

Biodiesel purification by solvent-aided crystallization using n-hexane as solvent

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Abstract. Biodiesel is a form of fuel that has a natural origin as it is derived from organic components such as vegetable oil and animal fats. However, biodiesel has to be purified based on the required biodiesel purity standards before it can be used as diesel fuel. This study focuses on a lab-based purification method which is solvent-aided crystallization (SAC) using a typical solvent used for oilseed extraction that is n-hexane. Response surface methodology was used to optimize the process parameters. The purified biodiesel was analyzed via GC-MS to determine its fatty acid methyl ester (FAME) content, reflecting the purity of the biodiesel. The effect of cooling temperature and the concentration of the solvent was studied. The highest purity was obtained at intermediate parameter levels; 12°C and 1.5 wt% of n-hexane. The predicted optimum process parameters within the experimental range were 9.924°C and 1.131 wt%, with FAME purity of 99.789%. The data was validated with an experimental run, and the FAME purity obtained was 99.88%, a 0.1% difference from the predicted value. The FAME purity obtained was above the biodiesel purity standards making this environmentally friendly process viable to be used on a much larger scale in the biodiesel industry.

Introduction

Biodiesel is a form of fuel that is derived from organic components such as vegetable oil, animal fats and waste cooking oil. Biodiesel is produced from a chemical process that converts the oils and fats of natural origins into fatty acid methyl esters (FAMEs) through a process known as transesterification [1]. In Malaysia, biodiesel consumption has seen a sharp increase in biodiesel consumption yearly since 2000, with an average annual rate of 76.06%. In 2019, Malaysia recorded the highest biodiesel consumption with a total of 16.2 thousand barrels per day and showing an increase of 42.42% from 2018 [2]. This shows that biodiesel consumption is certainly growing and has a promising future in the fuel industry, and has emerged as a viable replacement for diesel fuel derived from petroleum and natural gas.

However, biodiesel cannot be used directly without purification as its contaminants might cause fouling of the engine as well as engine failure [3]. The conventional method of biodiesel purification that has been used in the industry is wet washing, either using water, acid, ether or absorbents [4]. However, this method is not environmentally friendly as it uses a large amount of

water and produces undesirable by-products that must be treated before they can be discharged. It contains high BOD and COD components and high pH values. Hence, dry washing was introduced as a substitute that uses the application of the adsorption separation process using ion exchange resin and magnesium silicate [3, 5]. However, this method has its limitations, too, due to the lack of knowledge of its chemistry as well as the regeneration of the used adsorbent [6]. Currently, the application of membrane technology for biodiesel purification is being studied to be applied in the industry. However, this technology is considered very costly due to high membrane fouling which leads to higher energy demand and shortens the lifetime of the membrane. Crystallization has been used in various industrial applications as it is a high separation and purification efficiency for solutions with high concentrations or viscosity [7].

For biodiesel purification, solvent-aided crystallization (SAC) can be utilized as it is able to produce biodiesel with high purity or high content of FAMES [8]. The solvent will assist in reducing the viscosity of the solution and affecting the crystallization kinetics favourably, making the process more efficient. n-Hexane has been used as part of the conventional technology for oilseed solvent extraction; for example, to extract vegetable oils from crops like soybeans [9]. This is because it has various positive attributes such as low latent heat of vaporization, high selectivity, non-polar nature and is easy to be recovered or removed [10]. In a study carried out to compare a few available technologies for oil extraction from leaf feedstock, using n-hexane as the solvent in the solvent extraction technique produced the highest oil yield [11]. Hence, this solvent is expected to have similar attributes when used in the SAC process for biodiesel purification as palm oil is derived from organic components.

The final purity of the biodiesel should meet the purity standards such as the European EN14214 and American D6751 standards before it can be used as a fuel [12]. In Malaysia, the biodiesel standard, MS 2008:2008 conforms to the international standards mentioned earlier. In all these standards, the minimum ester or FAME content is 96.5%. Therefore, this study focuses on the utilization of n-hexane as the solvent for the SAC method. The purity was determined by measuring the fatty acid methyl ester (FAME) content via gas chromatography-mass spectrometry (GC-MS) which was also useful in determining the biodiesel composition. Response surface methodology (RSM) was applied to the design of the experiment (DOE) generated to predict the optimum process parameters.

Methodology

Materials. The palm oil used for the production of biodiesel was the cooking oil of the Saji brand. Methanol with 99.97% purity and potassium hydroxide were obtained from Avantis Laboratory Supply. For the SAC process, n-hexane was used. ethylene glycol solution of 50% (v/v) with water was used as a coolant in a temperature-controlled chiller.

Production of Biodiesel. The experimental setup for the transesterification is illustrated in Fig. 1 below. The necessary apparatus for this experimental procedure was a conical flask, a heating and stirring mantle, a magnetic stirrer and a thermometer. Approximately 300mL of the palm oil was poured into the conical flask, and the temperature was controlled and maintained between 55 to 60°C. 3.8 g of potassium hydroxide (KOH) was dissolved in 67.5mL of methanol. The methoxide solution was added to the heated oil. The mixture was then stirred rapidly at 1000rpm for 10-15 minutes. Once the reaction was completed, the mixture, crude biodiesel was poured into a separatory funnel, as shown in Fig. 2 below. The crude biodiesel was left for 24 hours. Once the crude biodiesel was separated into two visibly distinct layers that are the heavier glycerol at the bottom and the lighter biodiesel at the top, as shown in Fig. 3, 1mL of the biodiesel and glycerol were extracted and inserted into a glass vial separately. The two samples were then sent for differential scanning calorimetry (DSC) analysis to determine their crystallization point. The biodiesel sample was first equilibrated to 30°C and then cooled to -15°C. After one minute, the

sample was reheated at 30°C. The temperature range for the glycerol sample was between 0 to 30°C. The ramping rate for both samples was set at 5°C min⁻¹.

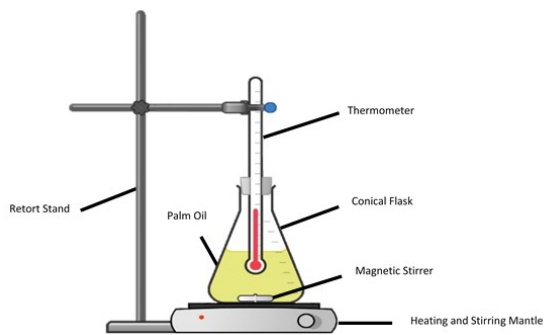


Fig. 1 Experimental Setup for Production of Biodiesel

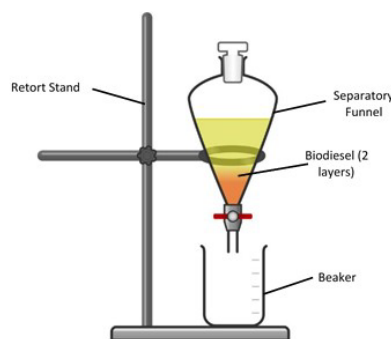


Fig. 2 Biodiesel Gravitational Settling Setup

Solvent-Aided Crystallization (SAC). The experimental setup for the solvent-aided crystallization (SAC) is illustrated in Fig. 3 below. The necessary apparatus for this experimental procedure was a chiller, a stainless-steel cylindrical vessel (crystallizer) and a stirrer. The temperature of the chiller was pre-eminently set to the desired temperature. The crude biodiesel was fed into the vessel. For the SAC process, the crude biodiesel did not undergo any gravity settling process as the purpose of the SAC is to separate and purify the biodiesel. n-Hexane was then added to the vessel as well. The amount of n-hexane required was calculated by weight percentage. Once the coolant temperature in the chiller reached the desired temperature, the vessel was placed in the chiller with the stirrer speed set at 220rpm. The SAC process was left for 40 minutes (cooling time). Two phases were formed in the vessel with the solidified glycerol melt at the bottom of the vessel. The purified biodiesel in the liquid phase was drained into a beaker, and a sample was collected. The solidified glycerol melt was quickly extracted, and a sample was collected. The biodiesel sample was then sent for analysis via GC-MS to determine its purity, while the glycerol sample was stored for future analysis. The entire experiment, the transesterification reaction followed directly by the SAC process, was repeated with different n-hexane concentrations (wt%) and cooling temperatures. The experiment was carried out based on the number of runs that were set by the design of the experiment (DOE) determined prior to the experiment.

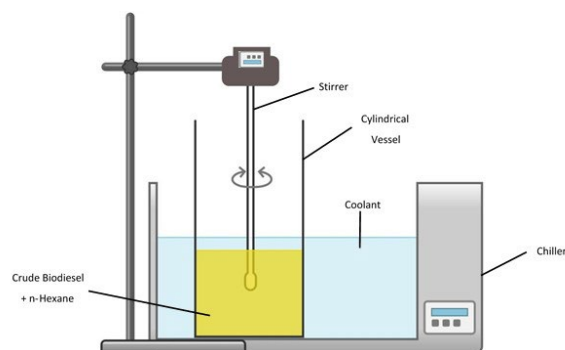


Fig. 3 Experimental Setup for Solvent-Aided Crystallization

Biodiesel **Purity**
 Assessment. A portion of the sample of the purified biodiesel was extracted and tested using gas chromatography-mass spectrometry (GC-MS). The initial oven temperature was set at 210°C with a holding time of 13 mins. The temperature was then raised to 230°C and was maintained for 15 mins. The ramping rate used was 5°C min⁻¹.

Process Optimization. The process optimization was carried out by applying response surface methodology (RSM) using Design Expert Software version 13.0.5. The software was utilized from the beginning of the experiment where the design of the experiment (DOE) was generated. Once the experimental results were obtained, the data was input into the software to generate quadratic models and to determine the optimum process parameters. For the DOE, a five-level-two factor central composite design (CCD) was used for this study. A minimum of 10 runs was required to construct the response surface model. The two parameters that were input were n-hexane concentration (A) and cooling temperature (B). There was only one response which was biodiesel purity (K). The biodiesel purity value was reflected by the FAME composition obtained from the GC-MS analysis carried out earlier. The values for the five levels of parameters are shown in Table 1. The SAC for each run was carried out based on the process parameters generated by the statistical DOE. Once all the runs were completed and the biodiesel purity for each run was obtained, the data was inserted into the software. The most suitable regression model was selected that fit the experimental data. Finally, the optimum process parameters were obtained by minimizing the parameters and maximizing the response. A final run of the experiment was carried out to validate the optimization results obtained through the RSM.

Table 1 Levels of Parameters used for CCD

Parameter	Type	Level				
		Min	Low	Central	High	Max
n-Hexane Concentration, A (wt%)	Numeric	0.79	1.0	1.5	2.0	2.21
Cooling Temperature, B (°C)	Numeric	4.48	8.0	12.0	16.0	20.0

Results and discussion

Production of Biodiesel. Based on the observation, the production of biodiesel via transesterification reaction was successfully carried out. The crude biodiesel that was left unattended for 24 hours had visibly separated into two distinct layers, as shown in Figure 3. The top layer is pure biodiesel comprising various types of fatty acid methyl esters (FAME) whereas the bottom darker layer is the contaminants, mainly glycerol. The visibly distinct formation of the two layers was caused by the difference in densities and polarities of the biodiesel and glycerol. From the crude biodiesel of approximately 370 mL, the glycerol obtained after the gravitational settling was approximately 35 mL. This value corresponds with the value reported by [13] stated that about 10 wt% of glycerol is produced as the major by-product in biodiesel production. Other studies also corroborate this data, proving that from every 100 pounds of biodiesel produced, approximately 10% of glycerol is produced [14, 15].

Differential scanning calorimetry (DSC) is a widely used thermal analysis technique for various purposes providing valuable test data for samples. For this study, DSC was carried out to determine the crystallization point of the biodiesel and the glycerol. The thermogram generated from the DSC analysis for the biodiesel sample is shown in Fig. 4, which illustrates the graph of heat flow (mW) against temperature (°C). A single clear peak can be observed, which shows that an exothermic process occurred during crystallization. The onset temperature of the nucleation process which is the point at which the peak begins, was approximately 7.5°C, whereas the crystallization point of the biodiesel at the top of the peak was 6.9°C. The maximum temperature of crystallization of the biodiesel is the end point of the peak at 3.8°C. Fig. 5 shows the thermogram generated from the DSC analysis of the glycerol sample. Unlike the graph in Fig. 4, the graph in Fig. 5 clearly shows no exothermic or endothermic peaks developed throughout the process. The result obtained can be corroborated by a recent study showing that no peak was found when DSC analysis was carried out for glycerol due to supercooling [16]. A similar study also stated that the melting point of glycerol is approximately 17.8°C. Since the crystallization temperature of the biodiesel sample

obtained from the DSC thermogram is approximately 7.5°C, the range of temperature selected for this study was from 8 to 16°C, which is below the melting point of glycerol, 17.8°C obtained from the study.

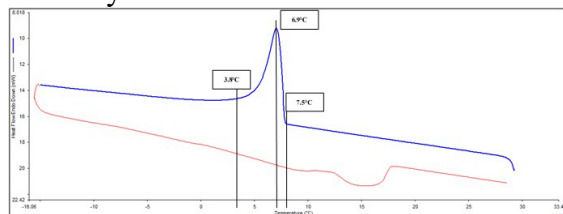


Fig. 4 Graph of Heat Flow vs Temperature (Biodiesel)

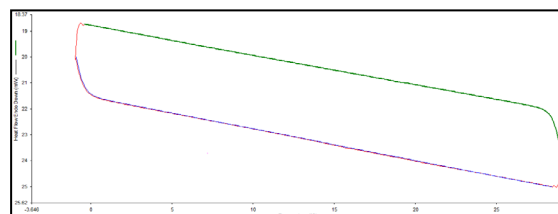


Fig. 5 Graph of Heat Flow vs Temperature (Glycerol)

Solvent-Aided Crystallization (SAC). Fig. 6 shows the pictures taken inside the vessel during and after the SAC process was completed. It can be clearly seen that after the SAC process was completed, two distinct phases were formed. The pure biodiesel was obtained in the liquid phase, and the glycerol crystallized at the bottom and sides of the vessel. n-Hexane is a non-polar solvent, and according to Bogataj and Bagajewicz [17], non-polar solvents can influence the solid crystals to be in an elongated form, as can be seen in Fig. 7. The solidified glycerol is in layer form. This observation concludes that the SAC process was successfully carried out.



Fig. 6 Left: During SAC; Right: After SAC

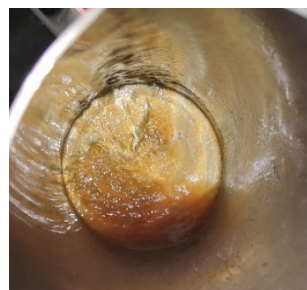


Fig. 7 Solid Glycerol in Layer Form

Biodiesel Purity Assessment. The purified biodiesel obtained from the SAC process was sent for analysis using GC-MS to determine its FAME content. Fig. 8 below shows the chromatogram obtained for the analysis of the first run of the experiment. The chromatogram shows the graph of signal intensity (abundance) against the retention time of the biodiesel sample. The peak data obtained from the GC-MS result is shown in Fig. 9. The percentage composition of the FAME is calculated using Eq. 1.

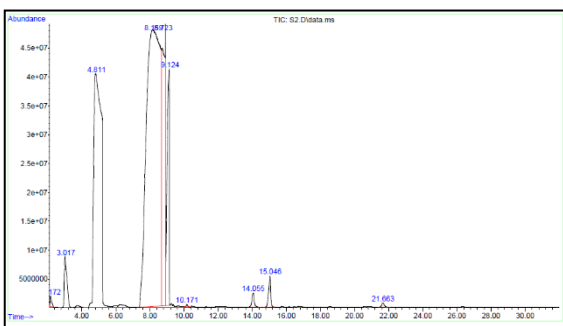


Fig. 8 Graph of Abundance vs Time (Sample from First Run)

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	2.172	5	15	54	BB	1773283	113459091	0.42%	0.220%
2	3.017	115	163	240	BB	48768916	961693857	3.59%	1.862%
3	4.811	384	476	632	BB	1040449119	12482249118	46.54%	24.165%
4	8.159	902	1061	1151	BV	1047995837	26822359763	100.00%	51.928%
5	8.723	1151	1160	1198	VV	944663845	6789445313	25.31%	13.144%
6	9.124	1198	1230	1243	VV	240694375	3705424598	13.81%	7.174%
7	10.171	1384	1413	1444	BB	3420628	21613862	0.08%	0.042%
8	14.055	2032	2092	2174	BB	22401407	224314990	0.84%	0.434%
9	15.046	2192	2265	2307	BV	5370705	452507347	1.69%	0.876%
10	21.663	3369	3421	3492	BB	5736501	80360171	0.30%	0.156%

Sum of corrected areas: 51653428112

Fig. 9 Peak Data from GC-MS Results (Sample from First Run)

$$\% \text{ Composition of FAME} = \frac{\text{Correction Area of Individual Component}}{\text{Sum of Correction Area}} \times 100\% \quad (1)$$

For example, the percentage composition of the FAME in the first peak is calculated as follows:

$$\% \text{ Composition of FAME} = \frac{113459091}{51653428112} \times 100\% = 0.22\%$$

The FAME present in the sample was identified based on the specific residence time, and the type of fatty acid was determined. The total FAME present was calculated by adding the percentage composition of each FAME present in the sample. The analyzed results are tabulated in Table 2. The total percentage of FAME for the purified biodiesel obtained from the first run of the experiment was 99.959% which is way above the biodiesel purity standards. To clarify, the composition of FAME obtained from this method may be different from the composition of raw palm oil as the FAME sample obtained in this study undergoes purification via SAC.

Table 2 GC-MS Analyzed Results for Sample from First Run

Peak Number	Retention Time (min)	Systematic Name (Library ID)	Trivial Name	Type	Composition of FAME (%)
1	2.172	Dodecanoic Acid	Lauric	Saturated	0.22
2	3.017	Methyl Tetradecanoate	Myristic	Saturated	1.862
3	4.811	Hexadecanoic Acid	Palmitic	Saturated	24.165
4	8.159	11-Octadecenoic Acid	Oleic	Unsaturated	51.928
5	8.723	9-Octadecenoic Acid	Oleic	Unsaturated	13.144
6	9.124	Methyl Stearate	Stearic	Saturated	7.174
8	14.055	cis-Methyl 11-Eicosenoate	Gadoleic	Unsaturated	0.434
9	15.046	Eicosanoic Acid	Arachidic	Saturated	0.876
10	21.663	Docosanoic Acid	Behenic	Saturated	0.156
TOTAL					99.959

Response Surface Methodology – Process Optimization. Various types of models could be used to fit the experimental design and the. Design Expert software suggested the most suitable polynomial model by using the Whitcomb score, which is a heuristic scoring system. The proposed model by the software was the quadratic model as it was not aliased and was adequately significant in representing the FAME purity that was the response for this study. The summary report comparing each of the parameters is shown in Table 3.

Table 3 Fit Summary of Each Model

Model	Sum of Squares	DF	Mean Square	F-value	p-value	Remarks
Mean	99482.87	1	99482.87	-	-	-
Linear	0.0533	2	0.0267	0.6586	0.5469	-
2FI	0.0130	1	0.0130	0.2875	0.6111	-
Quadratic	0.1302	2	0.0651	1.85	0.2692	Suggested
Cubic	0.1404	4	0.0351	-	-	-
Quartic	0.0	0	-	-	-	Aliased
Residual	0.0	0	-	-	-	-
TOTAL	99483.21	10	9948.32	-	-	-

Based on the selected model which was the quadratic model, the final empirical model in terms of the coded factor was generated as shown in Eq. 2.

$$K = 99.91 - 0.0071A - 0.0019B - 0.1197AB - 0.0906A^2 - 0.1251B^2 \quad (2)$$

The experimental and predicted response for each run is tabulated in Table 4. From Table 4, the data obtained from experimental and predicted were in the range of 99.46 to 99.96% since this study used cooking oil (refined oil) as the feed to produce biodiesel. For better clarification, biodiesel produced from refined oil is expected to have a high purity of FAME compared to unrefined oil such as crude palm oil processed from a palm mill. Another study using unrefined oil will be used to support this claim in the near future. On the other hand, the adequacy of the model was further justified by determining the absolute average deviation (AAD), as shown in Eq. 3 [18].

Table 4 Parameters and Response for Each Run

Run	Parameters		Response, K [FAME Purity (%)]		
	n-Hexane Concentration, A (wt%)	Cooling Temperature, B (°C)	Experimental	Predicted	Residual
1	1.5	12.0	99.96	99.91	0.0471
2	1.5	16.0	99.92	99.78	0.1331
3	1.0	8.0	99.51	99.59	-0.0755
4	1.0	20.0	99.46	99.56	-0.1024
5	0.79	16.0	99.87	99.78	0.0859
6	2.0	10.0	99.57	99.84	-0.2698
7	1.5	10.0	99.82	99.88	-0.0616
8	1.5	4.48	99.55	99.47	0.0716
9	2.0	8.0	99.88	99.81	0.0703
10	2.21	10.0	99.88	99.77	0.1012

$$AAD = \frac{1}{n} \sum_{i=1}^n \left| \frac{K_{i,exp} - K_{i,pred}}{K_{i,exp}} \right| \times 100\% \quad (3)$$

where n is the number of experiments, K_{exp} is the experimental value of the response and K_{pred} is the predicted value of the response. Hence, from the calculation, the AAD value obtained was 0.102%. Based on this significantly low AAD value, it can be interpreted that the model fitted precisely to the experimental data as a very low AAD value was obtained [19].

Effect of Parameters – Cooling Temperature. The first parameter that was studied was the cooling temperature. The cooling temperature was controlled by manipulating the temperature of the chiller to the desired temperature. Using Design Expert, a graph showing the relationship

between the temperature and FAME purity was generated as shown in Fig. 10 below. The value of the concentration of n-hexane kept constant at the central level is 1.5 wt%. The red dots are the expected design points, the black line indicates the trend of the findings, and the dotted blue lines are the bands of the confidence interval of 95%. The highest FAME purity can be achieved at the intermediate temperature of 12°C. Based on this finding, it can be concluded that the most desirable cooling temperature is at 12°C as the FAME is not solidifying while the glycerol and other by-products are well crystallized. According to a recent study [20], the solid grows in a more ordered pattern at a high temperature. This prevents the FAME from being trapped together with the glycerol during the SAC process, subsequently increasing the FAME purity. However, the FAME purity decreases as the temperature increases beyond 12°C. This is because the temperature is now approaching the melting point of the glycerol which is approximately 17.8°C. This reduces the crystallization efficiency of the glycerol, causing some of the glycerol to remain in its liquid form and combine with the FAME in one phase. Thus, for this experiment, the most desirable cooling temperature is in the intermediate region.

Effect of Parameters – Solvent Concentration. The next parameter studied was the concentration of the solvent, n-hexane. Using Design Expert, a graph showing the relationship between the n-hexane concentration and FAME purity was generated, as shown in Fig. 11. The value of the cooling temperature was kept constant at the central level which is 12°C. The most desirable concentration is at 1.5 wt% at which the efficiency of the SAC is at the optimum level. Almost all the glycerol is crystallized leaving only the FAME in the liquid phase. As a result, a high FAME purity can be observed. However, the FAME purity declines as the concentration of solvent is increased beyond 1.5 wt%. This shows that although the addition of n-hexane as the solvent in the SAC process helps to increase the solubility of the glycerol and reduce the density difference between the glycerol and the FAME, adding in too much solvent leads to a poor separation and purification process [21]. This finding is similar to a study carried out in 2015 [22] in which a higher separation of glycerol from the water was achieved with small quantities of the solvent, 1-butanol. The main point from this finding is that an increase in solvent concentration does not necessarily increase the FAME purity as an excessive amount of n-hexane creates a reverse effect by increasing the viscosity of the solution and subsequently, retarding the SAC process.

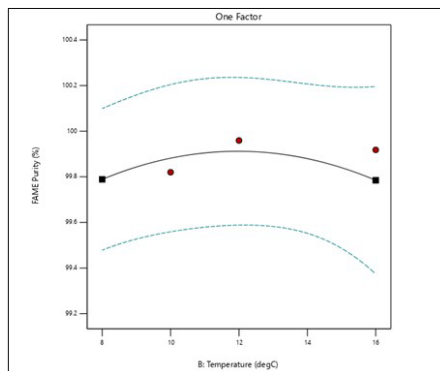


Fig. 10 Graph of Temperature vs FAME Purity

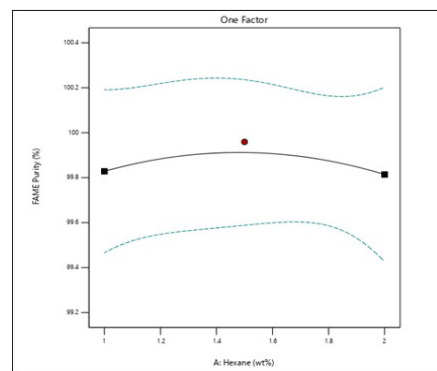


Fig. 11 Graph of n-Hexane Concentration vs FAME Purity

Optimum Conditions. Since there were only two parameters involved, the goal was to maximize the FAME purity while minimizing both parameters within the experimental range. The optimum operating conditions that were generated by the software based on the goals mentioned earlier are shown in Table 5. The desirability of the optimal solution selected was 0.758. The goal in determining the optimum conditions is to minimize the desirability value as a desirability of 1.00

translates that the goals were easy to reach and there might be better results available. Once the optimum conditions were obtained, the experiment was carried out again with the parameters generated by the software as shown in Table 5. The FAME purity obtained from the experiment was 99.88%. The reliability of the predicted biodiesel purity was evaluated by calculating the percentage error between the predicted and experimental value. The percentage error obtained was 0.1%. Since the value of percentage error is way lower than the maximum allowable percentage error of 10%, it can be concluded that the optimum conditions generated by the Design Expert as well as the predicted biodiesel purity are accurate as the model's prediction is almost equal to the actual biodiesel purity which was obtained through experiment. This value also justifies the regression model that was generated, and it confirms that this model was acceptable to be used for this project.

Table 5 Optimum Parameters with Predicted and Experimental Response Values

Parameters	Goal	Response Type	Optimum Conditions
A: Concentration of n-Hexane (wt%)	Minimize	-	1.131
B: Cooling Temperature (°C)	Minimize	-	9.924
K: FAME Purity (%)	Maximize	Predicted	99.789
		Experimental	99.880

Conclusion

This study focused on the utilization of SAC as a biodiesel purification method by studying the effect of two parameters, namely the concentration of the solvent, n-hexane and the cooling temperature. The purity of the biodiesel was reflected by its FAME content which was measured via GC-MS. The highest purity was obtained at intermediate parameter levels; 12°C and 1.5 wt% of n-hexane. Response surface methodology (RSM) was applied via Design Expert software. The adequacy of the selected quadratic model was justified with an absolute average deviation (AAD) value of only 0.102%, showing that the experimental data fitted well with the model. The predicted optimum process parameters within the experimental range were 9.924°C and 1.131 wt%, with FAME purity of 99.789%. The data was validated with an experimental run, and the FAME purity obtained was 99.88%. In conclusion, the biodiesel was well separated and purified as the FAME content is above the conformed purity standards.

Due to time and accessibility constraints caused by the pandemic, only two parameters could be studied. The effect of other parameters such as stirring speed and cooling time can be studied in the future, and the regression model generated can be further improved to provide a more comprehensive outcome. Besides that, other assessment methods can be carried out in future studies to completely characterize biodiesel. Also, different types of feed or oil sources can be used to produce biodiesel to compare the finding with this study. Currently, the use of green solvent has received a lot of attention in various industries as it is environmentally friendly and more cost-efficient. Hence, in future studies related to SAC purification of biodiesel, the effect of using green solvents can be studied, and the outcome can be compared to the results obtained from this study.

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