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Optimization of reaction conditions by response surface methodology for biodiesel production over different heterogeneous heteropoly acid-based nanomaterials

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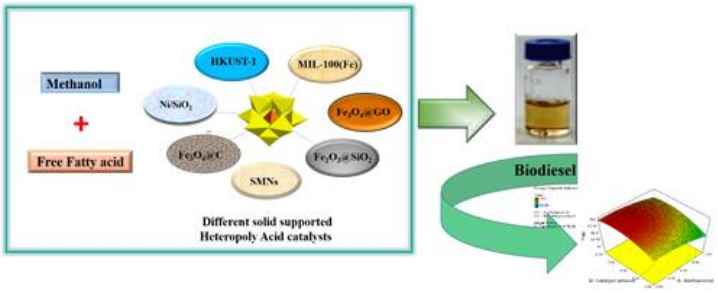
Abstract

A series of nanocatalysts based on heteropoly acid supported on various nanomaterials such as metal-organic frameworks (MOFs), carbon- and silica-based materials, have been synthesized for application in the esterification of oleic acid as catalyst. The effects of multiple parameters and their reciprocal interactions were investigated using a five-level three-factor design. The reaction conditions such as catalyst amount, methanol to oleic acid molar ratio, and reaction temperature have been optimized by Response Surface Methodology using the Central Composite Design model. The reaction temperature was the most significant factor, and the best conversion ratio of oleic acid could reach 99.27% with 5.97% of catalyst amount and 3.90:1 of methanol to oleic acid molar ratio at 74.0 °C. As a preliminary application, the best nanocatalyst was used in biodiesel production from castor oil and methanol. The yields of fatty acid methyl esters for castor oil were about 90.2%.



Keywords: *Biodiesel, Nanocatalyst, Heteropoly acid, Response Surface Methodology, Castor oil.*

Introduction

Biodiesel is a ''green fuel'' that gaining significant attention because of its crucial use to mitigate the increasingly serious problems of global energy shortage and environmental pollution.[1] The main process for the preparation of this fuel is catalytic esterification and transesterification of triglycerides with alcohols.[2, 3] Biodiesel has become a substitute for petroleum diesel because it possesses many advantages including low viscosity, nontoxicity, clean engine emissions, high cetane number, and low sulfur content.[4]

Common acid catalysts lead to corrosion and environmental problems.[5, 6] Therefore, the application of "green catalysts" for biodiesel production is important.

Many researchers believe that the heteropoly acids (HPAs), especially Keggin type 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, PW), are able to be active catalysts for biodiesel production.[7-18] It is because of their inherent advantages including, fewer side reactions, strong Brönsted acidity, high proton mobility, stability, environmentally benign nature, molecular and electronic structural diversity[19, 20] and less harmful and more active compared to mineral acids.[21] Above materials often have drawbacks, including low porosity and some technical problems in catalyst recovery. Encapsulation or immobilization of HPAs on different supports used as effective strategies to overcome these drawbacks.

Different immobilized HPAs on a wide number of solids including ZrO_2[22] montmorillonite K10[23] activated carbon fiber[24] zeolites,[25, 26] mesoporous silica,[27-30] and ionic liquids[4, 31, 32] have been performed for biodiesel production.

Since the properties of the solid support is very effective on stabilization and performance of the immobilized HPAs, it is important to choose the most suitable support for immobilization. In this study, a series of hybrid PW-based materials were synthesized according to our previously published procedures.[33-39] PW encapsulated in HKUST-1 ($Cu_3(BTC)_2$, BTC=1,3,5-benzene tricarboxylic acid), PW@HKUST-1; PW encapsulated in MIL-100(Fe) (mesoporous iron-carboxylate) PW@MIL-100(Fe); PW immobilized on magnetite graphene oxide, (PW/Fe_3O_4/GO); PW immobilized on carbon-coated Fe_3O_4 (PW/Fe_3O_4@C); composite of PW and starch coated magnetite nanoparticles, (PW/SMNs); PW supported on

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silica-coated magnetic nickel oxide, PW/Ni/SiO_2; PW supported on silica-coated magnetic nanoparticles, (PW/Fe_2O_3@SiO_2) were used as selected catalysts and activity of these PW-based nanomaterials were compared in biodiesel production.

The effect of temperature, methanol-to-free fatty acids (FFAs) ratio, and catalyst amount on the conversion of FFA to biodiesel, were studied by Central Composite Design (CCD) and for esterification reaction process optimization using the best catalyst, Response Surface Methodology (RSM) was carried out. This work also investigates the production of biodiesel from castor oil with high FFA by one-step heterogeneous acid-catalyzed esterification followed by heterogeneous catalyzed transesterification.

Experimental

General remarks

PW (> 99%), other reagents and solvents were commercially available and purchased from Fluka, Merck, and Aldrich chemical companies. Oleic acid (89.40 wt.%) was obtained from Carlo Erba. The feedstock and products were analyzed by the gas chromatographic-mass spectroscopy (GC-MS) using an Agilent 7890 gas chromatograph (Centerville Road, Wilmington, NC, USA) equipped with split/splitless inlet (MMI) with an electrospray ionization mode (ESI, 1200 eV) and the mass range was 50–700 a.m.u. The TEM image was taken out using a TEM microscope (Jeol JEM-2100 with an accelerating voltage of 200 kV).

Preparation of the catalysts

All catalysts including PW@HKUST-1, PW@MIL-100(Fe), PW/SMNs, PW/Fe_3O_4@C, PW/Fe_3O_4@GO, PW/Fe_2O_3@SiO_2, and PW/Ni@SiO_2 were prepared according to our previous reported procedures.[33-39]

Catalytic reaction

For esterification of oleic acid, catalyst and methanol were added to oleic acid under reflux conditions. The catalyst was recovered by centrifugation (5000 rpm) and MeOH as filtrate was recovered using a rotary evaporator. The obtained mixture was diluted with water/hexane, shaken for a few minutes, agitated and set aside to develop two phases: the non-polar phase containing hexane, fatty acid methyl esters (FAME) and FFAs, and the polar phase containing water. The non-polar phase was analyzed using GC-MS.

For the production of biodiesel from castor oil (commercial edible grade), the PW/Fe_3O_4@GO (6.0 wt.% to oil) was added to 1.0 g of castor oil and 3.90 g of methanol at 75 °C. The experiment was prolonged for about 2 h. Then, the catalyst was recovered by external magnet and MeOH as filtrate was evaporated by rotary evaporator. The obtained mixture was diluted with water/hexane, shaken for few minutes and agitated. After separation of the two phases using separating funnel, the upper layer was separated and analyzed using GC-MS.

Optimization of biodiesel production by RSM

The operational conditions of biodiesel production analysis were performed by RSM to optimize and get a high percent conversion. For fitting a quadratic surface and optimize the effective parameters with a minimum number of experiments, a standard RSM design called CCD was applied. The dependent variables selected for this study were (i) A, methanol:oil molar ratio; (ii) B, catalyst amount, and (iii) C, reaction temperature. Table 1 lists the range and levels of the three variables studied.

For each categorical variable, a 23 full factorial CCD for the three variables, consisting of 8 factorial runs, 6 axial runs and 6 center runs were employed, indicating that all together 20 experiments were required, as calculated from the following equation:

$$N = 2^n + 2n + n_c = 2^3 + (2 \times 3) + 6 = 20 \quad (2)$$

where N is the total number of experiments required and n is the number of factors.

Design Expert Version 8.0.7.1 was performed to develop the regression model and for the graphical analysis of the data. The complete design matrix of CCD and the experimental results were reported in Table 2. The three remained experiments are replicates of the central point for estimating the pure error. The fit of the model was investigated by coefficients of determination and a test for lack of fit, which was done by comparing mean square lack of fit to mean square experimental error, from the analysis of variance (ANOVA).

Table 1. *Experimental range and levels of the independent variables.*

Variables	Level				
	-2 (-α)	-1	0	+1	+2 (+α)
A: Methanol:oil molar ratio	1	3	5	7	9
B: Catalyst amount (wt.%)	2	4	6	8	10
C: Reaction temperature (°C)	65	70	75	80	85

Table 2. *The central composite design for optimizing biodisel reaction.*

Standard run	Level of variables			Yield%
	Methanol:oil molar ratio (A)	Catalyst amount (wt.%) (B)	Reaction temperature (°C) (C)	
1	0	-α	0	23.63
2	-1	+1	-1	86.49
3	0	+α	0	71.47
4	+1	+1	-1	76.53
5	0	0	0	100.00
6	-1	-1	+1	76.70
7	0	0	0	100.00
8	-1	-1	-1	50.37
9	+α	0	0	54.09
10	0	0	0	89.40
11	0	0	0	100.00
12	+1	+1	+1	40.52
13	+α	0	0	88.99
14	+1	-1	+1	34.72
15	+1	-1	-1	29.99
16	0	0	0	90.27
17	-1	+1	+1	71.46
18	0	0	+α	28.34
19	0	0	-α	46.20
20	+1	-1	0	100.00

Results and discussion

The esterification of oleic acid with methanol under reflux conditions was chosen as model reaction (reaction conditions: catalyst loading = 5.0 wt.% to oil, methanol:oil = 6:1, 65 °C, reaction time = 12 h). The composition of the sample was containing 89.40 wt.% oleic acid. First, the activity of different prepared catalysts was investigated in the model reaction as a qualitative factor. Table 3 (entries 1–8) shows the influence of various catalysts on the conversion of oleic acid. As can be seen, PW/Fe_3O_4/GO shows the highest oil conversion compare to other catalysts and presented a high conversion of 100.0% (entry 1). Hence, we have selected PW/Fe_3O_4/GO for further study. Figure 1 presents the GC-MS chromatogram of the oleic acid sample before starting the esterification reaction and after it by PW/Fe_3O_4/GO as the best catalyst. The morphology of PW/Fe_3O_4/GO nanocomposite was confirmed by the TEM image and corresponding surface plot (Figure 2).

Table 3. *Esterification of oleic acid with MeOH using PW-based catalysts.*

Entry	Catalyst (g)	Conversion (%)[a]
1	$PW/Fe_3O_4/GO$	100
2	$PW/Fe_3O_4@C$	92.20
3	PW/SMNs	49.84
4	PW@MIL-100(Fe)	63.54
5	PW@HKUST-1	46.12
6	$PW/Ni/SiO_2$	47.55
7	$PW/ Fe_2O_3@SiO_2$	30.13

[a] Catalytic activities were expressed as conversion of oleic acid and oleic acid proportion was analyzed using GC–MS. (Reaction conditions: catalyst loading = 5.0 wt.% to oil, methanol: oil = 6: 1, 65 °C, reaction time = 12 h)

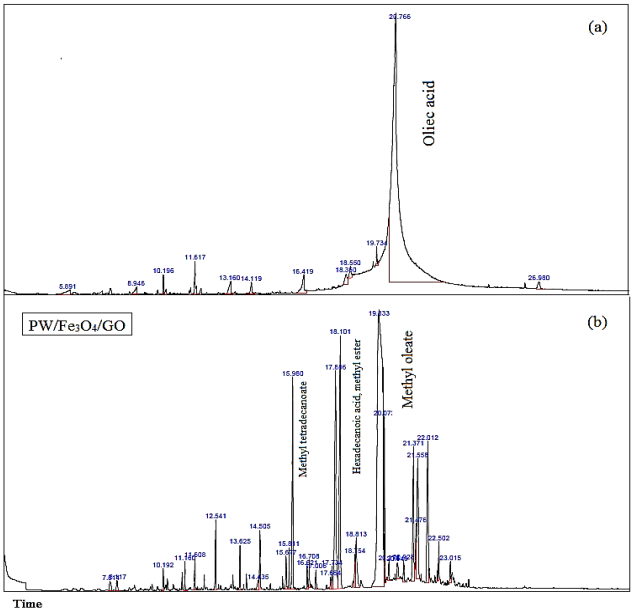

Figure 1. *GC-MS chromatograms of (a) oleic acid; (b) FAME products using $PW/Fe_3O_4/GO$.*

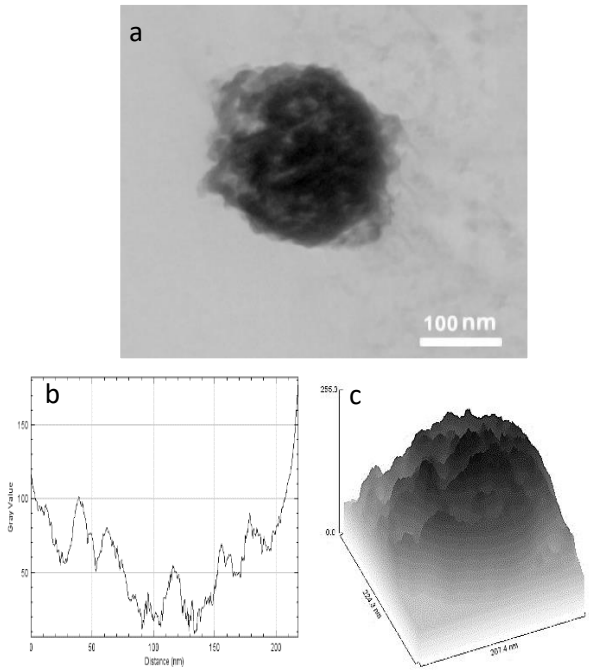

Figure 2. *(a)TEM image and (b) surface plot extracted by ImageJ® software of $PW/Fe_3O_4/GO$ nanocatalyst.*

After selection optimization of the best catalyst in biodiesel production, RSM was used to test the influence of other factors including methanol to oil molar ratio, catalyst amount and reaction temperature on the conversion to biodiesel by $PW/Fe_3O_4/GO$ as the best catalyst. Table 1 lists the range and levels of the three variables studied. Moreover, it can evaluate the relative interactions between variables. The results in Table 2 indicate the conversion of oleic acid to methyl oleate by $PW/Fe_3O_4/GO$ catalyst is in the range of 23.63–100%.

A polynomial equation (1) was obtained for the conversion yields by considering synthetic parameters and the equation in terms of coded factors was shown as follows:

$$Y= -4094.30261 + 47.26926A + 117.33761B + 99.80523C + 0.67063AB - 0.53225AC - 1.02625BC - 1.67824A^2 - 3.17761B^2 - 0.61122C^2. \quad (1)$$

Where Y is the conversion ratio of oleic acid (%), A is the weight ratio of the catalyst to FFA (wt.%), B is the molar ratio of methanol to acid, and C is the reaction temperature (°C). There is a positive and negative sign in front of terms that reveals synergistic effect and antagonistic effect respectively.

To justify the adequacy of the used model, ANOVA was carried out. From the ANOVA for response surface quadratic model (Table 4), the Model p-value of 0.0001 showed that the model was significant. According to the results, the catalyst loading and methanol:oil molar ratio are known as the most effective variables, and the interactive of catalyst loading and the reaction temperature is the most significant interaction factor. The interactive effect of methanol:oil molar ratio and the reaction temperature are significant to some extent. Moreover, the ''Predicted R-squared'' value of 0.8687 is in reasonable agreement with the ''Adjusted R-squared'' value of 0.9536.

Table 4. *ANOVA for the experimental results of the Response Surface Design.*

Source	Sum of squares	DF	Mean square	p-value
Model	13495.50	9	1499.50	< 0.0001
A-Methanol:oil	1871.86	1	1871.86	< 0.0001
B-Catalyst amount	2000.33	1	2000.33	< 0.0001
C-Temperature	193.91	1	193.91	0.0376
AB	57.57	1	57.57	0.2211
AC	226.63	1	226.63	0.0270
BC	842.55	1	842.55	0.0005
A^2	1133.03	1	1133.03	0.0002
B^2	4061.97	1	4061.97	< 0.0001
C^2	5870.66	1	5870.66	< 0.0001
Lack of Fit	199.78	5	39.96	0.3477
R^2=0.9756	Adj R^2=0.9536		Pre R^2=0.8687	

The interactions between the test variables can be presented by three-dimensional surface plots as the response is plotted against two of the variables and keeping the remaining variables at constant levels or by two-dimensional plots as the response is plotted against one of the variables in two levels of the second variable and constant value of the remaining variables.

Figure 3 shows the experimental values versus predicted values using the model equation developed. According to Figure 3, the regression model equation provided a very accurate description of the experimental data, demonstrated that it was successful in obtaining the correlation between the three test variables to the yield of biodiesel.

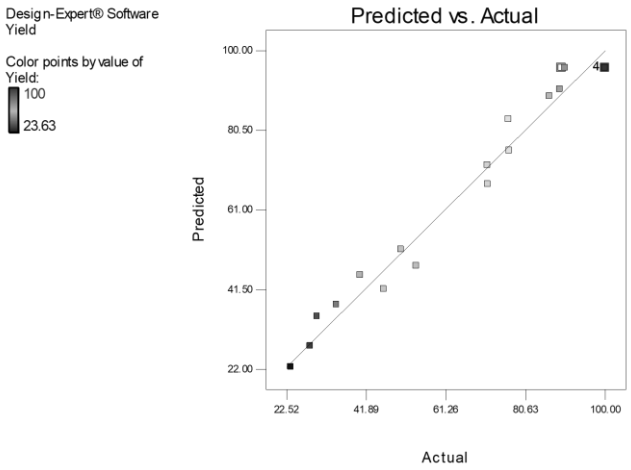

Figure 3. *Predicted versus experimental yield of methyl oleate by PW/Fe_3O_4/GO.*

The process variables were found to have significant interaction effects. Figures 4, 5, and 6 show the interaction between methanol:oil molar ratio and catalyst amount (AB), methanol:oil molar ratio and reaction temperature (AC) and catalyst amount and reaction temperature (BC), respectively on the yield of FAME.

Figure 4 shows the changes in yield as a function of methanol:oil ratio at the low and high amount of the catalyst. In this case, the temperature was kept constant at 75 °C. The low amount of the catalyst showed the lower yield of biodiesel compared to that of the high amount (Figure 4). Increasing methanol:oil molar ratio leads to the decline of the conversion of oleic acid at the higher and lower level of the catalyst amount. On the other hand, the interactive effect of the amount of the catalyst and methanol:oil molar ratio (AB) was not significant (p-value = 0.2211, Table 4).

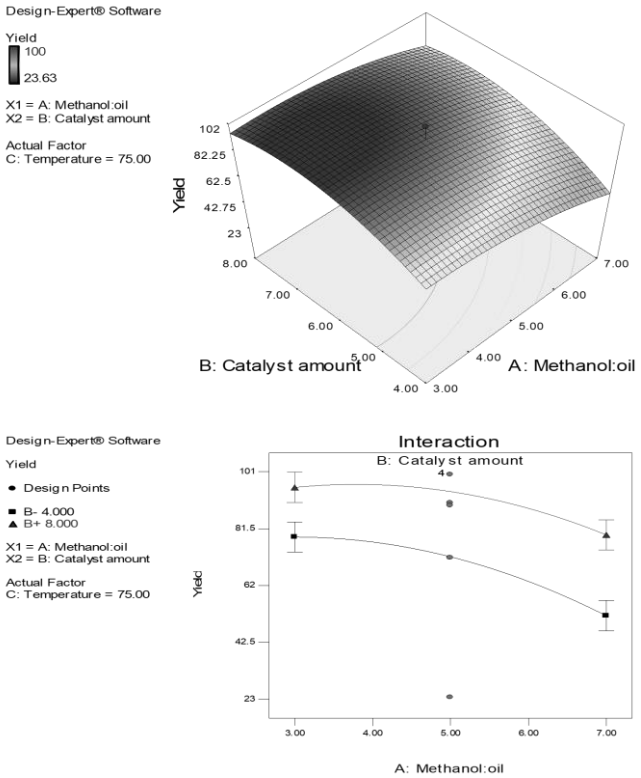

Figure 4. *Effect of reaction methanol:oil ratio and amount of the catalyst on biodiesel production by PW/Fe_3O_4/GO at 2 h: (up) response surface plot and (down) two intraction effect. (C is at middle level).*

The relationship between methanol:oil molar ratio and reaction temperature is shown in Figure 5. Amount of the catalyst was kept constant at 6 wt.%. A moderate interaction was found between methanol:oil molar ratio and reaction temperature. Referring to Figure 5, in high temperature with increasing of methanol:oil molar ratio, the yield of biodiesel was decreased while in low temperature the yield of biodiesel with increasing of the methanol:oil molar ratio was remained almost constant.

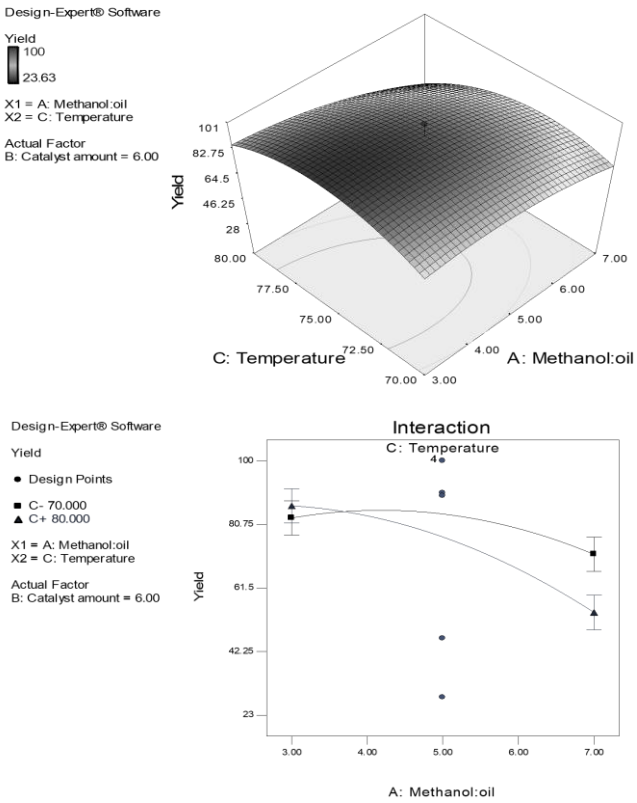

Figure 5. *Effect of reaction methanol:oil ratio and temperature on biodiesel production by PW/Fe_3O_4/GO at 2 h: (up) response surface plot and (down) two intraction effect. (B is at middle level).*

As shown in Figure 6, which depicted the effects of the amount of the catalyst and reaction temperature, oleic acid conversion increased with the increasing of catalyst loading. The figure also indicated that in low temperature with increasing of the catalyst amount, the yield of biodiesel was significantly increased while in high temperature the yield of biodiesel with increasing of the catalyst amount has remained constant. This indicated that the interactive effect between catalyst amount and temperature was significant (p-value = 0.0005, Table 4).

The optimal values of the selected factors were obtained by solving the regression equation (equation (1)) using Design-Expert software. The optimal conditions for biodiesel production in model reaction in the presence of PW/Fe_3O_4/GO are as follows: methanol-to-oil molar ratio 3.90:1, catalyst amount 5.97 wt.%, and reaction temperature 74 °C. The theoretical conversion to biodiesel predicted under the above conditions was 99.27%. The optimal conditions in the given solution could be tested for further validation. To confirm the prediction by the model, the optimal reaction conditions were applied to three independent replicates for biodiesel production using PW/Fe_3O_4/GO as a solid catalyst. The

average conversion yield reached 96.84 % and was close to the predicted value. The actual and predicted values are very close to each other and this indicates the eligibility of the selected model suggested by the software.

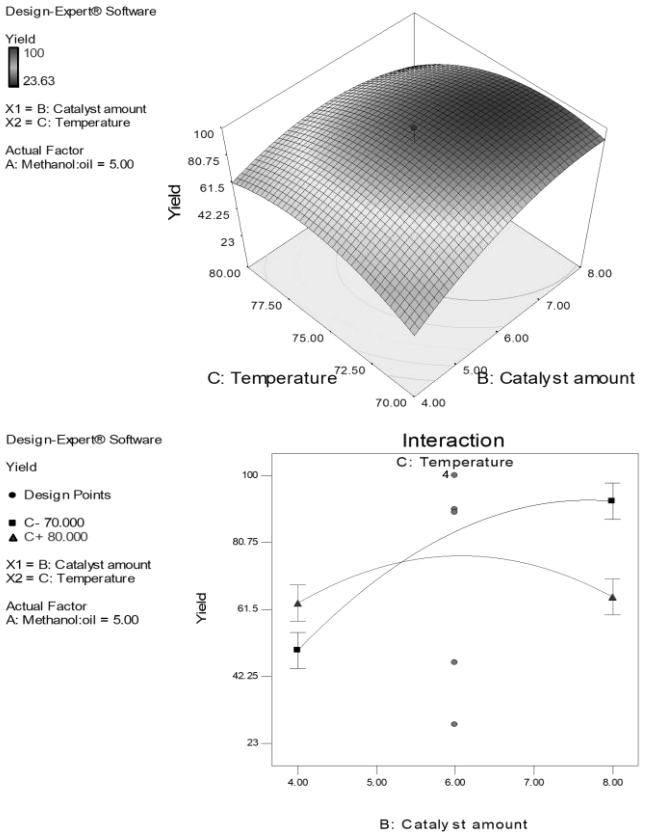

Figure 6. *Effect of reaction catalyst amount and temperature on biodiesel production by PW/Fe_3O_4/GO at 2 h: (up) response surface plot and (down) two intraction effect. (A is at middle level).*

The performance of different catalysts was investigated according to random reaction conditions before the optimization of reaction conditions (Table 3). Now, esterification of oleic acid with methanol using PW-based catalysts in optimized conditions was studied and shown in Table 5. As can be seen, PW/Fe_3O_4/GO shows the highest oil conversion obtained than other catalysts in optimized conditions too. Mechanism of the reaction in the presence of such kind of catalysts was reviewed in literature.[40,41]

Table 5. *Esterification of oleic acid with MeOH using PW-based catalysts in optimized reaction conditions.*

Entry	Catalyst (g)	Conversion (%)[a]
1	PW/Fe_3O_4/GO	96.84
2	PW/Fe_3O_4@C	90.10
3	PW@MIL-100(Fe)	86.34
4	PW/SMNs	54.04
5	PW/Ni/SiO_2	45.09
6	PW@HKUST-1	71.12
7	PW/Fe_2O_3@SiO_2	34.63

As an application of the above results, biodiesel production from castor oil with methanol over PW/Fe_3O_4/GO catalyst under optimized reaction conditions was carried out. The raw castor oil studied presented almost 82% of ricinoleic acid, linoleic acid was the second most abundant acid (around 10.4%), followed by the oleic acid (around 5.8%). Finally, around 2% of palmitic acid and stearic acid. The obtained results are agreed with the expected composition according to the literature.[42, 43] The yields of FAME for castor oil, were about 90.2%. There was no triglycerides existence. The data of GC-MS in Table 6 indicated methyl ester content.

Table 6. *Caster oil methyl ester composition.*

Retention time (min)	Substance	Peak area %
17.91	palmitic acid methyl ester	1.8
19.60	stearic acid methyl ester	1.1
19.71	oleic acid methyl ester	5.6
19.94	linoleic acid methyl ester	7.4
21.65	ricinoleic acid methyl ester	74.3

Conclusion

Hybrid PW-based nanomaterials were compared in the biodiesel production process of oleic acid and the catalyst containing PW, Fe_3O_4, and graphene oxide was the best one in this process. The morphology of the nanocatalyst was investigated using the TEM technique. The optimization of the esterification reaction using the CCD model has been explored by PW/Fe_3O_4/GO. Catalyst amount and the molar ratio of alcohol were variable with the largest effect and the interactive effect of catalyst amount and reaction temperature was more significant. The best conversion of oleic acid (99.27%) was obtained with R^2 = 0.9756 at the optimum operational conditions with 5.97 wt.% of the catalyst loading and 3.90:1 of methanol to oleic acid molar ratio at 74.0 °C. The present catalyst used in the single-step process for biodiesel production from castor oil with methanol under optimized reaction conditions and showed 90.2% FAME production.

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References

1. C.Z. Liu, F. Wang, A.R. Stiles, and C. Guo, *Appl. Energy*, 92, **2012**, 406.
2. M.K. Lam, K.T. Lee, and A.R. Mohamed, *Biotechnol. Adv*., 28, **2010**, 500.
3. W. Liu, P. Yin, X. Liu, and R. Qu, *Bioresource Technol*., 173, **2014**, 266.
4. H. Wan, C. Chen, Z. Wu, Y. Que, Y. Feng, W. Wang, L. Wang, G. Guan, and X. Liu, *Chem. Cat. Chem*., 7, **2015**, 441.
5. F. Ma, and M.A. Hanna, *Bioresource Technol*., 70, **1999**, 1.
6. R. Canioni, C. Roch-Marchal, F. Sécheresse, P. Horcajada, C. Serre, M. Hardi-Dan, G. Férey, J.M. Grenèche, F. Lefebvre, J.S. Chang, Y.K. Hwang, O. Lebedev, S. Turner, and G.V. Tendeloo, *J. Mater. Chem*., 21, **2011**, 1226.
7. F. Cao, Y. Chen, F. Zhai, J. Li, J. Wang, X. Wang, S. Wang, and W. Zhu, *Biotechnol. Bioeng.*, 101, **2008**, 93.
8. L. Xu, W. Li, J. Hu, K. Li, X. Yang, F. Ma, Y. Guo, X. Yu, and Y. Guo, *J. Mater. Chem.*, 19, **2009**, 8571.
9. L. Xu, Y. Wang, X. Yang, J. Hu, W. Li, and Y. Guo, *Green Chem.*, 11, **2009**, 314.
10. K. Srilatha, C.R. Kumar, B.L.A.P. Devi, R.B.N. Prasad, P.S. Sai Prasad, and N. Lingaiah, *Catal. Sci. Technol*., 1, **2011**, 662.
11. K. Srilatha, T. Issariyakul, N. Lingaiah, P.S. Sai Prasad, J. Kozinski, and A. K. Dalai, *Energy Fuels.*, 24, **2010**, 4748.
12. V.V. Bokade and G.D. Yadav, *Ind. Eng. Chem. Res.*, 48, **2009**, 9408.

13. A. Alsalme and E.F. Kozhevnikova, I.V. Kozhevnikov, *Appl. Catal.*, 349, **2008**, 170.
14. V. Brahmkhatri and A. Patel, *Ind. Eng. Chem. Res*., 50, **2011**, 6620.
15. M. Zabeti, W.M.A.D.M. Daud, and K. Aroua, *Fuel Process Technol*., 90, **2009**, 770.
16. S. Shanmugam, B. Viswanathan, and T.K. Varadarajan, *J. Mol. Catal. A: Chem*., 223, **2004**, 143.
17. Y. Liu, E. Lotero, and J.G. Goodwin, *J. Mol. Catal. A: Chem*.,242, **2006**, 278.
18. Z. Helwani, M.R. Othman, N. Aziz, W.J.N. Fernando, and J. Kim, *Fuel Process Technol*., 90, **2009**, 1502.
19. I.V. Kozhevnikov, *J. Mol. Catal. A: Chem*., 262, **2007**, 86.
20. M.N. Timofeeva, *Appl. Catal. A: Gen*., 256, **2003**, 19.
21. M. Balaraju, P. Nikhitha, K. Jagadeeswaraiah, K. Srilatha, P.S. Sai Prasad, and N. Lingaiah, *Fuel Process Technol*., 91, **2010**, 249.
22. C.F. Oliveira, L.M. Dezaneti, F.A.C. Garcia, J.L. de Macedo, J.A. Dias, S.C.L. Dias, and K.S.P. Alvim, *Appl. Catal. A: Gen*., 372, **2010**, 153.
23. K.Y. Nandiwale, P.S. Niphadkar, S.S. Deshpande, and V.V. Bokade, *Ind. Eng. Chem. Res*., 89, **2014**, 1507.
24. J. Alcañiz-Monge, G. Trautwein, and J.P. Marco-lozar, *Appl. Catal. A: Gen.*, 468, **2013**, 432.
25. A. Patel and N. Narkhede, *Energy Fuel*., 26, **2012**, 6025.
26. N. Narkhede and A.Patel, *Ind. Eng. Chem. Res*., 52, **2013**, 13637.
27. A.I. Tropecelo, M.H. Casimiro, I.M. Fonseca, A.M. Ramos, J. Vital, and J.E. Castanheiro, *Appl. Catal. A: Gen*., 390, **2010**, 183.
28. V. Brahmkhatri and A. Patel. *Appl. Catal. A: Gen*., 403, **2011**, 161.
29. S.Singh and A. Patel, *J. Clean Prod*., 72, **2014**, 46.
30. A. Patel and V. Brahmkhatri, *Fuel Process Technol.*, 113, **2013**, 141.
31. E. Rafiee and F. Mirnezami, *J. Mol. Struct*., 1130, **2017**, 296.
32. E. Rafiee and S. Eavani, *J. Mol. Liq*., 199, **2014**, 96.
33. E. Rafiee and N. Nobakht, *J. Mol. Catal. A: Chem*., 398, **2015**, 17.
34. E. Rafiee, N. Nobakht, and L. Behbood, *Res. Chem. Intermed*., 43, **2017**, 951.
35. E. Rafiee and M. Khodayari, *J. Mol. Catal. A: Chem*., 398, **2015**, 336.
36. E. Rafiee and M. Khodayari, *Res. Chem. Intermed*., 42, **2016**, 3523.
37. E. Rafiee and M. Khodayari, *RSC Adv*., 6, **2016**, 36433.
38. E. Rafiee, S. Eavani, and M. Khodayari, *Chin. J. Catal*., 34, **2013**, 1513.
39. S.M. Sadeghzadeh, *Res. Chem. Intermed*., 42, **2016**, 2317.
40. Shams, A. *Eng. J.*, 10, **2019**, 821.
41. H. Zhang, H. Li, Y. Hu, K.T. Venkateswara Rao, C.C. Xu, and S. Yang, *Renew. Sust. Energy Rev*., 114, **2019**, Article No. 109296.
42. J.M. Dias, J.M. Araújo, J.F. Costa, M.C.M. Alvim-Ferraz, and M.F. Almeida, *Energy*, 53, **2013**, 58.
43. A.K. Yusuf, P.A.P. Mamza, A.S. Ahmed, and U. Agunwa, *Int. J. Sci. Technol*., 4, **2015**, 1392.