CHEMICAL ENGINEERING TRANSACTIONS

VOL. 78, 2020

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš

ISBN 978-88-95608-76-1; **ISSN** 2283-9216

DOI: 10.3303/CET2078067

Optimization of Operating Conditions of Bio-Hydrogenated Diesel Production from Fatty Acid

Bulin Boonrod[a], Chutithep Rochpuang[a], Thitiwut Paisan[a], Chaiwat Prapainainar[b], Anusorn Seubsai[a], Nichakul Hongloi[a], Paweena Prapainainar[a,*]

[a]National Center of Excellence for Petroleum, Petrochemicals and Advance Materials, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University and Research Network of NANOTEC-KU on Nanocatalyst and Nanomaterials for Sustainable Energy and Environment, Bangkok 10900, Thailand.
[b]Department of Chemical Engineering, Faculty Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand.
fengpwn@ku.ac.th

Bio-hydrogenated diesel (BHD) is an interesting sustainable energy because of high heating value and environmentally friendly. This paper investigated parameters which affected to BHD production by catalytic deoxygenation reaction of fatty acid using nickel on silica catalyst. Three batches were firstly screened to find three parameters for optimization. The parameters consisted of type of solvent, oleic acid and palmitic acid, and the use of solvent. After that, Box-Behnken Design (BBD) in Design Expert program was used to optimize three operating conditions which were temperature, the amount of catalyst, and the amount of solvent using the selected reactant from screening experiment. The result of screening process showed that the conversions of fatty acid to fuel were almost 100 %. Therefore, the reaction temperature and the amount of catalyst were decreased to save the operating cost. Palmitic acid was selected as a reactant in optimization. In optimization, quadratic model was selected due to high r-square (0.9587) and p-value lower than 0.05. The model showed that the addition of solvent and high temperature reaction led to high selectivity of the desired product. The optimum operating condition was 53 mL of solvent, 1.4 g of catalyst, and 260 °C reaction temperature with selectivity of 61.06 %. It was also found that solvent had the highest effect to the selectivity of the desired product compared to the amount of catalyst and reaction temperature.

1. Introduction

Due to an increasing of petroleum fuels demand for transportation, there has been a rapid depletion in world's petroleum reserves along with an increasing of environmental concerns. Fossil fuels are not sustainable energy and their uses are not satisfactory from the economic, ecology, and environmental point of views. Presently, biomass is a major renewable energy source which produces fuels to meet the future energy (Pattanaik and Rahul, 2017). Biodiesel derived from fatty acid is one of alternate fuels which can be used instead of diesel. Less cold flow properties than diesel makes biodiesel usually be used as a mixture with diesel (Hossain et al., 2018). Bio-hydrogenated diesel (BHD) or greed diesel is a second generation of diesel that has total compatibility with diesel, high heating value, excellent storage stability, and very low combustion emissions (Orozco et al., 2017). Palm, which is economic plant in Thailand, normally is used to produce biodiesel. Thailand is one of large producers of palm oil in the world. Palm is easily grown in Southeast Asian (Boonrod et al., 2017). Crude palm oil has a ratio of unsaturated and saturated fatty acids. It contains oleic acid, linoleic acid, palmitic acid, and stearic acid. Palm fatty acid distillate (PFAD) is a co-product of palm oil refining which contains mainly palmitic acid and oleic acid. Production of BHD from these co-products are value-added to these materials. Hancsók et al. (2018) studied catalytic hydrodeoxygenation of fatty acid using waste fatty acid as reactant to produce paraffin at higher temperature than 300 ºC and 40 barg. Hossain et al. (2018) studied effect of solvent ratio in deoxygenation of fatty acid reaction at higher temperature than 300 ºC and pressure below 35 barg. They reported that increasing of solvent increased the production of paraffin. Pattanaik and Misra (2017) reviewed and reported parameter which effected to paraffin production which

Paper Received: 02/05/2019; Revised: 11/09/2019; Accepted: 29/10/2019
Please cite this article as: Boonrod B., Rochpuang C., Paisan T., Prapainainar C., Seubsai A., Hongloi N., Prapainainar P., 2020, Optimization of Operating Conditions of Bio-Hydrogenated Diesel Production from Fatty Acid, Chemical Engineering Transactions, 78, 397-402 DOI:10.3303/CET2078067

consisted of type of reactant, exist of solvent, temperature, amount of catalyst and etc. They performed experiment at high temperature and pressure and also no one had systematically design the experiment with statistical analysis. Response surface methodology (RSM), one of method in design experiment (DOE), was used to evaluate the influence of operating factors on the response in this research. Box-behnken design (BBD) was a design in RSM which was used to generate less experiment than central composite design. It was also more suitable to predict a data in this study range. In this field, there are few researches using DOE to investigate the effects of operating parameters to the conversion and selectivity of the design products. This work focused on BHD production using palmitic acid and oleic acid which are contained in PFAD in the present of solvent and free solvent systems. After that, optimization of operating conditions consisted of the amount of catalyst, reaction temperature, and the amount of solvent were optimized at a low temperature (lower than 300 ºC) and low pressure (10 barg).

2. Methods

2.1 Material and experimental set-up

Palmitic acid (98 %) was obtained from Sigma-Aldrich while oleic acid (88 %) was obtained from PanReac AppliChem. Dodecane (99 %) was purchased from Sigma-Aldrich. Commercial catalyst (Pricat Ni22/8D) was supplied by UAC Global Public Company Limited.

2.2 Liquid product analysis by GC-FID

After the experiment, liquid product was cooled down and it turned into wax. Wax was dissolved by adding of dichloromethane to separate hydrocarbon product and catalyst. Separated hydrocarbon product was brought into oven to evaporate dichloromethane. Then 0.08 g of hydrocarbon product was dissolved by 10 mL of hexane for analysis. The sample was brought to gas chromatography (Agilent-7890A) with flame ionization detector (FID) and a capillary column (ZB-1HT with dimension of 30 m * 0.32 mm * 0.1 micron). Finally, 1 µL of sample was injected to GC and 0.01 g of eicosane was used as standard for internal standard analysis. The amount of product was determined using relative between the product and eicosane.

2.3 Optimization of BHD production using Response Surface Method (RSM)

In screening experiment, the catalytic deoxygenation of fatty acid was taken in 300 mL high pressure stirred autoclave (Parr 5500). There were three experiments. First batch consisted of 96.31 g of palmitic acid without solvent. Second batch consisted of 106.10 g of oleic acid without solvent. Third batch consisted of 64.20 g of palmitic acid with 37.68 mL of dodecane as a solvent. Catalyst to reactant at a mass ratio of 1:37 was used. Reaction time was 6 h with the total pressure controlled at 10 bar. Sampling of liquid product was collected every 3 h (0 h, 3 h, and 6 h). BBD was used to optimize BHD production by using the Design Expert software (Stat-Ease Inc., Minneapolis, USA) in the optimization. Reaction parameters including ratio of solvent to reactant, amount of catalyst, and reaction temperature were varied to maximize the amount of pentadecane products. The influence of each independent variable and relations between these variables on the BHD production was discussed. Quadratic model was used to analyze the experimental data by using response surface regression. The amount of palmitic acid used was 51.15 g. The reaction time was 6 h. The total pressure was 10 bar with hydrogen feed. By using BBD, fourteen operating conditions were generated which are shown in Table 1. The levels of the independent variables were chosen based on the coded values of 0, +1 and -1.

Table 1: Variable values of factors

Box-Behnken values	A:Solvent (mL)	B:Catalyst (g)	C:Temperature (°C)
-1	0	0.35	230
0	26.5	0.7	245
1	53	1.4	260

2.4 Characterization of catalyst

Field emission scanning electron microscopes (FE-SEM) and energy dispersive X-ray spectrometer (EDX) were used for characterization of catalyst. Catalysts were brought to characterize by FE-SEM (JSM-760F). SEM was used to investigate the surface of catalyst. EDS was used to identify elemental distribution. Powder X-ray diffraction (XRD) pattern of commercial catalyst was recorded on diffractometer with a scanning rate of 0.02°, scan speed of 4° min^{-1}, and a scan range of 10-80° at 40 kV and 20 mA.

3. Results and discussion

3.1 Characterization of catalyst

Figure 1 shows characters of the commercial catalyst. SEM images and percent atomic element of the catalyst showed that the catalyst used was nickel supported on silica (Ni/SiO_2). The pore structure was irregular and non-uniform surface. The crystalline phase of the catalyst was analyzed and identified by XRD. The 2-theta of the peaks 43.496°, 51.492°, and 78.5° representing the metallic Ni. The 2-theta of the peak at 22° showed the strong and sharp peak of crystalline silica (Varkolu et al., 2015).

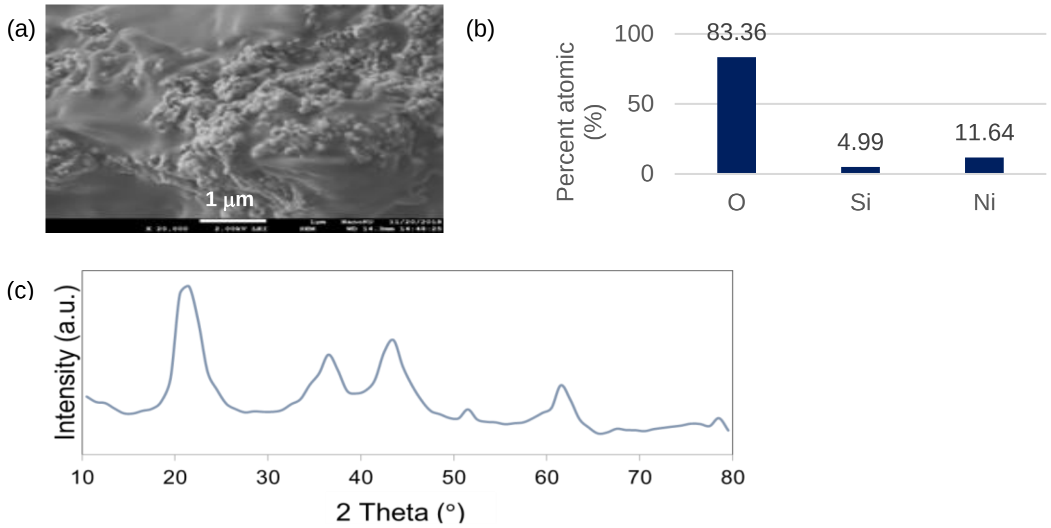

Figure 1: Result from (a) SEM image (b) SEM-EDS elemental analysis (c) XRD patterns of the catalyst.

3.2 Liquid product from investigated parameter

Percent conversions of palmitic acid from screening experiment are shown in Table 2. The conversion of palmitic acid (batch 1 and batch 3) was closed to 100 % from the beginning of the reaction. Deoxygenation of oleic acid (batch 2) was completely from 3 h.

Table 2: Conversions of batch at sampling time 0 h, 3 h, and 6 h.

Time (h)	Conversion (%)		
	Batch 1	Batch 2	Batch 3
0	97.22	21.99	98.56
3	98.04	100.00	99.12
6	98.49	100.00	99.63

Table 3 shows the selectivity of palmitic acid and oleic acid on pentadecane products. It showed that the presence of solvent improved mass transfer between reactant and product so the solvent increased the selectivity of paraffin (Hermida et al., 2015). Hermida et al. (2015) reported that organic solvent can increase diffusivity between reactant and catalyst. Comparison between palmitic acid and oleic acid, it was showed that oleic acid was completely converted to stearic acid by hydrogenation, whereas palmitic acid was converted to pentadecane directly. From previous result, it was found that solvent had significant effect to selectivity of paraffin, pentadecane. Therefore, the amount of solvent was selected as one of parameters for DOE. DOE was used in the next step by using palmitic acid and varying solvent, temperature, and the amount of catalyst. Oleic acid was not used because there were many unknown products at the end of the reaction.

Table 3: Selectivity of fatty acids at 6 h sampling time.

Batch	Pentadecane (%)	Hexadecanol (%)	Hentriacontanone (%)	Heptadecane (%)	Stearic acid (%)
1	12.03	0.43	87.54	-	-
2	-	-	-	92.21	7.79
3	53.08	0.30	46.62	-	-

3.3 Mechanism of the reaction

The reaction pathway of palmitic is shown in Figure 2a. The reaction involved four pathways which consisted of ketonization, decarboxylation, decarbonylation, and deoxygenation of palmitic acid. Ketonization was the main route in palmitic acid (batch 1). It coupled two fatty acids by forming carbon-carbon bonds (Romero et al., 2018). Decarboxylation and decarbonylation were two main routes to produce palmitic acid using dodecane as a solvent (batch 3). Deoxygenation of palmitic acid decomposed to hexadecanol. The results showed that the presence of solvent led to decarboxylation and decarbonylation rather than ketonization. The presence of solvent improved the mass transfer between reactant and product whereas pure reactant could not completely transform to the design liquid product at these operating conditions (Hermida et al., 2015). The reaction pathway of oleic is shown in Figure 2b. The pathway was hydrogenation of oleic acid to stearic acid. After that, stearic acid decomposed to hexadecane by decarboxylation and decarbonylation. The reaction pathway might not be completed because oleic acid can decompose to other substances beside paraffin which were not shown here.

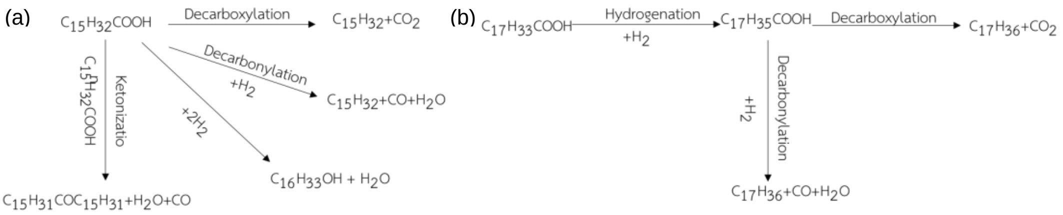

Figure 2: Scheme diagram of reaction pathways of deoxygenation of (a) palmitic acid (b) oleic acid.

3.4 Liquid product from design experiment

Table 4 shows liquid product at the end of reactions. The effect of three factors to desired product was shown. The selectivity of pentadecane was used as response for BBD. The conversions of all experiments were still almost 100 % (not shown here).

Table 4: Selectivity of palmitic acid using BBD

Run	Factor 1 A: Solvent (mL)	Factor 2 B: Catalyst (g)	Factor 3 C: Temperature (°C)	Selectivity (%) Pentadecane (%)	Hexadecanol (%)	16-hentriacontanone (%)
1	0	1.4	245	18.06	0.55	81.39
2	0	0.7	260	14.22	0.78	85.00
3	0	0.35	245	27.53	2.13	70.34
4	0	0.7	230	22.67	1.84	75.48
5	26.5	0.35	260	34.36	1.73	63.91
6	26.5	1.4	260	33.20	1.39	65.41
7	26.5	0.35	230	29.45	1.71	68.83
8	26.5	0.7	245	31.97	1.51	66.52
9	26.5	1.4	230	32.59	3.69	63.72
10	26.5	0.7	245	28.74	1.31	69.96
11	53	0.35	245	50.16	0.84	48.99
12	53	1.4	245	53.41	1.51	45.08
13	53	0.7	260	61.06	1.42	37.52
14	53	0.7	230	56.41	2.03	41.56

3.5 Response surface methodology

Quadratic model was selected due to its highest r-squared (0.9587). The suitable r-squared should be at least 0.8 in acceptable range (Saimon et al., 2019). It had high adjusted r-squared (0.8658) and low p-value (0.019). The acceptable p-value should be lower than 0.05. The quadratic equation in actual factors is given in Eq(1).

$$Y = 510.0008 - 1.9955A - 11.2431B - 3.8166C + 0.1527AB + 8.2946e\text{-}003AC - 0.0823BC + 9.3621e\text{-}003A^2 + 2.2067B^2 + 7.5002e\text{-}003C^2 \quad (1)$$

Figure 3a shows predicted data versus actual data. This indicated that the model was close to experimental data. Therefore, the data was suitable in the range of this study. From Figure 3b, the most standard residuals lied in the interval of ±5.00. The model was acceptable for the prediction.

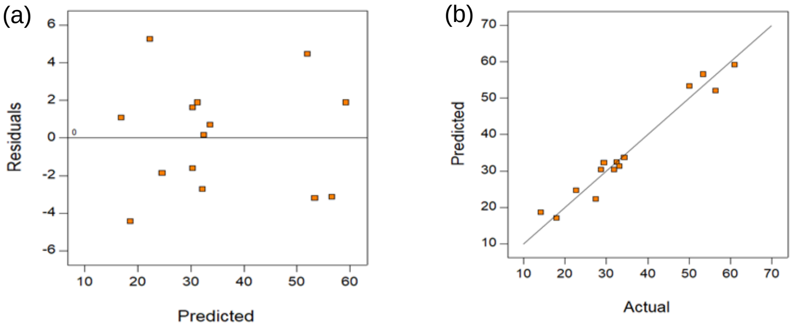

Figure 3: Graph of (a) predicted vs. actual data of quadratic model, (b) residual vs. predicted data.

The response surface was used to demonstrate the interaction between parameters and their effects on the selectivity of pentadecane. This study investigated three variables so the plots were formed with two parameters while the other factor was constant at zero value in codes. For the interaction of the amount of solvent (A) and the amount of catalyst (B) on pentadecane selectivity (Figure 4a), increasing the amount of solvent caused the favored pentadecane selectivity due to the enhancement of mass transfer of both reactants and catalyst for decarboxylation and decarbonylation reactions. Selectivity was slightly increased in solvent system. The selectivity of pentadecane slightly increased when decreasing the amount of catalyst in solvent free system. For the interaction of amount of solvent (A) and temperature (C) (Figure 4b), increasing in the amount of solvent increased the selectivity of pentadecane. It was found in Figure 4c that the interaction of temperature and amount catalyst was was nearly flat. It meant that this interaction was insignificant. The result indicated that solvent had the highest significant among all factors. From BBD, it was found that the optimum condition was 53 mL solvent, 1.4 g catalyst, and 260 °C reaction temperature. This led to the selectivity of pentadecane of 61.06 %.

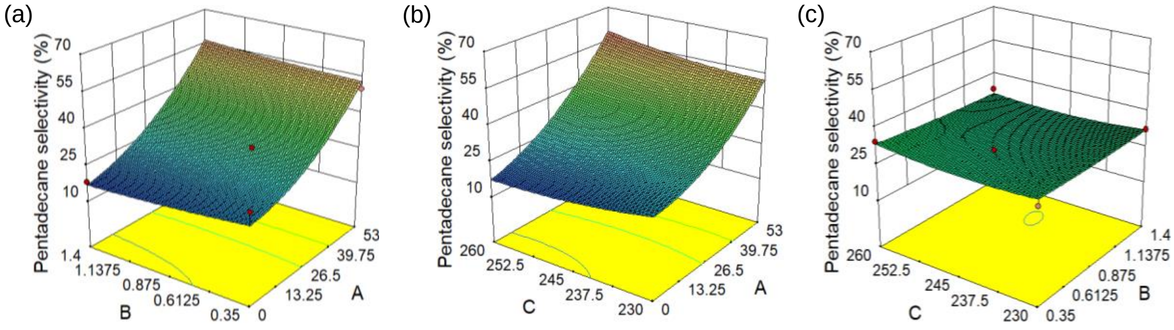

Figure 4: 3-D surface of interaction: (a) amount of catalyst (B) and amount of solvent (A), (b) reaction temperature (C) and amount of solvent (A), (c) amount of catalyst (B) and reaction temperature (C).

Comparing run 1 and run 12, run 2 and run 13, run 3 and run 11, run 4 and run 14, the reaction with solvent free system had less selectivity of pentadecane than that with the solvent system. This indicated that solvent affected to decarbonylation and decarboxylation reactions due to an improvement of mass transfer with the presence of solvent. The neighboring active site on the catalyst was couplinged to the reactant attached to the catalyst as shown in Figure 5.

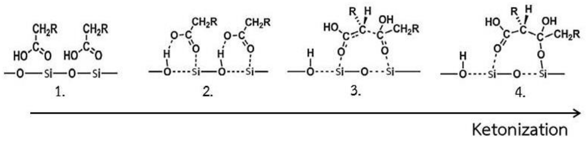

Figure 5: Step of neighbouring active site.

Then, the reactant reacted to the neighboring reactant via ketonization to create 16-hentriacontanone on the support surface. On the other hand, decarboxylation and decarbonylation consumed less active sites than ketonization did to produce pentadecane (Kordulis, 2016). In solvent free system, the reactant had low mass transfer to the active metal. Therefore, solvent improved the mass transfer between reactant and the active metal. Decarboxylation and decarbonylation subsequenly occurred.

4. Conclusion

In the production of BDH, hydrogenation was the main reaction for unsaturated fatty acid whereas saturated fatty acid converted to paraffin by deoxygenation. From BBD, the optimum operating conditions were at 53 mL solvent, 1.4 g catalyst, and 260 °C reaction temperature. Response surface data showed that the presence of solvent had the greatest effect among all studied factors and the interaction between the amount of catalyst and reaction temperature was insignificant. The optimum point was at the maximum boundary of experiment and the conversion was still almost 100 %. It was suggested that the reaction temperature and the amount of catalyst can be reduced and the amount of solvent can be increased to find the better operating condition.

Acknowledgments

This research is supported in part by the Graduate Program Scholarship from the Graduate School, Kasetsart University. Funding is also from Faculty of Engineering, Kasetsart University.

References

Boonrod B., Prpanainar C., Narataruksa P., Kantama A., Saibautrong W., Sudsakorn K., Mungcharoen T., Prapainainar P., 2017, Evaluating the environmental impacts of bio-hydrogenated diesel production from palm oil and fatty acid methyl ester through life cycle assessment, Journal of Cleaner Production, 142, 1210-1221.

Design Expert V10, 2016, Stat-Ease Inc., Minneapolis, USA.

Hancsók J., Visnyei O., Sági D., Holló A., 2018, Bio-paraffin mixture production from waste fatty acid mixture, Chemical Engineering Transactions, 65, 373-378.

Hermida L., Abdullah A.Z., Mohamad A.R., 2015, Deoxygenation of fatty acid to produce diesel-like hydrocarbons: A review of process conditions, reaction kinetics and mechanism. Renewable and Sustainable Energy Reviews, 42, 1223–1233.

Hossain Md. Z., Chowdhury M.B.I., Jhawar A.K., Xu, W.Z., Charpentier P.A., 2018, Continuous low pressure decarboxylation of fatty acids to fuel-range hydrocarbons with in situ hydrogen production. Fuel 212, 470–478. https://doi.org/10.1016/j.fuel.2017.09.092.

Kordulis C., Bourikas K., Gousi M., Kordouli E., Lycourghiotis A., 2016, Development of nickel based catalyst for the transformation of natural triglycerides and related compounds into green diesel: a critical review, Applied Catalysis B: environmental, 181, 156-196.

Orozco L.M., Echeverri D.A., Sánchez L., Rios L.A., 2017, Second-generation green diesel from castor oil: Development of a new and efficient continuous-production process, Chemical Engineering Journal, 322, 149-156.

Pattanaik B.P., Misra R.D., 2017, Effect of reaction pathway and operating parameters on the deoxygenation of vegetable oils to produce diesel range hydrocarbon fuels: A review, Renewable and Sustainable Energy Reviews, 73, 545–557.

Qiurong T., Zhang Z., Zhou F., Chen K., Fu J., Lu X., Ouyang P., 2017, Role of solvent in catalytic conversion of oleic acid to aviation biofuels, Energy Fuels, 31, 6163−6172.

Romero M., Pizzi A., Toscano G., Alessandro C., Busca G., Bosio B., Arato E., 2018, Deoxygenation of non-edible vegetable oil to produce hydrocarbons over Mg-Al mixed oxides, Chemical Engineering Transactions, 64, 121-126.

Saimon N.N., Isa S., Jusoh Y.M., Jusoh M., Ngadi N., Zakaria Z.Y., 2019, Optimization of esterification of palm fatty acid distillate to methyl ester using microwave-assisted titanium sulfonated incomplete carbonized Glucose (Ti-SO3H/ICG), Chemical Engineering Transactions, 72, 367-372.

Varkolu M., Velpula V., Ganji S., Burria D.R., Kamaraju S.R.R, 2015, Ni nanoparticles supported on mesoporous silica (2D, 3D) architectures: highly efficient catalysts for the hydrocyclization of biomass-derived levulinic acid, RSC Advances, 5, 57201-57210.