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Optimization of Esterification of Palm Fatty Acid Distillate to Methyl Ester Using Microwave-Assisted Titanium Sulfonated Incomplete Carbonized Glucose (Ti-SO_3H/ICG)

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An alternative feedstock, palm fatty acid distillate (PFAD) provides huge potential in solving the problem of high cost biodiesel production. The PFAD was esterified in batch mode using microwave-assisted titanium sulfonated incomplete carbonized glucose (Ti-SO_3H/ICG) catalyst. Microwave-assisted method was proposed to shorten the time and energy consumed during catalyst preparation. The process parameters which include molar ratio of methanol to PFAD, reaction temperature, catalyst loading and reaction time were optimized via response surface methodology (RSM) using central composite design (CCD). The optimization showed 99.63 % yield and 94.61 % conversion of PFAD to FAME under the following optimal conditions: molar ratio methanol to PFAD 11.30:1, reaction temperature 78.75 °C, 2.00 wt% catalyst loading and 1.8 h of reaction time. From this study, it can be shown that the costs for production can be reduced to its minimum level and the time consumed in catalyst preparation can be shorten.

1. Introduction

The high cost of biodiesel production has become a major obstacle for commercialization. In order to reduce the cost of biodiesel production, cheaper materials are necessary for consideration to replace the highly expensive feedstock. Palm fatty acid distillate (PFAD) has emerged to be a great potential as raw material for biodiesel production. PFAD is a by-product from the physical refining of crude palm oil consisting high free fatty acid (FFA) as a promising biodiesel feedstock candidate (Cho et al., 2012). Esterifying the high FFA feedstock will be best done with the existence of heterogeneous solid acid catalyst since the separation of the product will be more efficient (Sharma et al., 2011). In fact this type of catalyst can be regenerated and reused several times. In this paper, titanium-sulfonated/incomplete carbonized glucose (Ti- SO_3H/ICG) catalyst was prepared for esterification process of PFAD to fatty acid methyl ester (FAME). Ti- SO_3H/ICG catalyst was derived from incomplete carbonized of D(+)-glucose. D(+)-glucose was used due to its low-cost production, easy preparation process, high effectiveness, greener and suitable for esterification of waste oil containing high FFA (Tang et al., 2018). Titanium was selected as the catalyst support due to its capability in stabilizing the mesoporous structure catalyst (Bagheri et al., 2014). Yahya and colleagues prepared calcium titanate because of the titanium itself possessed dynamic support in accelerating the transesterification of the waste cooking oil (Yahya et al., 2017). The preparation of the heterogeneous solid acid catalyst however consumes a lot of time since the preparation involved a series of conventional heating methods (Lokman et al., 2015). Thus, microwave-assisted method was adapted in carbonization and sulfonation processes instead of using conventional method to shorten the period of time and energy consumed (Mello et al., 2014). By adapting this microwave-assisted method, the preparation of the catalyst can be shorten from 2 or 3 h to just few minutes (Ning and Niu, 2017). This study investigated the optimization of the biodiesel production using catalyst prepared via microwave-assisted method. The parameters involved were molar ratio of methanol to PFAD, heating time (h), temperature (°C) as well as catalyst loading (wt%). The optimum variables of the process were also investigated using Response Surface Methodology (RSM) to generate high FAME yield and PFAD

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conversion. Effect of the reaction conditions on the FAME content through analysis of variance (ANOVA) and correlation of FAME content with the process variables will also be analyzed.

2. Materials and methods

2.1 Materials

The feedstock palm fatty acid distillate (PFAD) was supplied by Mewaholeo Industries Sdn. Bhd., Pasir Gudang, Johor. Sulphuric acid (H_2SO_4), potassium hydroxide (KOH) and titanium (IV) Isopropoxide were purchased from J.T. Baker. The solvents such as methanol (95 %), ethanol (95 %) and analytical grade toluene were obtained from Merck chemical company. The FAME standards for chromatography analysis including methyl oleate, methyl palmitate, methyl linoleate, methyl myristate, methyl stearate and methyl heptadecanoate on the other hand were obtained from Fluka.

2.2 Catalyst preparation

20 g of D(+)-glucose was heated at medium high power level (560 W) for 20 min in a microwave. The resultant black carbon, incomplete carbonized glucose (ICG) was then crushed into powder form. Then, 4 g of the ICG was added into 100mL of concentrated sulphuric acid and heated inside a microwave for 3 ($SO_3H/ICG_{(3)}$), 5 ($SO_3H/ICG_{(5)}$), 7 ($SO_3H/ICG_{(7)}$) and 9 min ($SO_3H/ICG_{(9)}$). using power level of 560 W. The mixture was then filtered and washed using distilled water. The black precipitate was collected and washed again using hot distilled water with temperature of 80 °C. The process was basically carried out to eliminate any excess of sulphate ions and impurities from the precipitate. The precipitate was dried in a microwave for about 5 min using the same power level. 5 g of all SO_3H/ICG was impregnated with 7.5mL titanium(IV) Isopropoxide by immersed in 20 mL of toluene (Merck).The mixture (17 wt%) was then stirred until all the toluene was completely evaporated. Next, solid form inside the beaker was washed with ethanol to remove the residual toluene and subsequently dried at 110 °C for overnight. For activation, the Ti-ICG/SO_3H was calcined at 500 °C for 2 h in a furnace. The label of each catalyst was designated as Ti-$SO_3H/ICG_{(3)}$, Ti-$SO_3H/ICG_{(5)}$, Ti-$SO_3H/ICG_{(7)}$, and Ti-$SO_3H/ICG_{(9)}$ referring to the difference of heating time during sulfonation process.

2.3 Esterification of PFAD

PFAD was liquefied at 70 °C. The amount of methanol and Ti-SO_3H/ICG catalyst was prepared based on the molar ratio. The preheated PFAD was poured into the 100 mL of three-necks-round-bottom-flask. The reflux condenser was installed into the neck of the flask mainly to re-condense the evaporated methanol. The methanol and Ti-SO_3H/ICG catalyst were added and mixed with liquefied PFAD before it being heated at specified temperature inside a heating mantle. The mixture was stirred at 600rpm by a magnetic stirrer and reflux for specific reaction time. Then the liquid was poured into a separating funnel and was allowed to settle for around 60 min. The bottom layer containing FAME was collected and purified with distilled water. The FAME was analysed using GCFID.

2.4 Experimental design

4 parameters are chosen for optimization of biodiesel production which is molar ratio of PFAD to methanol, temperature of the process, catalyst loading and reaction time. Product yield and conversion will be the response in this experimental design. 4 Level Factorial design was being used in this study which amounted to 30 experimental runs. Each factor, or independent variable, was placed at one of three spaced values coded as -1, 0 and +1. The data were being coded as in Table 1. Based on the result of the experiments, the three dimensional response surfaces and contour plots were drawn to examine the influence of experimental variables on the responses.

Table 1: Coded variables for 4 Level Factorial Design

Independent Variables	Unit	Coded Levels		
		-1	0	+1
Molar Ratio	-	10	11	12
Temperature	°C	70	75	80
Catalyst loading	wt%	2	2.5	3
Reaction Time	h	1.5	2.0	2.5

2.5 ANOVA analysis

ANOVA is necessary to compare and test the significance between means. Compared means are from experimental result and response surface mathematical model. Test involves are the F-test for testing the adequacy of the fitted model, the Coefficient of Correlation (R) and the Coefficient of Determination (R^2) to test the fit quality of the model.

3. Results and discussion

Table 2 shows the screening of the catalyst prepared using microwave-assisted method. The catalyst prepared at 7 min during sulfonation process possessed high percentage yield of the methyl ester. Thus the Ti-SO_3H/$ICG_{(7)}$ was selected for further optimization using RSM.

Table 2: Screening of the percentage yield of catalysts prepared

Catalyst	Carbonization in microwave (min)	Treatment with H_2SO_4 (min)	Yield (%)
Ti-SO_3H/$ICG_{(3)}$	20	3	89.76
Ti-SO_3H/$ICG_{(5)}$	20	5	96.37
Ti-SO_3H/$ICG_{(7)}$	20	7	98.92
Ti-SO_3H/$ICG_{(9)}$	20	9	84.79

3.1 Model determination

The coefficient of determination (R^2) is defined as the ratio of the explained variation to the total variation, and is a measure of the degree of fit. A good model fit should yield at least 0.8 of R^2. Table 3 shows the statistical summary for each model. The quadratic model was selected although the cubic model was aliased. In cubic model, the least squares parameter estimated for alias models will not be unique and the resulting contour plots will be misleading. On the other hand, for linear and 2 factors interaction relationship have the least value of R^2 and adjusted-R^2 as shown in Table 3. It was clear that the relationships were not adequate for the experimental data. Therefore the value of R^2 and adjusted-R^2 for yield response were 0.9921 and 0.9841 and for conversion response were 0.9942 and 0.9884.

Table 3: Statistical summary for each model

Model	Standard Deviation		R^2		Adjusted-R^2		Predicted-R^2	
	Yield	Conv	Yield	Conv	Yield	Conv	Yield	Conv
Linear	10.76	11.99	0.2880	0.1821	0.1694	0.0457	-0.1335	-0.0323
2FI	11.72	12.66	0.3672	0.3168	0.0156	-0.0628	-0.1975	-0.2815
Quadratic	1.49	1.32	0.9921	0.9942	0.9841	0.9884	0.9497	0.9621
Cubic	1.15	0.58	0.9980	0.9995	0.9906	0.9712	0.5463	0.9712

3.2 Statistical analysis

The significance of each parameter which was evaluated by the probability value (*p*-value) are listed in Table 4 and Table 5. At 95 % confidence level, the *p*-values less than 0.05 indicate significant effects of those parameters. The model F-value of 124.89 implies the model is significant. The F-value for lack of fit which was 5.18 implies there is a 6.36 % chance that lack of fit this large could occur. The predicted-R^2 of 0.9497 is in reasonable agreement with the adjusted-R^2 of 0.9841 which have low difference value. In this case, A, B, D, AD, BC, CD, A^2, B^2, C^2 and D^2 showed as significant model term. F-value of model is 171.92 showed that the model is significant. The F-value for lack of fit which is 5.13 implies there is a 6.45 % chance that lack of fit this large could occur. The difference between predicted-R^2 and adjusted-R^2 also shows a small difference value indicates that it is in reasonable agreement. Based on the coded parameters, the quadratic regression model of the yield and conversion with determined coefficients was given in Eq(1) and (2).

$$\text{Yield} = -1{,}946.81 + 202.21A + 19.75B + 145.96C - 32.11D + 0.05AB - 0.57\,AC + 3.51AD - 1.56BC + 0.09BD + 3.79CD - 9.32A^2 - 0.11\,B^2 - 5.93C^2 - 6.46D^2 \quad (1)$$

$$\text{Conversion} = -2004.32 + 206.68A + 19.95B - 170.02C - 35.89D + 0.14AB + 1.28AC + 3.53AD - 2.09BC - 0.004BD + 8.29CD - 10.12A^2 - 0.11B^2 - 8.31C^2 - 6.61D^2 \quad (2)$$

Table 4: ANNOVA results of yield

Source	Sum of Squares	df	Mean Square	F Value	p-value, Prob >f	
Block	16.31	1	16.31			
Model	3,873.67	14	276.69	124.89	< 0.0001	significant
A-MR	1,052.45	1	1,052.45	475.04	< 0.0001	
B-Temp	19.71	1	19.71	8.90	0.0099	
C-Cat Loading	4.92	1	4.92	2.22	0.1582	
D-Time	47.63	1	47.63	21.50	0.0004	
AB	1.10	1	1.10	0.50	0.4931	
AC	1.31	1	1.31	0.59	0.4555	
AD	49.32	1	49.32	22.26	0.0003	
BC	242.04	1	242.04	109.25	< 0.0001	
BD	0.88	1	0.88	0.40	0.5389	
CD	14.35	1	14.35	6.47	0.0234	
A^2	2,384.06	1	2,384.06	1076.07	< 0.0001	
B^2	206.00	1	206.00	92.98	< 0.0001	
C^2	60.33	1	60.33	27.23	0.0001	
D^2	71.48	1	71.48	32.26	< 0.0001	
Residual	31.02	14	2.22			
Lack of Fit	28.79	10	2.88	5.18	0.0636	not significant
Pure Error	2.23	4	0.56			
Cor Total	3,920.99	29				

Table 5: ANNOVA results of conversion

Source	Sum of Squares	df	Mean Square	F Value	p-value, Prob >f	
Block	7.84	1	7.84			
Model	4,196.04	14	299.72	171.92	< 0.0001	significant
A-MR	646.05	1	646.05	370.59	< 0.0001	
B-Temp	22.31	1	22.31	12.80	0.0030	
C-Cat Loading	42.40	1	42.40	24.32	0.0002	
D-Time	57.60	1	57.60	33.04	< 0.0001	
AB	8.44	1	8.44	4.84	0.0451	
AC	6.55	1	6.55	3.76	0.0729	
AD	49.84	1	49.84	28.59	0.0001	
BC	435.14	1	435.14	249.61	< 0.0001	
BD	1.600E-003	1	1.600E-003	9.178E-004	0.9763	
CD	68.64	1	68.64	39.37	< 0.0001	
A^2	2,809.31	1	2,809.31	1611.48	< 0.0001	
B^2	198.35	1	198.35	113.78	< 0.0001	
C^2	118.43	1	118.43	67.93	< 0.0001	
D^2	74.94	1	74.94	42.99	< 0.0001	
Residual	24.41	14	1.74			
Lack of Fit	22.64	10	2.26	5.13	0.0645	not significant
Pure Error	1.77	4	0.44			
Cor Total	4,228.29	29				

3.3 Model adequacy check

First criteria being evaluated were the determination coefficient (R^2) which evaluated the suitability of the model. Hence, in this case, the obtained value of R^2 for biodiesel yield response and biodiesel conversion responses which were 0.9921 and 0.9942 indicated there is a good agreement between the observed and the predicted values of biodiesel yield from the model as sketched through Figure 1. These values represent that 99.21 % and 99.42 % of the sample variation could be attributed to the independent factors while only 0.79% and 0.58 % of the total variance could not be described by the model. The residuals indicate the difference between the predicted to the observed value.

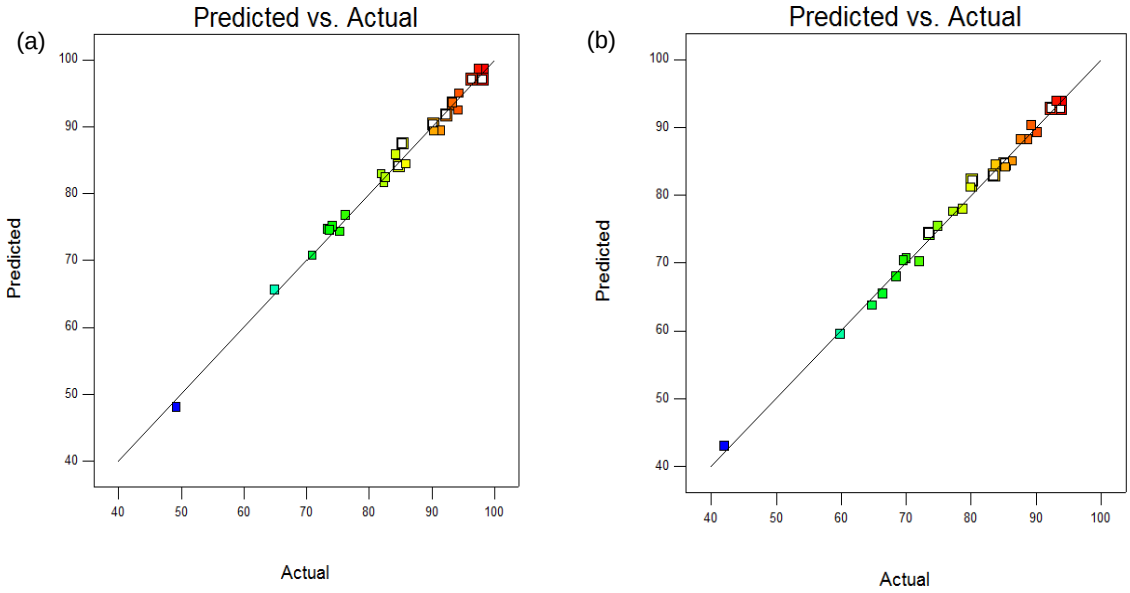

Figure 1: Comparison between predicted and experimental biodiesel yield: (a) Yield response; (b) Conversion response.

3.4 Interaction effects of the parameters

Figure 2 illustrates the surface plots of biodiesel yield and PFAD conversion as a factor of temperature, molar ratio of methanol to PFAD and time.

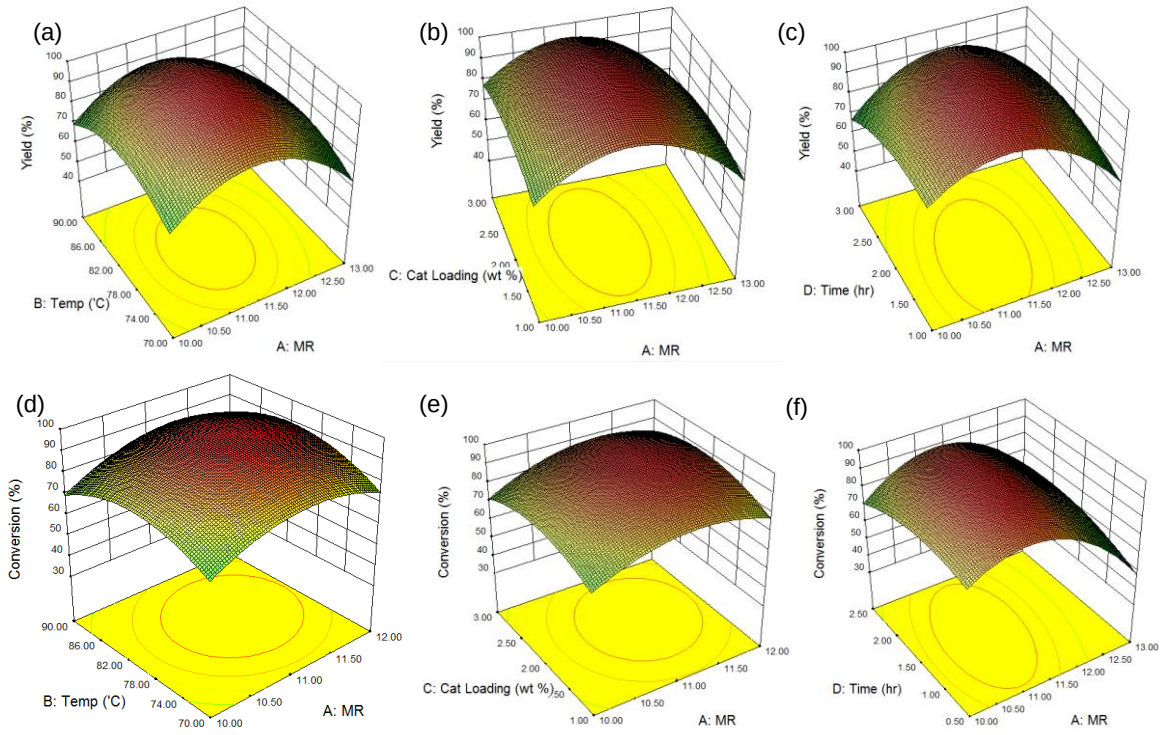

Figure 2: Surface plots (yield) for variable parameters – (a) molar ratio of methanol to PFAD & temperature; (b) molar ratio of methanol to PFAD & catalyst loading; (c) molar ratio of methanol to PFAD and reaction time. Surface plots (conversion) for variable parameters – (d) molar ratio of methanol to PFAD & temperature; (e) molar ratio of methanol to PFAD & catalyst loading; (f) molar ratio of methanol to PFAD & reaction time.

Figure 2a - c illustrate the response surface plot of the biodiesel yield for the combined parameters at the optimum condition. Figure 2d - f shows the response surface plot of the biodiesel conversion for the combined parameters at the optimum condition. The critical point, which is the optimum values from the overall interaction delivered 99.63 % FAME yield and 94.61 % PFAD conversion. These occurred at molar ratio methanol to PFAD 11.30:1, 78.75 °C reaction temperature, 2.00 wt% catalyst loading and 1.80 h of reaction time to obtain of PFAD to FAME. Due to several interaction effects between the variables, the parameter could not be analyzed independently. The most significance of the parameters in the model was obtained using statistical techniques. As in Table 4 and Table 5 for yield and conversion, mean square of parameter molar ratio PFAD to methanol were 1052.45 and 646.05 which resulting the highest value among the other factors. This shows that the parameter contributed the most significant effect to the results. Other supportive value was both on yield and conversion for molar ratio methanol to PFAD showed small p-value (< 0.0001).

4. Conclusion

Ti-SO_3H/ICG catalyst was prepared via microwave-assisted method for the esterification of PFAD to FAME. The optimum values of independent variable yield and conversion of PFAD to FAME are molar ratio methanol to PFAD 11.30:1, 78.75 °C reaction temperature, 2.00 wt% catalyst loading and 1.80 h of reaction time to obtain 99.63% yield and 94.61% conversion of PFAD to FAME. The coefficient of determination, R^2 obtained for yield and conversion responses are 0.9921 and 0.9942. This value shows good agreement between experimental data and predicted values. The most influential independent variable as the result from optimization process is the molar ratio methanol to PFAD which have the highest mean square of 1052.45 and 646.05 for percentage yield and conversion. The catalyst prepared via microwave-assisted shows remarkable yield percentage and conversion thus capable to be the alternative fuel along with sustainable and greener process.

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