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Optimization of Sulfonated Sago Pith Waste Catalyst for Conversion of Palm Fatty Acid Distillate to Biodiesel

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Carbon-based catalysts were reported to hold advantages such as being cost-effective, eco-friendly while having good stability and high selectivity in catalytic processes. Optimization of sulfonated sago pith waste (s-SPW) catalyst as a starch-rich biomass-derived solid acid catalyst for conversion of palm fatty acid distillate (PFAD) feedstock to biodiesel product was performed in this study. Synthesis condition of s-SPW catalyst was optimized through the design of experiment (DOE) optimization by employing Response Surface Methodology (RSM) using Statistica Software V10.0. Four independent variables for the synthesis of s-SPW catalyst, including carbonization temperature, carbonization time, sulfonation temperature and sulfonation time were studied for the optimization work with the response of biodiesel yield. DOE was carried out by utilizing Central Composite Design (CCD) of 4 factors with 26 runs. The optimum synthesis condition of s-SPW catalyst was found at a carbonization temperature of 338.49 °C, carbonization time of 69.44 min, sulfonation temperature of 156.32 °C and sulfonation time of 7.13 min with a biodiesel yield of 69.51 %. Conversion of PFAD with s-SPW catalyst is a promising, greener and cost-effective synthetic route for biodiesel production.

1. Introduction

Palm Fatty Acid Distillate (PFAD) had emerged as a potential feedstock oil for biodiesel production as it is a low-cost, low-value and low-quality oil that is rich in free fatty acids and glycerides (Zailan et al., 2021). Previously, researchers who studied the conversion of PFAD into biodiesel only considered the esterification of free fatty acid into biodiesel. In fact, free fatty acids and glycerides in PFAD can be converted into methyl esters (biodiesel) via esterification and transesterification processes, respectively, with the aid of a suitable catalyst. Unfortunately, the cost of producing a suitable heterogeneous catalyst is still relatively high and this lifted up the overall production cost of biodiesel and decreased its competitiveness as an alternative energy source (Tang et al., 2018). Sulfonated Carbon-Based Solid Acid Catalyst (CBASs) grabbed researchers' attention as it was reported to be able to tolerate high water and FFA content in the feedstock oil, have a high affinity for both esterification and transesterification and can catalyse both esterification and transesterification processes simultaneously (Clohessy et al., 2020). Carbon-rich biomass waste, which can be used to synthesize solid acid catalysts and may overcome the high catalyst costing issue while showing a promising performance came into researchers' focus recently (Tan et al., 2021). Indika et al. (2019) reported solid acid catalysts derived from coconut coir husk (CCH) and coconut meal residue (CMR) using in-situ incomplete sulfuric carbonization for conversion of waste palm oil to biodiesel. Zailan et al. (2021) investigated the sago pith waste (SPW) being used as a carbon-rich source for synthesis of sulfonated sago pith waste (s-SPW) catalyst to transform PFAD into biodiesel. Utilization of SPW, a starch-rich biomass waste for the synthesis of catalyst, could turn waste into useful substance, reduce waste disposal cost and have no competition with food supply and security issue. Laskar et al. (2022) conducted a process optimization of catalysts derived from flower petal ash using RSM for the conversion of waste cooking oil to biodiesel. The objective of this investigation is to perform process optimization of s-SPW catalyst for conversion of PFAD into biodiesel by RSM with Statistica Software. Variables considered to investigate the optimum synthesis condition in the preparation of the s-SPW catalyst were carbonization temperature, carbonization time, sulfonation temperature and sulfonation time.

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2. Material and methods

2.1 Materials

PFAD as feedstock oil was collected from Mewaholeo Industries Sdn Bhd, Pasir Gudang. SPW as a raw material of catalyst was collected from Hup Mop Kilang Sagu, Batu Pahat. Sulphuric acid (H_2SO_4, 98 %) as a sulfonating agent was purchased from RCI Labscan Group. Methanol (AR grade) and Chloroform (AR grade) were obtained from Merck Group. Fatty acid methyl ester standards, including methyl myristate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate were purchased from Sigma Aldrich (M) Sdn. Bhd.

2.2 Synthesis of catalyst

Raw SPW was put into the oven for 24 h at 110 °C for drying. After drying, SPW was ground and sieved to ensure consistent heating and reaction in subsequent processes. Carbonization of ground and sieved SPW was carried out in a furnace at temperatures range of 94.20 °C to 505.80 °C for 13.55 min to 116.45 min to produce partial carbonized SPW. 75 mL of concentrated H_2SO_4 was mixed with 5 g of partial carbonized SPW, and the mixture was subjected to a sulfonation process at a temperature range of 16.52 °C to 263.48 °C for 1.36 min to 11.64 min. After cooling down the sulfonated product mixture, distilled water was added for dilution purposes to ease the filtration process. The mixture was filtered and the filter cake consisting of s-SPW catalyst was rinsed and washed using hot distilled water to remove the excessive sulfate ions deposited on the surface of the catalyst post-sulfonation (Zailan et al., 2021). The s-SPW catalyst prepared will be placed in the oven for 24 h at 110 °C to be dried. The dried catalyst was ground, sieved and stored in a covered desiccator and ready to be used for biodiesel production.

2.3 Biodiesel production

50 g of PFAD was pre-heated at 70 °C for phase change from solid to liquid state. Liquefied PFAD, methanol and s-SPW catalyst were poured into a three-neck round bottom flask. Conversion of PFAD into biodiesel was carried out by heating under reflux in a water bath with a 10:1 methanol to PFAD molar ratio, 2 wt% catalyst loading, 500 rpm stirring speed and 60 °C reaction temperature for 60 min (Zailan et al., 2021). After that, the product mixture was filtered to remove the solid acid catalyst. Liquid product was transferred into a separating funnel as set aside for 30 min to allow settling and formation of 2 product layers. Biodiesel product layer was collected, washed and purified using hot distilled water. Biodiesel sample was diluted using chloroform with a dilution factor of 300 times to be analysed using GC-FID. Biodiesel yield % was calculated using Eq(1).

$$Yield\ (\%) = \frac{Actual\ Yield}{Theoretical\ Yield}\ x\ 100\% \quad (1)$$

2.4 Design of Experiment

Four independent variables for the synthesis of s-SPW catalyst, including carbonization temperature, carbonization time, sulfonation temperature and sulfonation time, were chosen in this study. Design of experiment (DOE) was done using Central Composite Design (CCD) of 4 factors with biodiesel yield as response with a study range of –α to +α. The coded variables were as shown in Table 1. Carbonization temperature of 94.20 °C to 505.80 °C, carbonization time of 13.55 min to 116.45 min, sulfonation temperature of 16.52 °C to 263.48 °C and sulfonation time of 1.36 min to 11.64 min were studied in this optimization work. 26 runs were carried out to study the optimization of conversion of PFAD to biodiesel using s-SPW catalyst. Response of biodiesel yield was investigated using multi regression analysis and second order polynomial was applied in this study as presented in Eq(2), where y is yield, x_i and x_j are the independent variables, β_o, β_i, β_{ii}, β_{ij} are intercept, linear, quadratic and interaction constant coefficients respectively.

$$y = \beta_o + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \quad (2)$$

Table 1: Coded variables

Variable	-α	-1	0	+1	+α
Carbonization Temperature (°C)	94.20	200.00	300.00	400.00	505.80
Carbonization Time (min)	13.55	40.00	65.00	90.00	116.45
Sulfonation Temperature (°C)	16.52	80.00	140.00	200.00	263.48
Sulfonation Time (min)	1.36	4.00	6.50	9.00	11.64

3. Result and discussion

3.1 Mathematical model

The experimental biodiesel yield of 26 runs using PFAD as feedstock with methanol and s-SPW catalyst was tabulated in Table 2. The data was subjected to RSM analysis to predict a mathematical model of the reaction through the regression coefficient of the factors involved. Significance of each variable was expressed in terms of probability value (p-value) where a p-value of less than 0.05 indicates significant effects of the variable at a 95 % confidence level. The adequacy of the mathematical model was also checked by using a coefficient of determination (R^2) and analysis of variance (ANOVA). The ratio of explained variation to total variation is presented as the coefficient of determination (R^2) and acts as a measure for the degree of fitness of the predicted mathematical, where $R^2 > 0.80$ indicates a good model fit (Saimon et al., 2019). Table 3 tabulates the regression coefficient of variables of the data under investigation.

Table 2: Experimental biodiesel yield for RSM Analysis

Run	Carbonization Temperature (°C)	Carbonization Time (min)	Sulfonation Temperature (°C)	Sulfonation Time (min)	Yield (%)
1	200.00	40.00	80.00	4.00	42.22
2	200.00	40.00	80.00	9.00	51.35
3	200.00	40.00	200.00	4.00	45.39
4	200.00	40.00	200.00	9.00	48.57
5	200.00	90.00	80.00	4.00	40.13
6	200.00	90.00	80.00	9.00	49.51
7	200.00	90.00	200.00	4.00	47.88
8	200.00	90.00	200.00	9.00	55.32
9	400.00	40.00	80.00	4.00	47.12
10	400.00	40.00	80.00	9.00	55.93
11	400.00	40.00	200.00	4.00	51.02
12	400.00	40.00	200.00	9.00	57.89
13	400.00	90.00	80.00	4.00	46.12
14	400.00	90.00	80.00	9.00	51.04
15	400.00	90.00	200.00	4.00	56.32
16	400.00	90.00	200.00	9.00	63.97
17 (c)	300.00	65.00	140.00	6.50	68.89
18	94.20	65.00	140.00	6.50	55.61
19	505.80	65.00	140.00	6.50	60.15
20	300.00	13.55	140.00	6.50	65.28
21	300.00	116.45	140.00	6.50	62.17
22	300.00	65.00	16.52	6.50	45.78
23	300.00	65.00	263.48	6.50	52.99
24	300.00	65.00	140.00	1.36	50.71
25	300.00	65.00	140.00	11.64	53.25
26 (c)	300.00	65.00	140.00	6.50	69.75

*(c) in the “Run column” denotes the centre value for the experimental design

Based on the regression coefficients obtained, the quadratic regression model was presented in Eq(3), where Y (%) = biodiesel yield %, X_1 = Carbonization Temperature (°C), X_2 = Carbonization Time (min), X_3 = Sulfonation Time (min), X_4 = Sulfonation Temperature (°C).

$$Y\ (\%) = -42.2463 + 0.2080\ X_1 + 0.2426\ X_2 + 11.4149\ X_3 + 0.3508\ X_4 - 0.0003\ X_1^2 - 0.0033\ X_2^2 - 0.7694\ X_3^2 - 0.0015\ X_4^2 - 0.002\ X_1X_3 + 0.002\ X_1X_4 + 0.0014\ X_2X_3 + 0.0013\ X_2X_4 - 0.0030\ X_3X_4 \quad (3)$$

The correlation of the predicted value of biodiesel yield using the mathematical model and experiment (observed) value was plotted in Figure 1 and the coefficient of determination (R^2) for this model is 0.8055 which implied a good model fit. The critical point for carbonization temperature, carbonization time, sulfonation temperature and sulfonation time is 338.49 °C, 69.44 min, 156.32 °C and 7.13 min, respectively. The optimized synthesis condition for s-SPW catalyst gave a biodiesel yield of 69.51 %.

Table 3: Regression coefficients of variables

	Regression Coefficient	Standard Error	t(11)	Probability Value (p)	-95 % Confidence Limit	+95 % Confidence Limit
Mean/Interc.	-42.2463	32.2502	-1.3100	0.2169	-113.2280	28.7358
(X_1) Carbonization Temperature (°C)(L)	0.2080	0.0923	2.2549	0.0455	0.0050	0.4111
Carbonization Temperature (°C)(Q)	-0.0003	0.0001	-2.8458	0.0159	-0.0010	-0.0001
(X_2) Carbonization Time (min)(L)	0.2426	0.3487	0.6958	0.5010	-0.5250	1.0100
Carbonization Time (min)(Q)	-0.0033	0.0019	-1.6960	0.1180	-0.0070	0.0010
(X_3) Sulfonation Time (min)(L)	11.4149	3.4867	3.2738	0.0074	3.7410	19.0891
Sulfonation Time (min)(Q)	-0.7694	0.1921	-4.0064	0.0021	-1.1920	-0.3467
(X_4) Sulfonation Temperature (°C)(L)	0.3508	0.1401	2.5046	0.0293	0.0430	0.6591
Sulfonation Temperature (°C)(Q)	-0.0015	0.0003	-4.5168	0.0009	-0.0020	-0.0008
X_1L by X_2L	0.0000	0.0005	0.0086	0.9933	-0.0010	0.0012
X_1L by X_3L	-0.0002	0.0052	-0.0423	0.9670	-0.0120	0.0112
X_1L by X_4L	0.0002	0.0002	0.7223	0.4852	0.0000	0.0006
X_2L by X_3L	0.0014	0.0208	0.0672	0.9476	-0.0440	0.0472
X_2L by X_4L	0.0013	0.0009	1.4618	0.1718	-0.0010	0.0032
X_3L by X_4L	-0.0030	0.0087	-0.3410	0.7396	-0.0220	0.0161

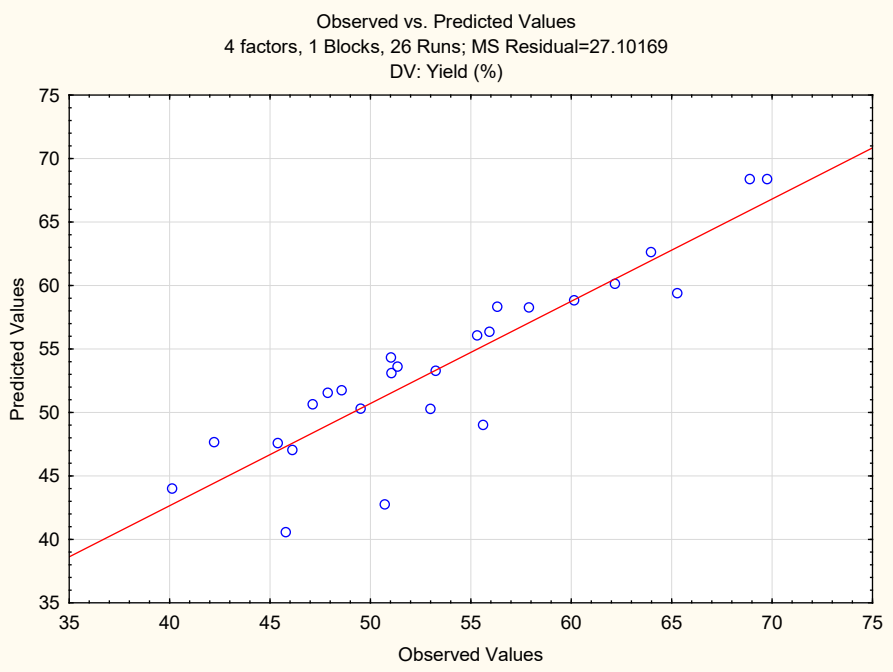

Figure 1: Graph of predicted values vs experimental (observed) values

ANOVA analysis for biodiesel yield from the conversion of PFAD using s-SPW catalyst is shown in Table 4. Fisher F-test is used by ANOVA method to validate the model's fitness obtained earlier. Using the data from the ANOVA table, F-value (calculated) was found to be 3.25, greater than F-value (tabulated) of 2.74, proving that the model is significant.

Table 4: ANOVA analysis

	Sum of square	Degree of freedom	Mean Square	F	p
(X_1)Carbonization Temperature (°C)(L)	139.2940	1.0000	139.2939	5.1397	0.0445
Carbonization Temperature (°C)(Q)	219.4800	1.0000	219.4801	8.0984	0.0159
(X_2)Carbonization Time (min)(L)	0.7910	1.0000	0.7910	0.0292	0.8674
Carbonization Time (min)(Q)	77.9560	1.0000	77.9558	2.8764	0.1180
(X_3)Sulfonation Time (min)(L)	160.1790	1.0000	160.1789	5.9103	0.0333
Sulfonation Time (min)(Q)	435.0060	1.0000	435.0056	16.0509	0.0021
(X_4)Sulfonation Temperature (°C)(L)	136.4210	1.0000	136.4211	5.0337	0.0464
Sulfonation Temperature (°C)(Q)	552.9180	1.0000	552.9181	20.4016	0.0009
X_1L by X_2L	0.0020	1.0000	0.0020	0.0001	0.9933
X_1L by X_3L	0.0480	1.0000	0.0484	0.0018	0.9670
X_1L by X_4L	14.1380	1.0000	14.1376	0.5217	0.4852
X_2L by X_3L	0.1220	1.0000	0.1225	0.0045	0.9476
X_2L by X_4L	57.9120	1.0000	57.9121	2.1368	0.1718
X_3L by X_4L	3.1510	1.0000	3.1506	0.1163	0.7396
Error	298.1190	11.0000	27.1017		
Total SS	1532.4300	25.0000			

3.2 Effects of s-SPW catalyst synthesis variables on biodiesel yield.

Pareto chart can visually present the absolute values of the effects of factors and the interaction of factors. The pareto chart includes a vertical reference line at the critical t-value for a p-value of 0.05 (magnitude for a 95 % confidence level) to indicate that the factors which passed through this line are statistically significant in the model. The pareto chart of standardized effects is shown in Figure 2. There are 3 variables in catalyst synthesis that showed significant effects on biodiesel yield: sulfonation temperature, sulfonation time and carbonization temperature. A suitable carbonization temperature promotes the formation of polycyclic aromatic ring and subsequent incorporation of sulfonic (SO_3H) groups while a higher carbonization temperature results in a stiff structure and inhibit insertion of functional groups. Sulfonation temperature and time affect the rate of incorporation of SO_3H groups and acidity of catalysts and a good balance between strong and weak acid sites density yields the best catalyst. Oxygen-containing functional groups (COOH and OH) provided a synergistic effect to SO_3H groups, resulting a high total acid density and enhanced catalytic activity of the catalyst (Yadav et al., 2023). This information is critical in providing which area to focus when design future of s-SPW catalyst.

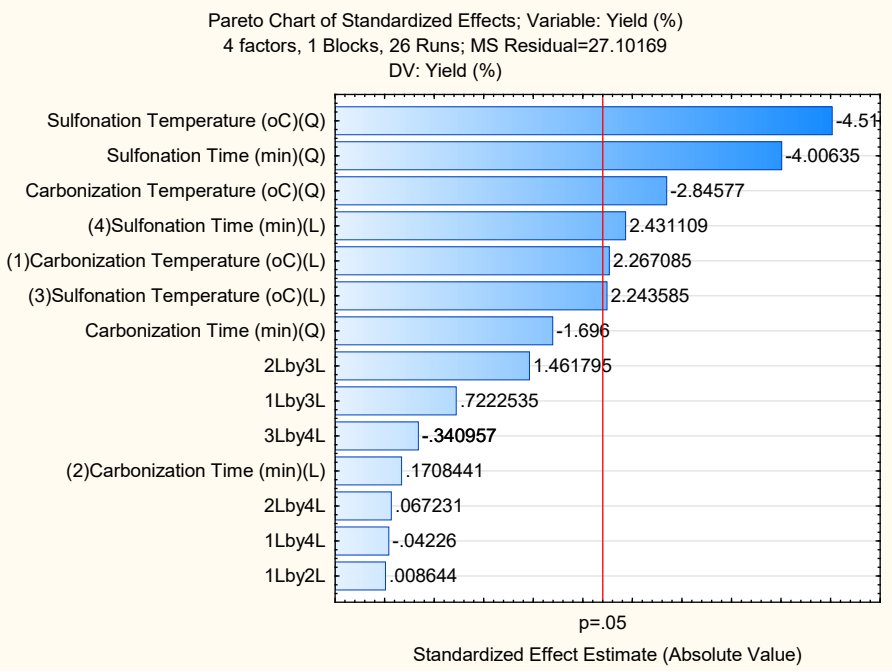

Figure 2: Pareto chart of standardized effects of variables

Figure 3 illustrated the surface plots of biodiesel yield as a function of the 3 most significant variables. It can be observed that deviation from the critical point of the synthesis condition of catalysts give lower yield % and the bigger the deviation, the lower the biodiesel yield % obtained.

(a) (b) (c)

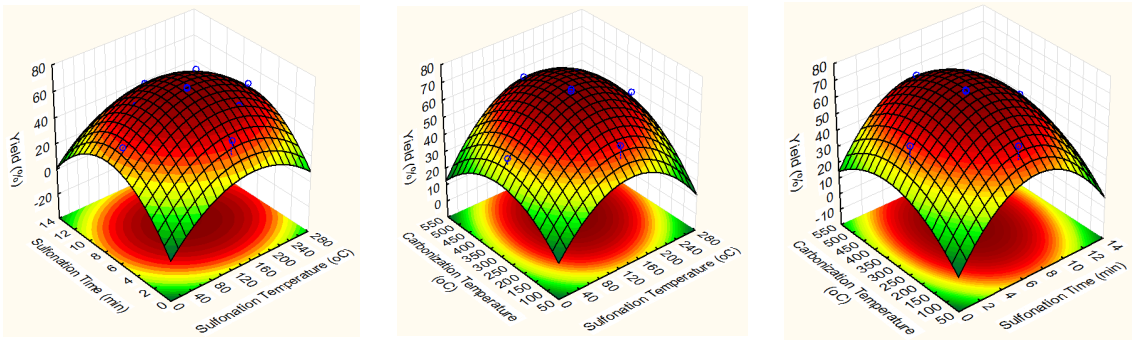

Figure 3: Surface plots of biodiesel yield as a factor of (a) sulfonation temperature and sulfonation time; (b) sulfonation temperature and carbonization temperature; (c) sulfonation time and carbonization temperature

4. Conclusion

s-SPW catalyst had been developed from raw SPW through carbonization and sulfonation process for conversion of PFAD to biodiesel. The optimum synthesis condition for s-SPW catalyst was found at a carbonization temperature of 338.49 ºC, carbonization time of 69.44 min, sulfonation temperature of 156.32 ºC and sulfonation time of 7.13 min with a biodiesel yield of 69.51%. Coefficient of determination (R^2), Fisher F-Test and ANOVA analysis had been applied to validate the mathematical model developed and showed that the model is significant. There are 3 synthesis parameters (variables) which have significant effects on the response (biodiesel yield), which are sulfonation time, carbonization temperature and sulfonation temperature. Further studies can be done on optimizing the process condition of conversion of PFAD to biodiesel, which favours the catalyst's activities, esterification and transesterification process and achieves higher biodiesel yield. S-SPW catalyst is a cost-effective catalyst which may decrease the overall production cost of biodiesel and increase its competitiveness against other alternative energy sources.

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References

Clohessy J., Kwapinski W., 2020, Carbon-Based Catalysts for Biodiesel Production - A Review, Applied Science 2020, 10, 918-934.

Indika T., Sandhya B., Chanatip S., 2019, Biodiesel production in an autoclave reactor using waste palm oil and coconut coir husk derived catalyst, Renewable Energy, 134, 125-134.

Laskar I.B., Deshmukhya T., Biswas A., Paul B., Changmai B., Gupta R., Chatterjee S., Rokhum S.L., 2022, Utilization of biowaste-derived catalysts for biodiesel production: process optimization using response surface methodology and particle swarm optimization method, Energy Advances, 1, 287-302.

Saimon N.N., Isa S., Jusoh Y.M., Jusoh M., Ngadi N., Zakaria Z.Y., 2019, Optimization of esterification palm fatty acid distillate to methyl ester using microwave-assisted titanium sulfonated glucose acid catalyst, Chemical Engineering Transactions, 72, 367-372.

Tan W.T., Jusoh M., Zakaria Z.Y., 2021, Starch-derived Solid Acid Catalyst for Biodiesel Production: A Mini Review, Chemical Engineering Transactions, 89, 487-492.

Tang Z.E., L. S., 2018, Synthesis of biomass as heterogeneous catalyst for application in biodiesel production: State of the art and fundamental review, Renewable and Sustainable Energy Reviews, 92, 235-253.

Yadav N., Yadav G., Ahmaruzzaman Md., 2023, Biomass-derived sulfonated polycyclic aromatic carbon catalysts for biodiesel production by esterification reaction, Biofuels, Bioproducts and Biorefining, 17(5), 1334-1367.

Zailan Z., Tahir M., Jusoh M., Zakaria Z., 2021, A review of sulfonic group bearing porous carbon catalyst for biodiesel production, Renewable Energy, 175, 430-452.