CHEMICAL ENGINEERING TRANSACTIONS

VOL. 81, 2020

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

Guest Editors: Petar S. Varbanov, Qiuwang Wang, Min Zeng, Panos Seferlis, Ting Ma, Jiří J. Klemeš

ISBN 978-88-95608-79-2; **ISSN** 2283-9216

DOI: 10.3303/CET2081176

Optimization of Biodiesel Production from Neem Oil using KOH Supported with Activated Carbon

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Fossil fuel reduction and environmental degradations are the two crises that the world threatened by generally and UAE specifically. Biodiesel is a fuel produced through a chemical reaction of animal fat or vegetable oil with alcohol, and consider a potential alternative of diesel engines. However, this reaction needs a catalyst to complete successfully. The current article contains transesterification of neem oil with KOH catalyst supported with activated carbon (KOH/AC). This study included experimental work by applying KOH/AC as an effective catalyst for transesterification of local neem oil. The response surface methodology (RSM) software tool was used in this study to determine the optimal conditions of reaction time, amount of catalyst and ratio of methanol to oil in order to obtain the highest percentage of biodiesel product. The optimal settings obtained were 60 min reaction time, a ratio of oil to methanol 1:6 and 1 wt% of catalyst, which lead to the highest yield of biodiesel (100 wt%). The specific features of biodiesel were checked and compared to ASTM standards.

1. Introduction

As fossil fuels expected to be depleted in the future, biomass-based biofuels (especially biodiesel) are gaining attention as novel sustainable petroleum substitutes (Costa et al., 2019). The derived biodiesel has more benefits than that of petroleum alternatives, in terms of biodegradability, nontoxicity, eco-friendliness, and usefulness in reutilization of CO_2 quickly (Chuah et al., 2016). Neem seeds are a very abundant type of biomass available in United Arab Emirate, and it contains a good amount of oil that can be extracted easily from it to use it in many applications like biodiesel production. It doesn't contribute to food consumption because it comes in non-edible oil category (Akhabue et al., 2020). There are three different processes for converting oils into biodiesel such as direct blending, catalytic cracking and transesterification. Effect of catalyst, time and temperature of the reaction and mole ratio are parameters that can affect biodiesel production (Sarno and Iuliano, 2020). Most often, the catalyst used for biodiesel production from biomass is KOH and NaOH (Inayat et al. 2019). It is a common perception that when KOH is concentrated between 2 – 12 %, the transformation will take about 8 h, and the biodiesel will increase from 20 to 95 % (Tiwari et al., 2018). Some advantages of using the activated carbon as a catalyst are the reutilization of catalytic material in the manufacturing procedure, which will make biodiesel production more reliable and decrease in soap formation. Due to its large surface spread (800 – 1,500 m^2/g), it has good adsorption properties such as resistant to radiation and heat, stable in alkaline and acidic environments and can be castoff again actively. The separation between biodiesel and glycerol will be easier, and the purity of the glycerol will increase by using this. Due to the surface properties and the surface oxides of the activated carbon, it has high catalyst activity. In addition, the production of the activated carbon cost is low (Konwar et al., 2018). This study includes both simulation and experimental work by applying KOH/AC to check the catalytic effect on the transesterification of local neem seed. The central idea of this study is to evaluate the influence of process parameters (time of reaction, amount of catalyst and molar ratio of

Paper Received: 30/04/2020; Revised: 06/06/2020; Accepted: 07/06/2020
Please cite this article as: Inayat A., Ghenai C., Hammad D., Almarzooqi S., Tariq R., Jamil F., Bokhari A., Ayoub M., 2020, Optimization of Biodiesel Production from Neem Oil using KOH Supported with Activated Carbon, Chemical Engineering Transactions, 81, 1051-1056 DOI:10.3303/CET2081176

methanol to oil) on the production profit of biodiesel and to analyze the best-fitted reaction conditions with the help of RSM tool to attain maximum possible yield. The features of methyl ester (biodiesel) produced from this procedure were investigated and examined with respect to Petro-diesel.

2. Material and methods

2.1 Raw material and catalyst preparation

Neem seeds were purchased from a local shop. Methanol with a purity of 99.5 % and Potassium Hydroxide (KOH) were purchased from a local company. The heterogeneous natured catalyst was KOH which was placed upon AC. It was produced according to the specific method. 110 °C temperature was used to dry AC to obtain a dry mass. Subsequently, the appropriate weight of the AC (of the captivative capacity of 1.06 g H_2O/g AC) was mixed to a saturated solution of water and KOH. The mixing of suspension was done at 30 °C with a magnetic stirrer at a speed of 160 rpm continuously for a day. After that, the drying of the catalyst was done at 60 °C in order to make the mass dry.

2.2 Experimental procedure

There were five main steps for the small scale of biodiesel production. The first step was preparing the solution of KOH using 250 g of KOH with 500 mL of deionized water in a medium beaker and stirred it using a magnetic stirrer for a few minutes until all KOH dissolved completely. The electric balance was used to measure the 250 g of the KOH. The second step was titration by taking 10 mL of isopropyl alcohol, 1mL of oil and 3 drops of phenolphthalein as an indicator by mixing them in a small plastic testing vial. Titration solution was prepared by 1 g of KOH with 50 mL of distilled water. In the third step, RSM data had been used, and some parameters and quantities were fixed during the whole 20 experiments which were: an amount of oil (100 mL) and 55 °C as reaction temperature. At the beginning of each experiment, the activated carbon was prepared by measuring how many grams of AC will be needed using an electronic balance and then the required amount of KOH solution will be added into it, all in one small beaker and let the mixture stirred at 180 rpm using the magnetic stirrer for 2 h. After 2 h the stirrer was turned off. The amount of methanol was prepared using a graduated cylinder, and the 100 mL of oil was prepared in a medium beaker. After that both of methanol and activated carbon poured into the oil and then placed on the magnetic stirrer with heat, a thermocouple was used to be able to set the reaction temperature to be around 55 °C while the stirrer was off. Once it reached 55 °C, the magnetic stirrer started to stir for the required reaction time. The last step was to turn off the heater and stirrer and pour the mixture into a separation funnel using glass funnel on the top of it. After that, the separation funnel was kept close and left for 1 day for the separation. The separation of biodiesel and glycerol was clear, and the glycerol with the remaining of the catalyst was extracted from the lowest side of the separation conduit, while the extraction of biodiesel was done from the top. These steps were the same for the 20 experiments.

2.3 Design of experiments

RSM stands for response surface methodology. This software can be utilized to evaluate the outcome of the parameters (reaction time, amount of catalyst and ratio of methanol to oil) on the optimal production of biodiesel. In addition, RSM help to know the optimum conditions that can be operated in terms to obtain maximum production of biodiesel. It provided 20 different runs with different operating conditions that were used to do the experimental work to find the maximum yield of biodiesel.

Table 1: Ranges of the parameters in RSM

Numeric factor: 3	Categoric factors: 2		
Name	Units	-1 Level	+1 Level
A: Reaction time	min	30	60
B: Amount of catalyst	wt%	0.5	1.5
C: Methanol to oil	Ratio	3	6

2.4 Biodiesel characterization

High kinematic viscosities (like in vegetable oils and animal fats) can cause many problems such as the deposition on an engine which can influence on the performance of the engine (Chuah et al., 2015). Cannon-Fenske Routine was used to measure the viscosity of the biodiesel. Digital Portable Density Meter DA-130N apparatus was used to measure the density of the biodiesel. Parr 6400 Calorimeter was used to measure the high heating value of diesel fuel. The ASTM and EN standards properties of biodiesel for edible and non-edible oil sources will help to know if the biodiesel's properties within these ranges or not in order to know whether the biodiesel will be accepted as an alternative fuel to be used in engines or not (Mahmudul et al., 2017).

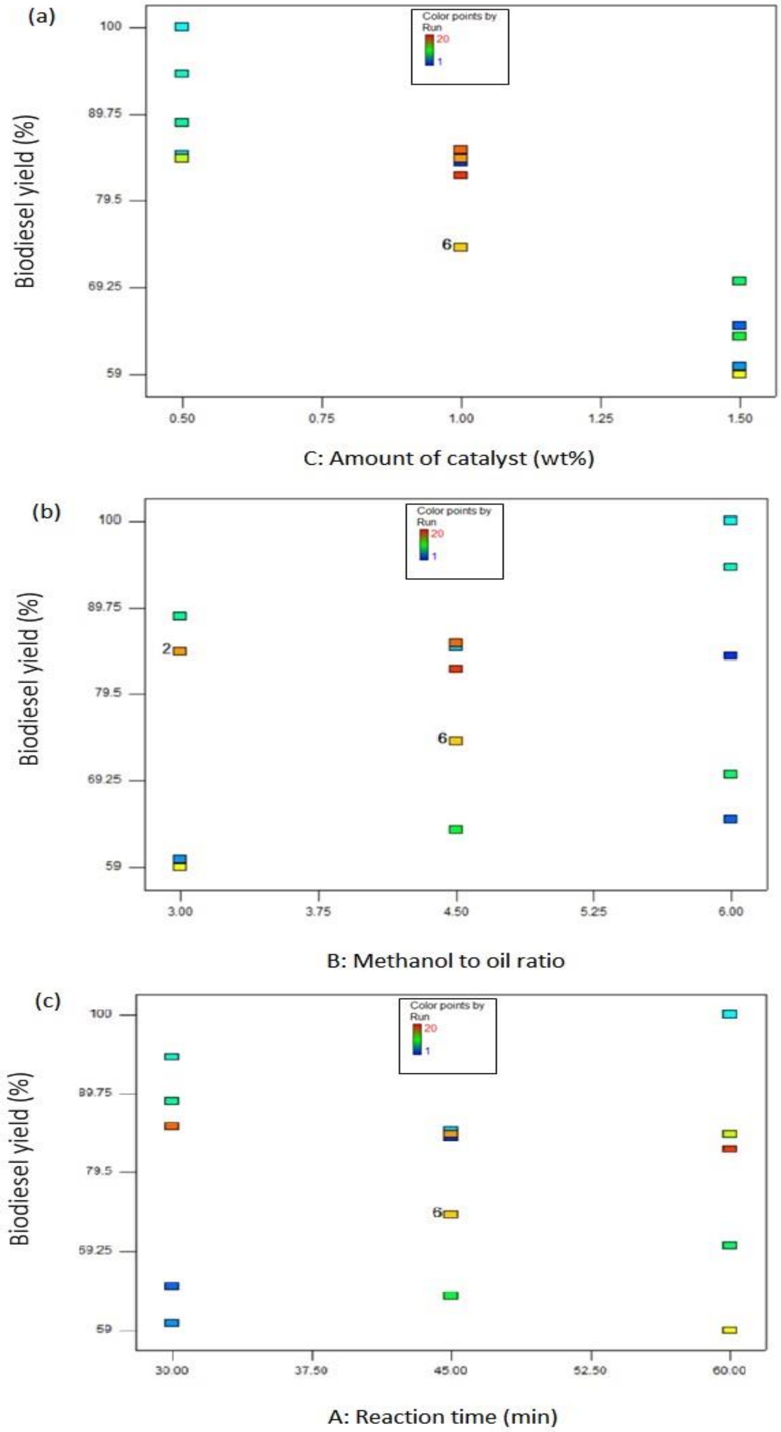

Figure 1: (a)- Impact of the amount of catalyst on the percentage of biodiesel, (b)- Impact of methanol to oil on the percentage of biodiesel, (c)- Impact of the reaction time on the percentage of biodiesel

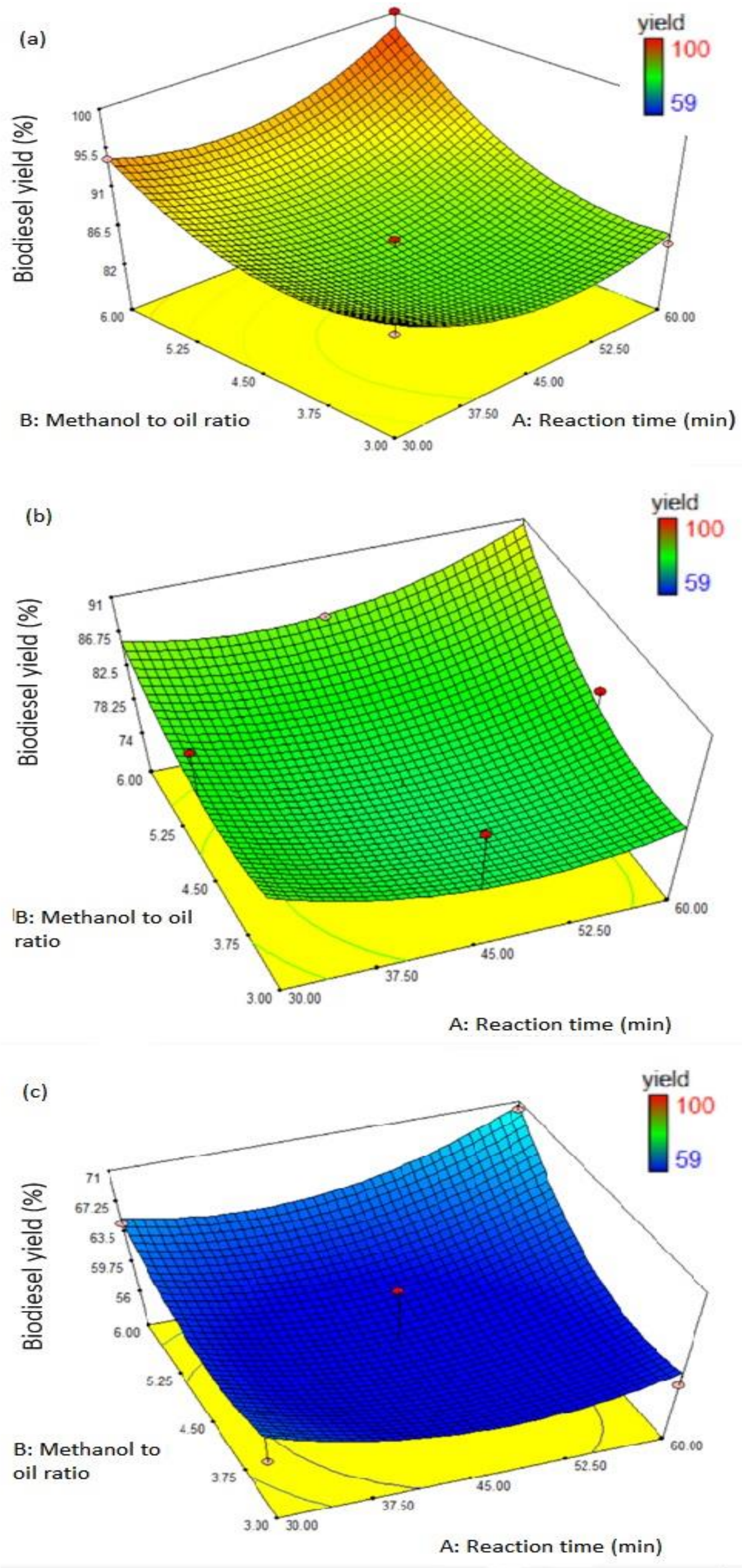

Figure 2: (a) 3D graph for yield vs reaction time and methanol to oil ratio at 0.5 wt% of catalyst from design expert, (b) 3D graph for 1 wt%, (c) for 1.5 wt% of catalyst from a design expert.

3. Results and discussion

Table 2 shows the RSM results for the small-scale biodiesel production. It can be seen that the maximum yield of biodiesel which is 100 % experiment 6 the optimum conditions were: 6 part methanol and one part oil, 1/2 wt% of catalyst and 60 min of reaction time.

Table 2: RSM data for the small scale of biodiesel production

Std	Amount of oil (mL)	Amount of Activated Carbon (g)	Amount of methanol (mL)	Amount of KOH solution (mL)	Methanol to oil ratio	Amount of catalyst (wt.%)	Time of reaction (min)	Biodiesel production (%)
1	100	0.35	22	5.25	4.50	1.00	45	74
2	100	0.35	29	5.25	6.00	1.00	45	84
3	100	0.52	29	7.8	6.00	1.50	30	64.8
4	100	0.52	14.6	7.8	3.00	1.50	30	60
5	100	0.17	22	2.6	4.50	0.50	45	85
6	100	0.17	29	2.6	6.00	0.50	60	100
7	100	0.17	29	2.6	6.00	0.50	30	94.5
8	100	0.17	14.6	2.6	3.00	0.50	30	88.7
9	100	0.52	29	7.8	6.00	1.50	60	70
10	100	0.52	22	7.8	4.50	1.50	45	63.5
11	100	0.35	22	5.25	4.50	1.00	45	74
12	100	0.35	22	5.25	4.50	1.00	45	74

3.1 Parametric study

Figure 1a explain the graph at lowest catalyst amount (0.5 wt%) which gave us higher yield than the runs where the amount of catalyst was relatively high (1 wt%) and also even higher than the middle experiments where the amount of catalyst was the highest (1.5 wt%). As shown in Figure 1b, 6:1 methanol to oil ratio gave us a maximum percentage of bio-diesel that than of ratio 4.5:1 or 3:1, because usually methanol keeps the reaction forwards and prevents it from going in a back way and also helps in increasing the amount of biodiesel extracted. Figure 1c illustrates the consequence of time of reaction to the production capacity of biodiesel. The yield was maximum (100 % of biodiesel) when 60 min was chosen other than 45 or 30 min because the more time the transesterification process will be, the more oil will be reacted with the methanol and catalyst to produce biodiesel until certain limits. Besides that, 60 min was enough for the effective separation of biodiesel from the glycerol.

It could be seen that in Figure 2a that the yield is getting closer to 100 % as methanol to oil and time of reaction increase if the catalyst amount was fixed. Using 0.5 wt% of catalyst will let the red area appears in the graph where we have a very high yield of biodiesel.

The intersect point between the highest amount of methanol to oil ratio (6:1) and the highest reaction time (60 min) gives us about 100 % of yield. In Figure 2b it can be seen that 1 wt% of catalyst was used instead of 0.5 wt%. However, if 6:1 methanol to oil ratio and 60 min reaction time were used it will give us 91 % as the highest yield instead of 100 % (There is no red area appears in this figure), the green areas indicated intermediate yield %. Figure 2c shows that 1.5 wt% of catalyst was used. However, if 6:1 methanol to oil ratio and 60 min reaction time were used it will give us 71 % as the highest yield, which can be considered as low yield compared to the % of biodiesel yield obtained when 0.5 wt% and 1 wt% catalyst were used. Neither red areas nor green areas have appeared in this figure. Besides, the dark blue areas indicate the very low % of biodiesel yield.

3.2 Biodiesel properties

The core characteristics of the optimal bio-diesel sample were measured experimentally. Then, calculated values were compared with the standard ones, as shown in Table 4. The experimental properties almost met the standard value

Table 4: Properties of biodiesel

Property	ASTM Standard	Experimental
Viscosity ($\mathbf{cST}$)	5.213	4.8
Density (kg/m^3)	868	888
HHV (MJ/kg)	39.81	36.1

4. Conclusion

The core purpose of this research was to explore the usage of KOH supported with activated carbon and their influence on the production percentage of biodiesel from neem seed using transesterification method. The calculations were needed for the design as well as for the usage of the RSM software. This was done to give the number of experiments (20 runs) with different conditions (reaction temperature, time, catalyst amount and methanol to oil ratio) to obtain the optimum conditions such as the maximum yield of biodiesel. In experiment 6 (6:1 methanol to oil ratio, 1/2 wt% of catalyst and 60 min time of reaction) the maximum percentage of bio-diesel (100 wt%) obtained. Some of the properties of biodiesel were measured and compared to the standards, such as kinematic viscosity (4.8 cSt), high heating value (36.15 MJ/kg) and density (888 kg/m^3).

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