

Mesoporous SBA-15-Pr-SO₃H Catalysed Biodiesel Production from Maize Acid Oil

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Received 04 January 2018; revised 19 September 2018; accepted 20 December 2018

Mesoporous SBA-15-Pr-SO₃H catalyst has been synthesized via one-pot co-condensation method. The synthesized catalyst has been characterized by small and wide angle XRD, SEM-EDS, BET surface area, FT-IR, ¹³C and ²⁹Si CP-MAS-NMR and TGA analysis. The performance of SBA-15-Pr-SO₃H catalyst was evaluated in biodiesel production from low-cost maize acid oil (MAO) feedstock containing high free fatty acid (127.21 mgKOH / g). Optimization of various reaction parameters has been carried out using Box-Behnken design (BBD). Under optimized reaction condition, 99.53% biodiesel conversion is obtained.

Keywords: Renewable Feed Stock, Maize Acid Oil, SBA-15-Pr-SO₃H, Box-Behnken Design, Biodiesel Properties

Introduction

Production of biodiesel on industrial scale from edible feed stock is difficult as it imbalances the world food demand and increased the cost of edible oils as the later contributes 70 – 95 % to the overall biodiesel production cost¹. These problem can be solved by using non-edible oils², acid oil and animal fats as a low-cost feedstock for the biodiesel production. In this context, herein an attempt has been made to utilize maize acid oil (MAO) for the biodiesel production. MAO is the by-product of distilled maize oil refinery. Soap formation is a major problem in the case of solid base catalysed biodiesel production from low-cost oil feed stock containing high FFA³. To overcome this problem, several solid acid catalysts are reported⁴⁻¹² for the biodiesel production. Reported protocols are associated with certain drawbacks such as, more consumption of catalyst concentration, deactivation of catalyst during regeneration and leaching of active component from supported catalyst etc.⁹⁻¹¹ In the present case, the mesoporous solid acid SBA-15-Pr-SO₃H catalyst has been selected for biodiesel production from MAO containing high FFA, owing to its good reactivity result from underlying functional groups, non-corrosive and less hazardous nature and ease of separation. The optimization of three reaction parameters such as MAO to methanol

molar ratio, the amount of catalyst loading and reaction time were studied to obtain maximum biodiesel conversion using Box-Behnken design (BBD). In order to reduce the number of experiments, the reaction temperature parameter for the first time is considered out of box during the calculation of total number of experiments.

Materials and methods

Materials

Tetraethyl orthosilicate (TEOS, 98 %), Pluronic P-123, (3-Mercaptopropyl)-trimethoxy-silane (95 %) Hydrogen peroxide (30 %), Methanol (99.99%) have been purchased from Sigma-Aldrich and Finar chemical. MAO was obtained from Ashwin Vanaspati India Pvt. Ltd. (Baroda, India).

Catalyst preparation

Functionalized SBA-15 material has been synthesized by the reported method⁸. In a typical one-pot synthesis, 4 g of Pluronic P-123 was dissolved in 125 g of 1.9 M HCl at 40 °C temperature with continuous stirring. Upon dissolution, TEOS was added dropwise and allowed to pre-hydrolyzed for approximately 45 mins. prior addition of MPTMS-H₂O₂ solution. The molar composition of the resulting mixture was 0.0369 TEOS: 0.0062 MPTMS: 0.0554 H₂O₂. It was continuously stirred for 24 h at 40 °C and thereafter, aged in a teflon coated auto-clave reactor for 20 h at 130 °C under static conditions. The product

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was filtered and dried at 120°C for 3 h. Then, Pluronic P-123 was removed by performing 24 h Soxhlet extraction using ethanol. The resultant product was collected and dried at 120°C for 4 h.

Application of SBA-15-Pr-SO₃H in esterification of maize acid oil

A biodiesel synthesis from MAO was performed at 65°C temperature at stirring speed of 400 rpm using conventional reflux technique. In this reaction, 5 ml of MAO was mixed with the calculated amount of methanol and catalyst. Upon reaction completion, the reaction mixture was filtered and the biodiesel is separated using separating funnel. Biodiesel was collected and heated at about 80 °C temperature for purification. Reaction conversions calculated using the equation, $[AV_f \times AV_p / AV_f] \times 100$ ¹³; where, AV_f and AV_p are the acid values of the feedstock and the product, respectively.

Results and Discussion

Catalyst characterization

Small and wide angle XRD patterns of SBA-15-Pr-SO₃H shows three diffraction peaks, which are indexed as (1 0 0), (1 1 0) and (2 0 0). Very low intensity of 1.38° and 1.82° (2 θ) peaks were observed which may be due to inner hexagonal pore structure of SBA-15 with functionalization of -Pr-SO₃H groups. In wide angle XRD patterns, broad peak was observed between 15°- 30° 2 θ angle indicating amorphous nature of SBA-15-Pr-SO₃H catalyst⁴. The SEM images of SBA-15-Pr-SO₃H catalyst exhibited many wheat-like structures with uniform sizes⁸. The presence of Si, C, O and S elements are confirmed by SEM-EDS analysis. The absence of other elements indicated absence of impurity in the catalyst. BET surface area, pore volume and pore size of SBA-15-Pr-SO₃H catalyst are found to be 464.14 m²/g, 0.68 cm³/g and 37.46 Å respectively. The C₁, C₂ and C₃

carbon of -Pr-SO₃H groups were confirmed by peaks at 11.26, 18.19 and 54.00 ppm in ¹³C CP-MAS-NMR spectra of catalyst. The organo-siloxane network is confirmed by peaks observed at -61.52, -66.07 ppm and silica framework of SBA-15 is confirmed by -102.22 and -111.23 ppm in ²⁹Si CP-MAS-NMR spectra of SBA-15-Pr-SO₃H catalyst⁸ (Figure-1). In TGA analysis, the first weight loss is observed upto at 100 °C due to water desorption and the second weight loss is observed in the range of 320-600 °C, which is attributed to the decomposition of propyl sulfonic acid groups. In FT-IR spectrum, the band corresponding to -SO₂ stretching vibrations of SO₃H, Si-O-Si and OH stretching and CH₂ groups of propyl chain are observed in the range of 1000-1200 cm⁻¹, 3200 - 3600 cm⁻¹ and 1500 cm⁻¹ respectively⁸.

Optimization of reaction parameters

In this study, the effects of reaction parameters such as catalyst concentration, MAO to methanol molar ratio and reaction time have been investigated using BBD. Each variable has three levels i.e. the low levels (-1), centre levels (0) and high levels (+1) (table-1). The table-1 represents coded and encoded values of three variables and percentage conversion of biodiesel during the experiment for the development of BBD. The BBD approach is developed in order to finalize number of experiments to be performed using the equation, $N = [2V (V-1)] + C_0$, where V = Number of variables and C₀ = Number of central points. Fifteen experiments (N) have been performed for the investigation of three variables. Predicted conversion and the effect of each variable on the biodiesel production were analyzed by a following polynomial quadratic equation using Minitab 17 (Trial version) software.

$$Y = -1.0 - 1.57X_1 + 4.74X_2 + 0.647X_3 - 0.094(X_1)^2 - 0.791(X_2)^2 - 0.002098(X_3)^2 + 0.701X_1 \cdot X_2 + 0.00991X_1 \cdot X_3 - 0.0066X_2 \cdot X_3;$$

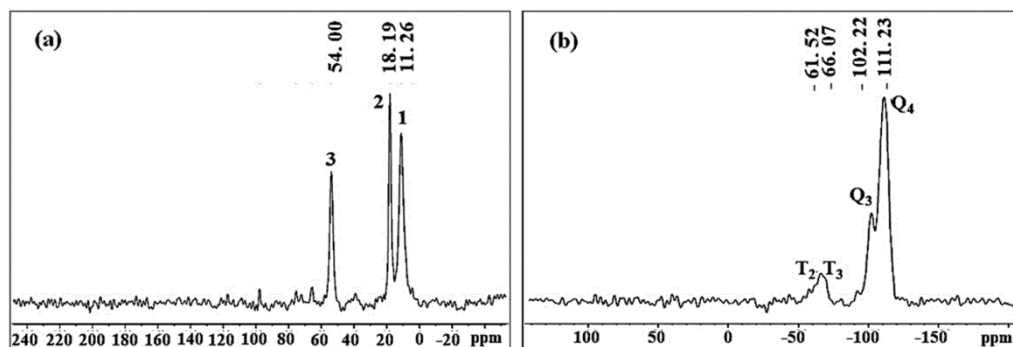


Fig. 1 — (a) ¹³C CP MAS NMR of SBA-15-Pr-SO₃H catalyst (b) ²⁹Si CP MAS NMR of SBA-15-Pr-SO₃H catalyst

Where Y is the theoretical response of biodiesel conversion; X_1 , X_2 and X_3 are molar ratios of MAO to methanol, catalyst concentration and reaction time respectively; -1.0 is the intercept; 1.57, 4.47 and 0.647 are linear coefficients; 0.094, 0.791 and 0.002098 are the squared term coefficients; 0.701, 0.00991 and 0.0066 are the interaction coefficients. Table 1 clearly revealed close matching of experimental and predicted values. Pearson's r for experimental conversion against the predicted conversion is 0.96493 that means the total variation in the results was 3.507 %. It may be due to the non-independent

variables such as human (experimental) or instrumental (stirrer speed, temperature) errors¹⁴. The statistical analysis for the response surface model is shown in Table-2. The F-value of reaction time is 29.1 which is larger as compared to catalyst concentration and MAO to methanol ratio which indicates the most significant factor was reaction time, followed by catalyst concentration and the molar ratio of MAO to methanol in biodiesel synthesis. Besides, P-value for the model is less than 0.05, which indicates that it is a significant and desirable model¹⁵. Figure-2 depicts the interaction of

Table 1 — Experimental design and % yield of biodiesel

Standard Run	Molar ratio with respect to MAO	Catalyst concentration (%)	Time (min.)	Experimental conversion (%)	Theoretical conversion (%)
1	-1 (5)	-1 (1)	0 (130)	56.86	50.52
2	-1 (5)	-1 (5)	0 (130)	61.11	61.06
3	+1 (15)	+1 (1)	0 (130)	35.88	35.92
4	+1 (15)	+1 (5)	0 (130)	68.17	74.50
5	0 (10)	0 (1)	-1 (60)	15.85	22.70
6	0 (10)	0 (1)	+1 (200)	48.44	48.87
7	0 (10)	0 (5)	-1 (60)	48.55	48.11
8	0 (10)	0 (5)	+1 (200)	77.44	71.58
9	-1 (5)	-1 (3)	-1 (60)	39.01	39.49
10	+1 (15)	+1 (3)	-1 (60)	37.88	31.97
11	-1 (5)	-1 (3)	+1 (200)	51.96	57.86
12	+1 (15)	+1 (3)	+1 (200)	64.71	64.23
13	0 (10)	0 (3)	0 (130)	60.77	61.01
14	0 (10)	0 (3)	0 (130)	60.58	61.01
15	0 (10)	0 (3)	0 (130)	61.70	61.01
opt.	+1 (15)	+1 (5 %)	182 min.	80.13	81.73

opt. = Optimization reaction condition (excluded optimized temperature)

Table 2 — Analysis of Variance for response surface quadratic model of BBD

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Model	9	3155.27	350.59	7.96	0.017
Linear	3	2488.75	829.58	18.83	0.004
Ratio	1	0.66	0.66	0.02	0.907
Catalyst	1	1206.39	1206.39	27.39	0.003
Time	1	1281.7	1281.7	29.1	0.003
Square	3	418.38	139.46	3.17	0.123
ratio*ratio	1	20.32	20.32	0.46	0.527
Catalyst*Catalyst	1	37.01	37.01	0.84	0.401
time*time	1	390.26	390.26	8.86	0.031
2-Way Interaction	3	248.15	82.72	1.88	0.251
ratio*Catalyst	1	196.56	196.56	4.46	0.088
ratio*time	1	48.16	48.16	1.09	0.344
Catalyst*time	1	3.42	3.42	0.08	0.792
Error	5	220.24	44.05	--	--
Lack-of-Fit	3	219.53	73.18	203.7	0.005
Pure Error	2	0.72	0.36	--	--
Total	14	3375.51	--	--	--

DF - Degree of Freedom; Adj. SS - Adjusted Sum of Squares; Adj. MS - Adjusted Mean of Squares; F - Probability distribution; p - Probability

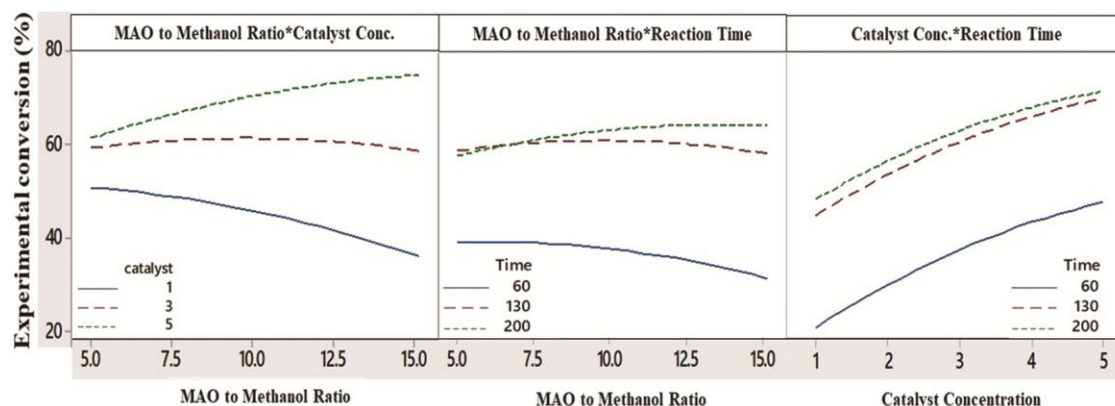


Fig. 2 — Experimental conversion Vs interaction between MAO to methanol molar ratio, catalyst concentration and reaction time

catalyst concentration with reaction time and the MAO to methanol ratio indicates that when the catalyst concentration and reaction time increases from 1 to 5 wt. % and 60 to 200 minutes, respectively, the experimental biodiesel conversion was found to be increased. On the other hand when MAO to methanol ratio increases from 5 to 15 molar, only biodiesel conversion increased with 5 wt. % catalyst, and in the case of 1 wt. % catalyst, the conversion was found to be decreased. Which may be due to use of high MAO to methanol molar ratio leads to more water formation, during esterification, which in turn causes deactivation of catalyst¹⁶. Finally, 80.13 % biodiesel conversion was obtained under optimized reaction condition using BBD. The additional reaction temperature parameter is considered as out of BBD design parameter, due to which, the number of experiments is reduced to 18 from 28 (according to Eq.-3). Further experiments were performed in an autoclave reactor at a different temperature. 82.34%, 92.23% and 99.53% biodiesel conversions obtained at 65, 85 and 105 °C temperature, respectively. Thus, the optimized reaction conditions are found as catalyst concentration, 5 %; MAO to methanol ratio, 1:15; temperature, 105 °C and reaction time, 182 min for getting maximum biodiesel conversion. The present protocol has an advantage of getting better biodiesel quality (i.e. with acid value <0.50 mg KOH /g) without any additional treatment.

Conclusion

In the present study, the biodiesel was synthesized using low-cost feedstock such as maize acid oil containing high FFA (127.21 mg KOH/g) using mesoporous SBA-15-Pr-SO₃H catalyst. BBD is used for optimization of reaction parameters. 80.13 % biodiesel conversion is obtained under optimized

reaction conditions (excluding reaction temperature). Amongst the studied reaction parameters, reaction time and catalyst concentration are found more influencing. The thought of considering the reaction temperature parameter out of box is found beneficial to reduce the number of experiments from 28 to 18. Under optimized reaction conditions (including reaction temperature), 99.53 % biodiesel conversion is obtained. Owing to good quality of produced biodiesel, one can utilize it in petro-diesel engine without any further modification.

Acknowledgement

The authors gratefully acknowledge the Sardar Vallabh bhai National Institute of Technology, Surat, Gujarat, India for providing support for this research work.

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