAME) was removed, and the lower, methanol/sulfuric acid/sodium sulfate/impurity layer was poured off as white solid pellet. The FAME fraction was vacuum filtered for further removal of impurities followed by neutralization using sodium hydroxide for catalyst removal and recovering excess methanol using rotary evaporator. The FAME fraction out from the rotary evaporator was subjected to dry washing by magnesium sulfate (anhydrous) to absorb water formed by the reaction, and silica gel was used to adsorb the un-reacted free fatty acid and soap. It was packed to a size of 4 cm in 10 cm diameter column above which magnesium sulfate layered to a thickness of 2 cm to dry

water. Each run was passed through similar procedure and the biodiesel yield was recorded.

III. RESULTS AND DISCUSSIONS

A. Physical and chemical characteristics of soapstock

Soapstock is found to be quite alkaline, pH 11.9, and viscous (3.21pa.s @ 40°C) with a saponification value (SV) of 37.67 mg KOH /g or 26.34 mg NaOH/g indicating that relatively little additional alkali (no >3 wt.% caustic soda) is required to achieve full saponification/hydrolysis of all lipid-linked fatty acid ester bonds. Approximately half the weight of soapstock (48.71 wt. %) is found to contain water and this warns to subsequently remove much of the water from the saponified soapstock in order to conduct acid-catalyzed esterification as the reaction proceeds essentially spontaneously. Soapstock under analysis had relatively higher density showing up the presence of impurities of higher density. TABLE I summarizes the properties of soapstock under analysis.

Property	Results obtained in laboratory
Density	1143 kg/m^3
Dynamic viscosity	3.21pa.s @ 400 C
pH	11.9
Saponification value	37.67 mg KOH /g
Water content	48.71 wt.%

TABLE I
PHYSICO-CHEMICAL PROPERTIES OF SOAPSTOCK

B. Soapstock saponification

In attempts to achieve full saponification at elevated temperature (100°C), it was found that the addition of NaOH to hot soapstock to a final concentration of 3% (wt. of NaOH/wt. of soapstock) quantitatively hydrolyzes all lipid-linked fatty acid ester bonds in soapstock. Complete saponification was achieved after 4 hours. The 100°C saponification is preferred, since it achieves full hydrolysis more quickly, requires less alkali, will consequently require less acid in subsequent steps. Achievement of full saponification was assured by withdrawal of samples from the saponification reactor in period of 30 minutes and making analysis using

saponification value test method described so far in the methods section. TABLE II shows the course of saponification in an incubation time and the saponification curve (Fig. 1.) suggests soapstock saponify exponentially.

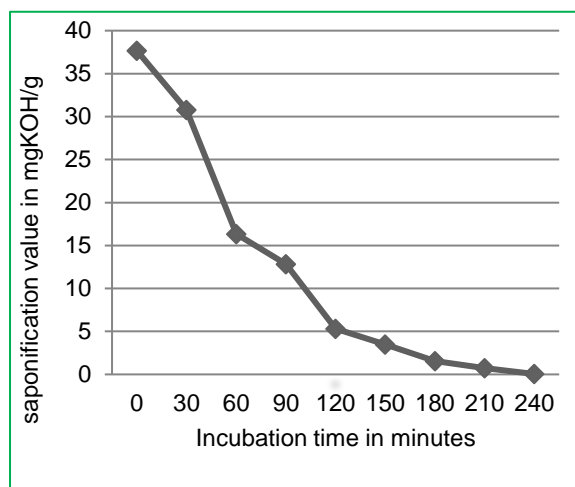| Incubation time in minutes	Saponification value in mg KOH/g
0	37.67
30	30.77
60	16.34
90	12.82
120	5.33
150	3.48
180	1.56
210	0.75
240	<0.05 (complete

TABLE II
SAPONIFICATION PROCESS

Fig. 1. Saponification curve

After tray drier and sundry, the water content of saponified soapstock was reduced to 8.4 %, and that is passed through a 0.5 mm size sieve and was used as a feedstock for biodiesel production. The amount of saponified, dried and sieved soapstock obtained from a kilogram of raw soapstock and 3 wt% NaOH (30g) was 656 g averagely showing that much of the soapstock contained sodium salt of fatty acids and water.

C. Optimization of the esterification reaction

Studies indicated that high degrees of fatty acid esterification could be achieved by incubation of fully saponified soapstock in acidic alcohol solutions at mild temperatures and ambient pressure (Haas et al., 2000). In this study statistical experimental design techniques were employed to determine the effects of the amounts of saponified soapstock to methanol ratio, reaction time and temperature on the efficiency of esterification. A total of 16 experiments were conducted for optimization purpose where the effect of each factor was analyzed by taking lower and higher values from optimized conditions of similar previous work. The biodiesel yield obtained from each experiment was used as a response parameter for optimization and TABLE III shows respective yields of each run.

Run number	Level of factor (A*, B*, C*)	Biodiesel yield (wt. %)	Run number	Level of factor (A*, B*, C*)	Biodiesel yield (Wt. %)
1	- - -	60.8	9	- - -	59.0
2	+ - -	57.0	10	+ - -	50.0
3	- + -	60.9	11	- + -	58.0
4	+ + -	56.0	12	+ + -	56.4
5	- - +	55.9	13	- - +	52.4
6	+ - +	47.5	14	+ - +	50.5
7	- ++	47.3	15	- + +	48.8
8	+ ++	57.1	16	+ + +	55.2
+ = high level, - = low level					
*A - temperature (high 45ºC, low 35ºC), B - SS to methanol ratio (high 1:35, low 1:25), C - reaction time (high 4 hours, low 3 hours).					

TABLE III
BIODIESEL YIELD PER RUN

The resulting data, TABLE III, were analyzed using Design expert® (v.7) software to determine the effects of operating temperature, the amounts of saponified soapstock to methanol ratio (mol/mol) and reaction time. The dependent variable used as a response parameter was the biodiesel yield. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to extraneous factors.
A cubic polynomial regression model was assumed for predicting response. In order to determine whether or not the cubic model is significant, it was necessary to conduct analysis

of variance (ANOVA), TABLE IV. The probability (*p*-values) values were used as a tool to check the significance of each coefficient, which also indicated the interaction strength of each parameter. The smaller the *p*-values are, the bigger the significance of the corresponding coefficient.

Source	Sum of Squares	df	Mean Square	F Value	*p*-value Prob > F
Model	296.56	7	42.37	8.53	0.0036*
A- temperature	16.61	1	16.61	3.34	0.1050
B-SS to Meth. ratio	5.64	1	5.64	1.14	0.3178
C-Rxn time	133.98	1	133.98	26.96	0.0008
AB	55.88	1	55.88	11.24	0.0100
AC	49.35	1	49.35	9.93	0.0136
BC	1.76	1	1.76	0.35	0.5687
ABC	33.35	1	33.35	6.71	0.0321
Pure Error	39.76	8	4.97		
* significant, SS – soapstock					

TABLE IV
ANALYSIS OF VARIANCE (ANOVA)

F- Value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. Here the Model F-value of 8.53 implies the model is significant.

There is only a 0.36% chance that a "Model F-Value" this large could occur due to personal error or disturbance. Probablity values and/ or "Prob > F" values less than 0.0500 indicate model terms are significant. In this case C (reaction time), AB (temperature and soapstock to methanol ratio interaction), AC (temperature and reaction time interaction), ABC (temperature, soapstock to methanol ratio and reaction time interaction) are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Coefficient of Variation (C.V.), the standard deviation expressed as a percentage of the mean; Predicted Residual Error Sum of Squares (PRESS), which is a measure of how the model fits each point in the design; the R-Squared, measure of the amount of variation around the mean explained by the model; Adj R-Squared that is a measure of the amount of variation around the mean explained by the model, Pred R-Squared, a measure of the amount of variation in new data explained by the model, and Adequate Precision, this is a signal to disturbance ratio due to random error, presented in the TABLE V, are used to decide whether the model can be used or not.

Std. Dev.	2.23	R-Squared	0.8818
Mean	54.73	Adj R-Squared	0.7784
C.V. %	4.07	Pred R-Squared	0.5872
PRESS	159.02	Adeq Precision	8.152

TABLE V
MODEL ADEQUACY MEASURES

The "Pred R-Squared" of 0.5872 is as close to the "Adj R-Squared" of 0.7784 in less than 0.2 difference as one might expect. "Adeq Precision" measures the signal to disturbance ratio due to random error. A ratio greater than 4 is desirable. Here ratio of 8.152 indicates an adequate signal. Therefore, this model can be used to navigate the design space.

The regression coefficients and the corresponding 95% CI (Confidence Interval) High and Low were presented in Table 6. 95% CI High and Low columns represent the range that the true coefficient should be found in 95%

of the time. If this range spans 0 (one limit is positive and the other negative) then the coefficient of 0 could be true, indicating the factor has no effect.

Factor	Coefficient Estimate	95% CI Low	95% CI High
Intercept	54.73	53.45	56.02
A-temper.	-1.02	-2.30	0.27
B-SS to Meth. Ratio	0.59	-0.69	1.88
C-Reaction	-2.89	-4.18	-1.61
AB	1.87	0.58	3.15
AC	1.76	0.47	3.04
BC	-0.33	-1.62	0.95
ABC	1.44	0.16	2.73

TABLE VI
REGRESSION COEFFICIENTS AND THE CORRESPONDING 95% CI HIGH AND LOW

From the 95% CI High and Low values of each model term, it could be concluded that the regression coefficients of C (reaction time), and the interaction terms of AB, AC, and ABC had significant effect on the methyl ester yield.

Using the designed experimental data of TABLE III, the polynomial model for the methyl conversion was regressed and shown as in term of coded factors;

*Biodiesel yield = +54.73 - 1.02 * [A] + 0.59 * [B] - 2.89 * [C] + 1.87 * A * B + 1.76 * A * C - 0.33 * B * C + 1.44 * A * B * C*   (1)

Where, [A] = A3+AB2+AC2, [B] = B + B3 + A2B + BC2, [C] = C + C3 + A2C + B2C, A temperature, B = soapstock to methanol molar ratio, and C = reation time.

Final Equation in Terms of Actual Factors:

*Biodiesel yield = - 231.38750 + 7.22250 * temperature + 13.76250 * soapstock to meth. ratio + 108.68750 * Rxn time - 0.32950 * temperature * soapstock to meth. ratio - 2.76250 * temperature * Reaction time - 4.75250 *soapstock to Meth. ratio * Reaction time + 0.11550 * temperature * SS to Meth. ratio * Rxn time*   (2)

The actual versus predicted values using model equation, Eq. (2) are tabulated in TABLE VII,

Standard Order	Actual Value (wt.%)	Predicted Value (wt. %)	Residual	Internally Studentized Residual	Externally Studentized Residual	Run order
1	60.	59.90	0.90	0.571	0.545	1
2	59.	59.90	-0.90	-0.571	-0.545	14
3	50.	53.50	-3.50	-2.220	-3.353	8
4	57.	53.50	3.50	2.220	3.353	12
5	60.	60.90	0.00	0.000	0.000	11
6	60.	60.90	0.00	0.000	0.000	2
7	56.	56.20	-0.20	-0.127	-0.119	9
8	56.	56.20	0.20	0.127	0.119	10
9	55.	54.15	1.75	1.110	1.129	5
10	52.	54.15	-1.75	-1.110	-1.129	13
11	47.	49.00	-1.50	-0.952	-0.945	3
12	50.	49.00	1.50	0.952	0.945	15
13	48.	48.05	0.75	0.476	0.452	7
14	47.	48.05	-0.75	-0.476	-0.452	6
15	57.	56.15	0.95	0.603	0.577	4
16	55.	56.15	-0.95	-0.603	-0.577	16

TABLE VII
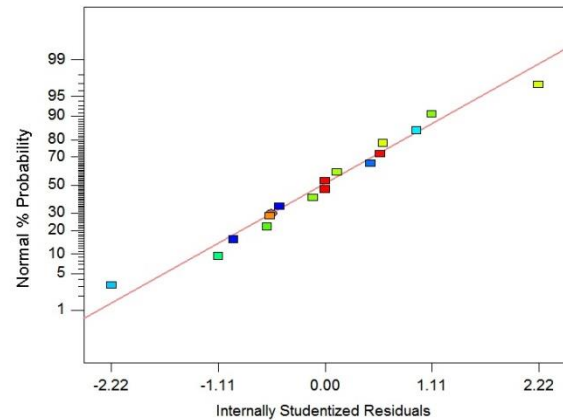ACTUAL VS. MODEL PREDICTED BIODIESEL YIELDS

Fig. 2. Normal plots of residuals

(2)

To see how well the model satisfies the assumptions of the analysis of variance (ANOVA), the plots of residuals (TABLE VII) were analyzed.

The normal probability plot, (Fig. 2.), indicates the residuals following a normal distribution, in which case the points follow a straight line assuring the model satisfies ANOVA assumptions. A plot of the residuals versus the ascending predicted response values (Fig. 3.), tests the assumption of constant variance. The plot shows random scatter (constant range of residuals across the graph) which is welcome deserving no need for a transformation to minimize personal error.

variables by holding the other one at middle value.
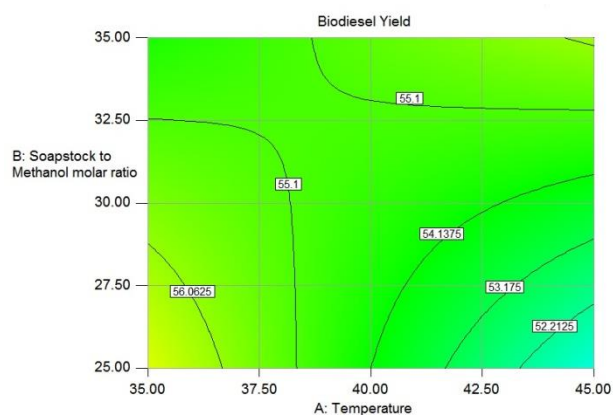
(a)

(b)

Fig. 3. Plot of residuals vs. model predicted values

Many parameters can influence the performance of methyl ester yield from cottonseed soapstock. Eq. (2) shows that methyl ester conversion has a complex relationship with independent variables that encompass first, second and third-order polynomials and may have more than one maximum point. The best way of expressing the effect of any parameter on the yield within the experimental space under investigation was to generate response surface plots of the equation. The three dimensional response surfaces, contours and interactions were plotted in figures (4), (5) and (6) as a function of the interactions of any two of the
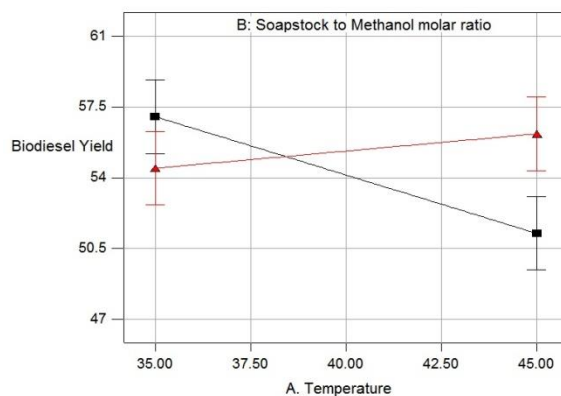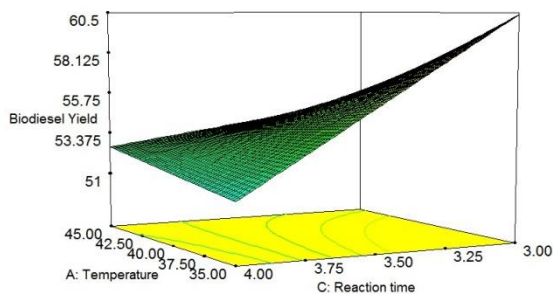
(c)

Fig. 4. Response surface curve (a), contour plot (b) and interaction plot (c) of temperature and soapstock to methanol ratio
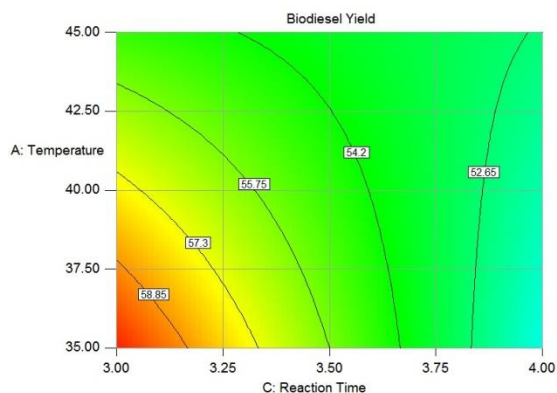
The response surface, Fig. 4 (a), obtained from operating temperature and soapstock to methanol ratio is flatly convex but had sharply up warded edges at one symmetry suggesting that there are well-defined optimum operating conditions. However, the convexity was not high enough, as the surfaces were rather symmetrical about the yield (vertical) axis and a little flat near the optimum which meant that the response optimized value based on combined effects reaction temperature and soapstock to methanol molar ratio may not vary widely from the single variable optimized condition.

Contour plot and interaction graph showing predicted response of methyl ester yield as a function of reaction temperature and soapstock to methanol molar ratio is shown in Figs. 4(b) and (c). It is indicated that the methyl ester yield is sensitive to reaction temperature and SS to methanol molar ratio. An increase in methyl ester yield is observed with the increasing of reaction temperature, Fig. 4 (c), red line) at higher soapstock to methanol molar ratio, but the yield decreases when lower SS to methanol molar ratio is used, Fig. 4 (c), black line. It could be interpreted that, under much excess amount, the methanol was used to improve the solubility of soapstock in methanol and reaction mixture would become well mixed. But when lower amount of alcohol were used the increase in temperature decreases the methyl ester yield, this could be due to the reversible nature of the esterification reaction. That is, as the reaction temperature was increased at lower excess alcohol amount the yield is initially maximum and a further rise in temperature favors the water formed during the reaction to hold a reversible reaction to form soap decreasing the yield.
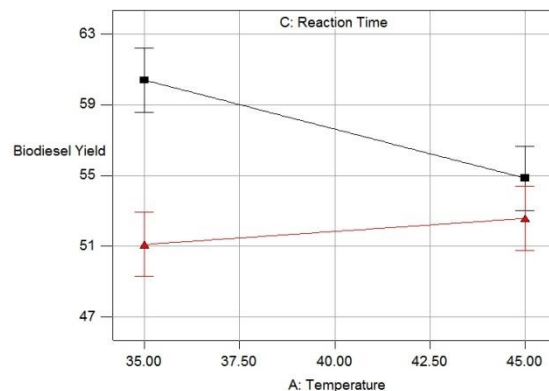
The profile of the contour plot, Fig. 4(b), indicated that the interaction between the reaction temperature and amount of soapstock to methanol ratio is strong.
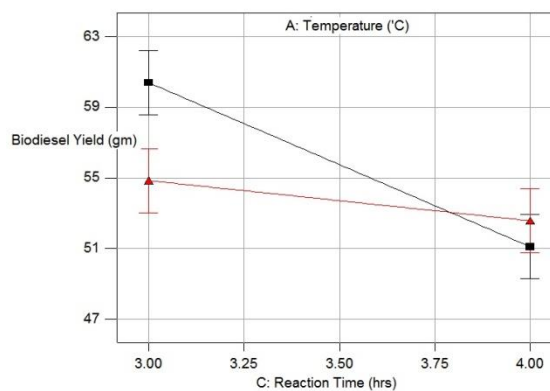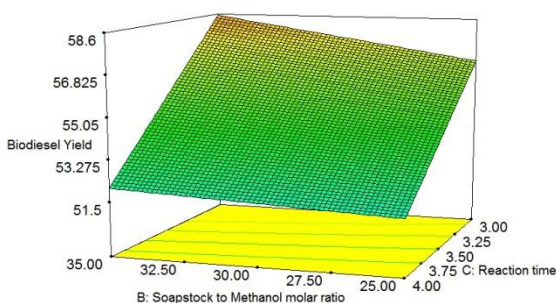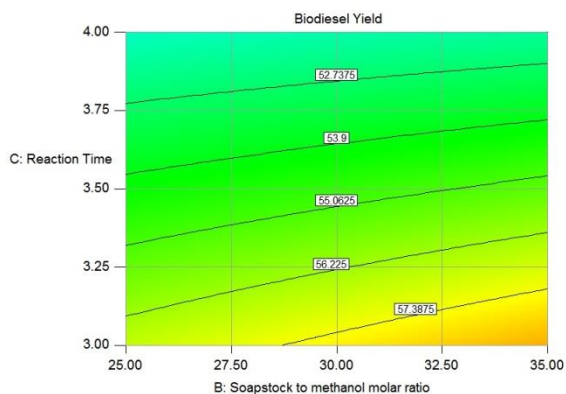
(b)

(c)

(d)

Fig. 5. Response surface curve (a), contour plot (b) and interaction plots (c) and (d) of temperature and reaction time

The response surface, Fig. 5 (a), obtained from operating temperature and reaction time is

(a)

faintly flat and sloppy which has one up warded edge at one end suggesting that there are well-defined optimum operating conditions. Moreover, the surface is somewhat flat near the optimum which meant that the response optimized value based on combined effects reaction temperature and reaction time may not vary widely from the single variable optimized conditions.Interaction of temperature and reaction time on methyl ester yield is presented in Figs. 5 (c) and (d). A decrease in methyl ester yield is observed with the increasing of reaction time, (Fig. 5 (d)), and temperature, Fig. 5 (c) square indicator, although very small increment in yield is observed with the increase of reaction temperature in short reaction period, Fig. 5 (c) triangle indicator. It could be interpreted that, at higher reaction temperatures, there is a chance of loss of methanol when the reaction time increases. The profile of the contour plot, Fig. 5 (b), indicated that the interaction between the reaction temperature and amount of soapstock to methanol ratio is strong.

(a)

(b)
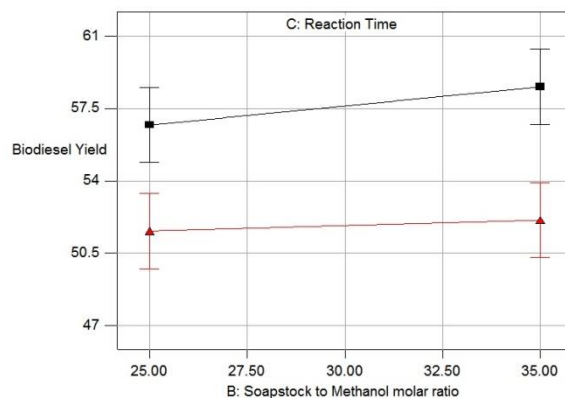
(c)
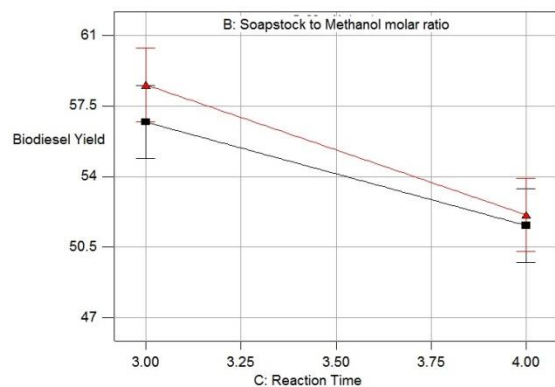
(d)

Fig. 6. Figure 6 Response surface curve (a), contour plot (b) and interaction plot of SS to methanol ratio and reaction time (c) and (d).

The response surface, Fig. 6 (a), obtained from soapstock to methanol molar ratio and reaction time was sloppy flat and which had one up warded edge at one end suggesting that there were a dominance of reaction time in the in the interaction of these two factors.

The profile of the contour plot, Fig. 6 (b), indicated that the interaction between the reaction duration and amount of soapstock to methanol ratio is dominated by reaction duration.

Interaction of soapstock to methanol molar ratio and reaction duration on methyl ester yield is presented in Figs. 6 (c) and (d). A slight increase in methyl ester yield was observed with the increasing of soapstock to methanol molar ratio, Fig. 6 (c), where as a relatively strong

decrease of the yield is observed and when the reaction time increased. It could be interpreted that, at higher reaction temperatures, there is a chance of loss of methanol with longer reaction duration and basically the esterification reaction was kinetics limited so that the yield was faster initially but later the yield decreases due to reversible nature.

The optimum reaction temperature, soapstock to methanol molar ratio and reaction duration for the maximum methyl ester conversion are 35 ^{0}C, 1:25 and 3 hours, respectively with 59.9 methyl ester yields.

The optimization criteria used are summarized as,

Name	Goal	Lower Limit	Upper Limit
Temperature (^{o}C)	minimize	35	45
soapstock to Meth.(ml/mol)	minimize	25	35
Reaction time (hours)	minimize	3	4
Biodiesel yield (wt.%)	maximize	47.3	60.9

Optimum possible solutions and corresponding surface plot are presented in TABLE VIII.

TABLE VIII
OPTIMUM POSSIBLE SOLUTIONS

Number	Temperature (°C)	Soapstock to Methanol Ratio	Reaction time (hours)	Biodiesel yield (wt.%)	Desirability
1	35.00	25.00	3.00	59.9	0.973*
2	35.02	25.04	3.00	59.8913	0.972
3	35.00	25.09	3.00	59.9071	0.971
4	35.00	25.00	3.01	59.8702	0.971
5	35.05	25.02	3.00	59.867	0.971
6	35.22	25.00	3.00	59.7584	0.965
7	35.00	25.60	3.00	59.9601	0.962
8	35.31	25.00	3.00	59.6994	0.961
9	35.00	25.75	3.00	59.9745	0.959
10	35.00	25.95	3.00	59.9946	0.955
11	35.00	25.00	3.06	59.5423	0.950
12	35.00	27.22	3.00	60.1225	0.928
13	36.43	25.00	3.00	58.983	0.916
14	35.00	28.57	3.00	60.2574	0.894

* selected as optimum conditions with diserablity near

D. Validation of the model

According to the 2-level factorial design result using Design-Expert® v.7 software, an experiment with reaction temperature of 35^{0}C, SS to methanol molar ratio of 1:25, and reaction duration of 3 hours was conducted in order to investigate the effect of the design used. The experiment was carried out at the optimized conditions. Methyl ester yield of 59.6% (average) has been obtained and was in good agreement with the predicted one. The accuracy of the model is validated with triplicate experiments under the aforementioned optimal reaction conditions. As a result, the model is considered to be accurate and reliable for predicting the yield of methyl ester.

E. Product purification and property analysis of biodiesel

The FAME produced at all conditions goes similar purification procedure, centrifuge, neutralization, methanol recovery in rotary evaporator, and water, soap, and FFA removal using adsorbents magnesium sulfate and silica gel. TABLE IX shows results obtained in centrifuge and methanol recovery processes. From the results, Table 9, it was clearly shown that the excess methanol could be readily recovered and improves the efficiency aspect of production. On the other hand, the absorption nature of anhydrous magnesium sulfate for water removal showed promising effect.

Run order	Centrifuge			Methanol Recovery (weight in grams)		
	Before (weight in grams)	After (weight in grams)		Recovered methanol	FAME before MgSO$_4$ absorption	FAME after MgSO$_4$ absorption
		FAME/methanol layer	White solid pellet			
1	528.2	444.7	63.5	308.8	64.5	60.8
2	536.1	459.8	56.3	303.2	60.5	57.0
3	561.2	476.9	64.3	307.9	64.5	60.9
4	558.8	478.2	60.2	313.4	59.4	56.0
5	532.2	458.1	54.1	317.8	59.4	55.9
6	532.9	465.3	57.6	308.6	50.4	47.5
7	557.2	488.5	58.7	311.5	50.2	47.3
8	556.5	447.7	61.8	300.4	60.4	57.1
9	524.2	441.4	62.8	305.7	63.6	59.0
10	533.3	461.6	61.7	318.4	53.0	50.0
11	562	486.3	55.7	322.3	61.5	58.0
12	558.8	478.2	60.6	309.1	59.8	56.4
13	531.5	440.2	53.3	306.8	55.6	52.4
14	526.6	453.8	52.8	306.4	53.4	50.5
15	559.7	490.8	58.9	309.6	51.7	48.8
16	558.8	483.4	55.4	307.3	58.5	55.2
17	526.2	479.7	52.5	316.7	62.2	59.6

TABLE IX
PURIFICATION RESULTS ON CENTRIFUGE
AND ROTARY EVAPORATOR

The solid white material formed during esterification was averagely 58.24% in mass to the amount of dry SS in the reaction used for the reaction; this indicates there were impurities that have to be initially removed from the saponified SS. It was largely water soluble and had an inorganic content, determined by ashing.

This study evaluated the use of silica gel in a column with bed diameter of 10 cm and silica gel packing thickness of 4cm. To dry the biodiesel, a 2 cm layer of magnesium sulfate was placed above the silica gel. This study analyzed the biodiesel density, kinematic viscosity, and acid value. It was found that there was no significant change in density, kinematic viscosity, due to purification by silica gel but the

acid value was reduced from 1.12 to 0.56 mg KOH/g by 50%. This study compared the results from purification with silica gel to that of water washing. It was found that silica gel produced yields of about 59.6% compared from water washing which cause emulsification and an able to separate thereafter.

The density, viscosity, acid value and flash point of each run were measured and presented in TABLE X.

The use of density as an expedient check of fuel quality may not be as useful for biodiesel as it is for petro-diesel and it is not as such important parameter though the range expected is in between 0.86 and 0.90 g/m^3.

Run order	Density (kg/m^3)	Kinematic viscosity (mm^2/s) @ 40 ^{0}C	Acid Value (mg KOH/g)	Flash point (^{0}C), open cup
1	893	2.78	0.56	143
2	867	1.16	0.67	156
3	878	4.15	1.12	123
4	890	1.43	0.67	127
5	912	4.23	0.89	136
6	886	2.72	0.78	158
7	876	2.05	1.00	160
8	889	5.63	0.56	118
9	885	3.35	0.67	123
10	875	4.53	0.56	134
11	873	2.96	0.78	143
12	892	5.43	0.67	120
13	878	4.74	0.67	180
14	896	3.62	0.56	160
15	876	3.61	0.56	172
16	883	3.45	0.67	167
17*	872	4.27	0.56	193
*average value at optimum conditions				

TABLE X
SOME PROPERTIES OF BIODIESEL

Most of the runs did fall in the range but few didn't showing that there were impurities remaining mainly sulfated salts.

The viscosities of the biodiesel produced at lower temperature (runs 1, 3, 5, 9, 11, 13 and 15) are higher than that of the corresponding experiments conducted with the same feed ratio but at higher temperature (runs 2, 4, 6, 10, 12 and 16) this could be because as the temperature

increase the esterification reaction was facilitated and the excess alcohol was diluting the mixture hence resulting in a decrement of viscosity.

The acid value of most runs (except run 3, 5 and 7) fulfill the requirements in ASTM (0.8 mg KOH/g maximum) and witnessed the good performance of silica gel in adsorbing free fatty acid from FAME. The odd result from runs 3, 5, and 7 may show as the activity of the silica gel was inhibited and a rinse using methanol was mandatory.

The elimination of excess reactant alcohol is ensured through measurement of the flash point. The results of this study show widely varying results, runs 3, 4, 7, and 8 (with corresponding replicates) had relatively lower flash points in comparison with runs 1, 2, 5, and 6.The interpretation could lie on the efficiency of the rotary evaporator to recover the excess alcohol. Since runs with lower flash point were observed at higher excess methanol amounts, it is reasonable to suggest that there were un-reacted alcohol in final FAME of these products. The flash point is the temperature at which fuel vapors can be ignited by externally supplied ignition. It is important for determining the fire hazard and the subsequent safety measures in the storage and distribution systems. As a result when using too much alcohol could lead to lower flash point and care is needed when purifying.

IV. CONCLUSION

Soapstock was found to be quite alkaline, pH value 11.9. Therefore, relatively little additional alkali, 3 wt. % caustic soda, was required to achieve full saponification of its fatty acid esters. Soapstock contained approximately half its weight water (48.71wt %), and highly viscous. The free fatty acid obtained as sodium salt from a kilogram of SS and 3 wt % NaOH was 656 gm (63.69%) indicating that SS can be a good source of free fatty acid for biodiesel production via esterification.

By means of simple chemical methods, a low-quality underutilized feedstock has been used to produce biodiesel. The quality specification of the product is comparable in composition with other oil based biodiesels that achieve standards. A hydrolysis route for efficient FAME synthesis from soapstock is used to esterify both free and ester-linked fatty acids, and showed a promising result of 59.6% yield that is in good comparison with similar other works of Haas. et al. 2000, and Kempers et al. 2008.

Optimization of acid catalyzed esterification of cottonseed soapstock was carried out with the aid of Design Expert® software (V.7). A 2-lvel factorial design method was used and a cubic polynomial regression model was assumed to for predicting response. The probability (p) value of 0.0036 demonstrates a high significance for the regression model. Methyl yield of 59.9 wt. % was obtained when optimum conditions of were a temperature of 350C, soapstock to methanol molar ratio of 1:25, soapstock to catalyst molar ratio of 1:5 and reaction duration of 3 hours. Validation experiments verified the availability and the accuracy of the model. The predicted value was in agreement with the experimental value (59.6 wt.%). Consequently, the study also provided useful information and reference for the conditions optimization of other acid catalyzed processes.

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