Homogeneous-Base Catalysed in Situ Transesterification of Desert Date Kernels: Biodiesel Yield and Methanol Recovery Maximization

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Abstract. Depletion of petroleum reserves and environmental-related problems such as climate change have triggered research towards sustainable and green substitutes for petroleum-based products. Biodiesel has been identified as a good replacement for conventional diesel. The traditional two-step biodiesel production approach can increase the capital and operating costs due to the requirement of two different units for extraction and the reaction. To overcome the problem, this research was carried out to produce biodiesel from desert date seeds through *in situ* potassium-hydroxide-catalysed methanolysis. Experimental investigations were conducted under different operating conditions, including temperature, time, and catalyst dosage. The optimal yield of 98.1% was achieved in 120 minutes at 50 °C using 3 g of catalyst. The one-factor at-time designed experimental data were analysed using Design Expert 13. Catalyst dosage was a significant model term, while time and temperature were not statistically significant, corroborating the experimental observation. The optimisation results predicted an optimal biodiesel yield of 86.9% at a reaction temperature of 50 °C, a reaction time of 160 minutes, and a 3 g catalyst dosage, which is close to the result obtained from the experimental investigation. The results from the characterisation showed that the product has the properties of biodiesel, and the cake can be useful for pyrolytic production of bio-oil and biochar since the cake had fat and carbohydrate contents of 38.432 and 43.911%, respectively.

Keywords: desert date kernels; biodiesel; insitu-transesterification; alcohol recovery; optimisation.

INTRODUCTION

Research on clean and renewable energy sources is increasing due to the high cost of conventional petroleum products, environmental and health issues associated with their use and non-renewability of the sources. One of the significant advantages of biodiesel is that it is considered carbon-neutral, meaning there is no net carbon output in the form of carbon dioxide (CO_2), as the same amount of CO_2 emitted during its combustion is absorbed during the growth of the oil crop. Biodiesel is also non-toxic, free of sulphur, biodegradable, safe to handle, and improves lubricity [6]. The power output of biodiesel is affected by the quality, blend, and load conditions under which it is burnt. The thermal efficiency of a fuel is a function of physicochemical properties such as viscosity, specific density, and flashpoint. The American Society for Testing and Materials has set standards for these properties that biodiesel must conform to before application.

Biodiesel is a renewable and cleaner liquid fuel obtained from fatty-acid-rich sources, such as vegetable oils, animal fats, and mineral oils, through chemical processes. Biodiesel consists of long-chain fatty acid methyl esters (FAME), and its production involves the catalytic transesterification of fatty acid with alcohol to form ester and glycerol [6]. Conventionally, the feedstock of transesterification is oil from the seed obtained through pressing and solvent extraction. The approach requires a separate unit for extraction and transesterification. This traditional method produces a high product yield when optimal operating conditions are selected. However, more unit operations can translate to high capital and operating costs. In optimising the pathway to increase yield with low capital and operating costs, researchers found *in situ* transesterification suitable for biodiesel production. *In situ,* alcoholysis is a reactive extraction method of producing biodiesel from ground seed kernels and alcohol in the presence of a catalyst. This process from the conventional method does not require extracting oil; instead, the oil-rich kernel is used in ground form, and both extraction and reaction occur in a single unit. Some researchers have investigated the use of *in situ* transesterification for biodiesel production. Authors [2] studied the suitability of desert dates *(Balanites aegyptiaca* L. Delile) for large-scale, sustainable, industrial biodiesel production. Both conventional and *in situ* transesterification were carried out. The conventional transesterification reaction was performed at a 6:1 methanol to oil molar ratio, 25 °C for 1 hour. On the other hand, the *in situ* transesterification was carried out using 2% (w/w) potassium hydroxide; the reaction mixture was shaken at the reflux temperature in an orbital shaker for 6 h. The two-step and in situ reactions yielded 82.16–93.2% and 91.54–93.35% respectively. The authors concluded that both approaches can use desert date seeds for sustainable biodiesel production. [8] conducted a critical review of the *in situ* transesterification process for biodiesel production. Their article provides an overview of the *in situ* transesterification process, the parameters that significantly affect it, and the advantages and disadvantages of the *in situ* technique. Their research found that the *in situ* transesterification process can effectively produce biodiesel, provided researchers can reduce the amount of alcohol used in the reaction. Additionally, technical feasibility has been demonstrated for various feedstocks, catalysts, and alcohols.

In their study, [4] conducted *in situ* transesterification experiments using milled jatropha seeds. They tested varying conditions such as methanol to seed ratio (2:1–6:1), amount of alkali (KOH) catalyst (0.05–0.1 mol/l in methanol), stirring speed (700–900 rpm), temperature (40–60 C) and reaction time (3–5 h). The findings revealed that the highest biodiesel yield (87% with a fatty acid methyl ester purity of 99.7%) was achieved with a methanol-to-seed ratio of 6:1, KOH catalyst of 0.075 mol/l in methanol, a stirring speed of 800 rpm, a temperature of 50^{o}C, and a reaction time of 5 h. It was observed that increasing the temperature favoured the reaction up to 50°C, beyond which a decrease in yield was encountered. Furthermore, the biodiesel yield remained relatively constant as the reaction time increased from 3 to 5 hours, indicating that the equilibrium composition had already been reached after 3 hours. The stirring speed did not affect the biodiesel yield, and the resulting yield remained constant as the stirring speed increased from 700 to 900 rpm, suggesting that a stirring speed of 700 rpm was sufficient to mix the reactants efficiently.

Authors [10] carried out *in situ* transesterification on Karanja seed powder. The operating conditions used for this study are temperature (50°C), the molar ratio of methanol to oil (3:1-8:1), KOH concentration (0.25-2 wt%), and time (10-60 min). The results showed that the *in situ* transesterification reaction of karanja oil seed powder depends on the increase of catalyst concentration and the ratio of methanol to Karanja oil seed powder. The yield obtained was about 62.5 %. The optimum conditions for maximum yield are observed at 30 min, 6:1, and 1.0 wt %. Authors [11] investigated using microalgae (Nannochloropsis gaditana) as feedstock for *in situ* transesterification. Several reaction conditions were tested, including methanol/biomass (ml/g) from 30 to 120, reaction temperature from 60 to 90^{o}C, and reaction time from 0.5–2.5 h. The optimal yield of 10.04% ± 0.08% by weight was obtained at a methanol/biomass ratio of 90 ml/g, a temperature of 70^{o}C, and a reaction time of 1.5 h. The results indicate that an excess of methanol favours the formation of glycerol and FAME and reaches equilibrium within a reasonable time. While a high temperature ensures a thorough reaction, raising the temperature to 90 °C led to a drop in biodiesel yield due to methanol evaporation, resulting in a shortage of reactants and harming biodiesel production. Moreover, prolonging the reaction time from 1.5 to 2.5 h did not increase the biodiesel yield, as the reaction had already reached equilibrium at 1.5 h.

Many of the reported work on *in situ* transesterification focused on other seeds. Though many reported experimental studies [1, 11, 4] on desert date biodiesel production via two-step transesterification, the only study found on the in situ transesterification of these seeds lacked observations on process variables. As a result, no research currently examines the effects of process variables on the *in situ* transesterification of a desert date seed. Also, almost all the works reported using desert dates did not take into account the alcohol recovery alcohol. Therefore, further research is needed to explore the impact of different process variables on the efficiency and yield of biodiesel production from desert date seeds using this method. This research aims to produce biodiesel from desert date kernels using the *in situ* transesterification method at various temperatures, times, and catalyst dosage operating conditions. The specific objectives were to investigate the effects of process variables such as temperature, time, and catalyst dosage on the yield of biodiesel and alcohol recovery, model and optimise the experimental data and characterise the biodiesel produced and the cake.

METHODS

Pretreatment of Desert Date Seed

Collection and preparation of desert date seeds. To begin the process, desert date fruits (Figure 1) were first obtained from the market. These seeds were then meticulously washed, graded, and dried. Once fully dried, the shells were carefully cracked open to extract the kernels (Figure 2), which were then further dried to ensure the removal of any residual moisture. This thorough preparation of desert date seeds is a crucial initial step in producing biodiesel from these seeds.

Figure 1 – Desert Date Fruits

Grinding of the Seeds into Powder. Once the seeds were dried, they were pounded and ground into a fine powder (Figure 3) using a blender. Then, the crushed particles were sieved using a 0.6 mm sieve. This powder was used as the starting material for the production of biodiesel.

Figure 2 – Desert Date Kernels

Figure 3 – Desert Date Kernels after Grinding

In Situ Transesterification

10 g of the desert date seeds powder was measured and loaded into the thimble. A mixture of methanol and Potassium Hydroxide (KOH) as a catalyst was measured and poured into a round bottom flask. The concentration of the catalyst was varied. The Soxhlet extractor was set up by placing the thimble containing the desert date seed powder into the main chamber of the extractor. The Soxhlet extractor containing the methanol and catalyst mixture was then attached to the round bottom flask. A reflux condenser was attached above the extractor, and cold water was circulating to control the temperature. The setup used for the experiments is given in Figure 4. The apparatus was heated to reflux and left

to extract for a defined time and temperature during the in-situ transesterification process. The experiment was repeated at varying catalyst dosages, times and temperatures to optimise the biodiesel yield.

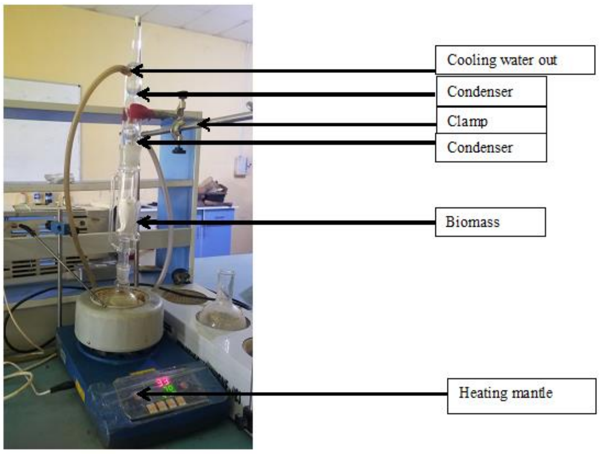

Figure 4 – The Experimental Setup for the In Situ Transesterification

Product Separation and Recovery of Alcohol

In Situ, Transesterification is a biodiesel production method that involves the simultaneous transesterification and alcohol recovery process. After the transesterification reaction, the seed powder was removed from the reactor shown in Figure 8, leaving the mixture of biodiesel and excess alcohol. The mixture was then heated to evaporate the excess alcohol. The evaporated alcohol vapour was then condensed using a condenser, which converted the alcohol vapours into liquid form, and the liquid methanol rose in the extraction chamber. Still, its level was not allowed to reach the siphon arm of the soxhlet to avoid reflux (Figure 5).

The biodiesel yield and alcohol recovery were calculated using Equations 1 and 2, respectively.

$$\text{Biodiesel Yield (\%)} = \frac{\text{Mass of biodiesel obtained}}{\text{Mass of ground desert date kernels used}} \times 100 \tag{1}$$

$$\text{Alcohol recovery (\%)} = \frac{\text{Mass of alcohol recovered after } \textit{in situ} \text{ transesterifiction}}{\text{initail mass of alcohol added for the reaction}} \times 100 \tag{2}$$

The recovered alcohol was then reused in the next batch of transesterification reaction, thus reducing the overall cost of biodiesel production. At the same time, the remaining biodiesel was allowed to cool. Overall, alcohol recovery using the *in situ* transesterification method is an efficient and cost-effective way of producing biodiesel while minimising waste and maximising the use of resources.

Figure 5 – The Setup for Alcohol Recovery

Optimisation of reaction conditions

The experimental data were collected and optimised using design expert 13. The process of optimisation of yield and alcohol recovery of biodiesel produced at varying times, temperatures, and catalyst dosage using the one-factor approach pre-designed experiments. The experimental data were inputted into Design Expert using a blank sheet with rows equal to the number of experiments carried out at different values of time, temperature, and catalyst dosage as factors. The optimal conditions were determined using the numerical approach available in the software by setting the optimisation goal to be within range of the factors and maximise the responses. The results were validated by performing additional experiments under the optimised conditions, and the yield and alcohol recovery were analysed.

Characterisation of biodiesel

The biodiesel produced at optimum conditions was characterised by physicochemical properties such as cloud point, flash point, pour point, dynamic viscosity, refractive index, acid value, saponification value, flash point, iodine value, etc. These properties were measured according to the methods indicated in Table 1. The procedures for those parameters not measured according to the American Society for Testing Materials Standards are below.

Table 1 – Characterisation Methods

Parameters	Standard Method
Density / Specific Gravity	ASTM method D – 129 –12b (2017)/ By calculation
Dynamic viscosity	ASTM D- 445
Kinematic Viscosity	Calculation
Refractive index	Direct method using a refractometer
Acid value	ASTM – D 974
Free Fatty Acid	Calculation
Saponification value	ASTM method- D94 -07 (2017)
Flash point	ASTM D 93
Iodine value	Wij and Hanus Method
Cloud point	ASTM D2500-11
Pour point	ASTM D97
Peroxide value	Titration
Heating value	ASTM D 2382-88
Cetane number	ASTM D 613

Determination of refractive index. An Abbey Refractometer was used in this Determination. A sample drop was transferred into a glass slide of the refractometer. Water at 30 °C was circulated on the glass slide to keep its temperature uniform. Through the eyepiece of the refractometer, the dark portion viewed was adjusted to align with the cross's intersection. At no parallax error, the pointer on the scale pointed to the refractive index. This was repeated, and the mean value was recorded as a refractive index.

Iodine Value Determination. This measures the degree of unsaturation in any vegetable oil or animal fat. It is the weight of iodine absorbed by 100 parts by the weight of the sample. It is expressed in (mg/g). The oil sample was poured into a dry glass-stopper bottle of about 250 ml capacity and added a small rod. The weight (g) of the oil was obtained by dividing the highest expected iodine value by 20. 10 ml of carbon tetrachloride and 20 ml of Wiji's solution were dissolved in the bottle. The stopper was moistened with potassium iodine solution, and the solution was inserted and kept in the dark for 30 minutes. 15 ml of potassium iodide solution and 100 ml of water were mixed and titrated with 0.1 M of thiosulphate solution using starch as the indicator just before the endpoint. A blank was carried out simultaneously with 10 ml of carbon tetrachloride. The iodine value (IV) was later calculated using Equation 3.

$$\mathrm{IV} = \frac{12.69\left(\mathrm{B\text{-}S}\right)}{\text{weight of sample}} \tag{3}$$

where B – the blank titre value, S – the sample titre value.

Peroxide value determination. This is the measure of its oxygen content. It is expressed in mol/kg. 2 g of oil sample and 1 g of powdered potassium iodide was added into 2 test tubes containing 20 ml of solvent mixture each (2 vol. glacial acetic acid + 1 vol. of chloroform), i.e. (60:30). Step 1 was carried out in a blank tube (without sample). The tubes were placed in a water bath and allowed to boil vigorously for 30 seconds. The contents were poured quickly into a conical flask containing 10 ml of 5% potassium iodide solution. The tubes were washed with 5ml of water each and poured into each conical flask with contents, and four drops of phenolphthalein were then added into each conical flask. They were titrated with 0.01M thiosulphate until a colour change was obtained. The biodiesel's peroxide value (PV) was calculated according to Equation 4.

$$\mathrm{PV} = \frac{\left(\mathrm{B\text{-}S}\right)*0.01*1000}{\text{weight of sample}} \tag{4}$$

Proximate Analysis of the Cake

Determination of Moisture Content. The Moisture Content was determined using the procedure described by AOAC. The moisture content of each sample was determined by weighing 5g of the sample into an aluminium moisture can. The sample was then dried to constant weight at 105±2°C. The moisture content of the sample was measured by comparing the weight of the moist sample and the dried sample per weight of the moist sample by 100.

Determination of Crude Protein. The Protein Content was determined using a Foss Tescator protein digestor and KJECTEC 2200 distillation apparatus (Kjeldahl method) according to the procedure of AOAC. Concentrated H_2SO_4 (12 ml) and 2 catalyst tablets were put into a Kjeldahl digestion flask containing 1g of the sample. The flask was placed in the digestor in a fume cupboard and switched on, and digestion was done for 45 minutes to obtain a clear, colourless solution. The digest was distilled with 4% boric acid, 20% Sodium hydroxide solutions were automatically metered into it in the KJECTEC 2200 distillation equipment until distillation was completed. The distillate was then titrated with 0.1 M HCl until a violet colour formation indicated the endpoint. A blank was run under the same condition as with the sample. Total nitrogen content was then calculated according to the formula given in Equation 5.

$$\mathrm{CP} = \frac{(\mathrm{S\text{-}B}) \times 0.01 \times 14.007 \times 6.25 \times 1000}{1000 \times \text{weight of sample}} \qquad (5)$$

Determination of Crude Fat Content. Crude fat was extracted in a Soxhlet extractor with hexane and quantified gravimetrically. 1 g of sample was weighed into an extraction thimble and then stopped with grease-free cotton. Before extraction commenced, the round bottom cans were dried, cooled, and weighed. The thimble was placed in an extraction chamber, and 80 ml hexane was added to extract the fat. The extraction was performed at 135oC, lasting 1 hour and 40 minutes. After this, the fat collected in the bottom cans was cooled in a desiccator. The fat content was calculated as the ratio of the weight of the extracted fat to the weight of the sample, all multiplied by 100.

Determination of Ash Content. 2 g of the sample was weighed into well-incinerated crucibles and then ashed in a muffle furnace at 600^0C for 3 hours. The ash content was calculated as the weight of the sample obtained per weight of the sample before incineration, all multiplied by 100.

Determination of Crude Fiber. 2 g of the sample was transferred into a 1-litre conical flask. 100 ml of sulphuric acid (12.5M) was heated to boiling and then introduced into the conical flask containing the sample. The contents were then boiled for 30 minutes, ensuring the acid level was maintained by adding distilled water. After 30 minutes, the contents were filtered through a muslin cloth held in a funnel. The residue was rinsed thoroughly until its washing was no longer acidic to litmus. The residue was then transferred into a conical flask. 100 ml of sodium hydroxide (12.5 M) was brought to a boil and introduced into the sample's conical flask. The contents were then boiled for 30 minutes, ensuring the acid level was maintained by adding distilled water. After 30 minutes, the contents were filtered through a muslin cloth held in a funnel. The residue was rinsed thoroughly until its washing was no longer alkali. The residue was introduced into an already-dried crucible and ashed at 600°C ±200°C. Equation 6 was then used to calculate the crude fibre.

$$\text{Crude Fiber} = \frac{\text{Final weight of crucible -initial weight pf crucible}}{\text{weight of sample}} \times 100 \qquad (6)$$

RESULTS AND DISCUSSION

Experimental Data. Table 2 shows the experimental data from biodiesel production from desert date seeds by varying temperature and catalyst dosage using the *in situ* transesterification method.

Table 2 – Experimental Data Obtained from the Production of Biodiesel

No	Time (min)	Temp (°C)	Catalyst dosage	Yield (%)	Methanol Recovery (%)
1	60	55	1	24.8	40
2	60	55	2	20.8	52
3	60	55	3	49.6	46
4	40	50	3	80	45
5	80	50	3	95.2	60
6	120	50	3	98.1	70
7	160	50	3	95.1	66
8	40	60	3	80.4	46
9	80	60	3	64.6	50
10	120	60	3	65	56
11	160	60	3	63.8	60
12	40	70	3	53.2	62
13	80	70	3	83.5	54
12	120	70	3	95.5	56
15	160	70	3	56.8	58

The effect of reaction time and temperature on biodiesel production from desert date seeds through the *in situ* transesterification method is shown in Table 2. The impact of reaction time on biodiesel yield is noteworthy. Usually, a longer time is expected to result in a high biodiesel yield at low temperatures. For instance, the yield increased from 70% at 40 minutes to 98% at 120 minutes, both at a temperature of 50°C and a constant catalyst dosage of 3. This suggests that allowing more time for the reaction to proceed enhances feedstock conversion into biodiesel. However, at 60ºC, yield decreased with an increase in time. Also, at 70 °C, the yield increased with time for up to 120 min but decreased thereafter. It was noticed that for all reactions, after 120 mins, there was a decrease in the yield, which suggests that the composition had reached equilibrium at 120 min. In their study, [3] also observed an increase in yield as the reaction time increased. A yield 90% was achieved within an hour for biodiesel production; however, there was no effect on the biodiesel yield as the reaction time was increased up to 3 h. The trend in this reaction shows that lower temperature favours high biodiesel yield. This observation aligns with the report by [8], which observed that reaction temperature had little impact on biodiesel yield, especially from 40°C to 52.5°C. However, a further increase in temperature shows no effect on the yield. When the reaction temperature approaches methanol and n-hexane boiling points, they partially vaporise and form some bubbles, interrupting the reaction [5].

Effect of catalyst dosage. The results demonstrate a clear trend regarding catalyst dosage. As the catalyst dosage increased from 1 to 3, the biodiesel yield also increased significantly. This is evident from the yield of 16.8% at a catalyst dosage of 1, compared to 39.6% at a dosage of 3 (Table 2). The substantial increase in yield suggests that the catalyst plays a crucial role in facilitating the transesterification process.

Experimental Data Fitting and Analysis of Variance (ANOVA) of Biodiesel Yield. The linear model obtained when the experimental data were analysed was given in Equation 7. This model is based on three variables: Time (A), Temperature (B), and Dosage (C).

$$R_1 = 44.3189 + 3.9973A - 7.6021B + 30.9836C \quad (7)$$

where R1 is the yield of biodiesel, A represents Time, B is the temperature, and C is the factor representing the catalyst dosage.

The coefficients (4.00, -7.60, and 30.98) represent the change in the biodiesel yield (R1) for a one-unit change in their respective variable, holding all other variables constant. The intercept (44.32) is the expected value of biodiesel yield (R1) when all variables (time, temperature and dosage) were 0.

Analysis of Variance (ANOVA) of biodiesel yield. The ANOVA (Table 3) reveals the significance of the model and the individual predictors in explaining the variability of the response variable.

Table 3 – Analysis of Variance for Biodiesel Yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4750.80	3	1583.60	4.66	0.0245	significant
A-Time	164.18	1	164.18	0.4834	0.5013	
B-Temp	477.02	1	477.02	1.40	0.2610	
C-dosage	3785.52	1	3785.52	11.14	0.0066	
Residual	3736.31	11	339.66			
Cor Total	8487.11	14				

The ANOVA table proves that the model is significant, and the predictor Dosage (C) significantly influences predicting the response variable. However, the predictors Time (A) and Temp (B) seem not to have a significant impact on the yield. The F-value of 4.66 with a corresponding p-value of 0.0245 indicates that the overall model is statistically significant at a 95% confidence level. This suggests that at least one of the predictor variables has a significant effect on the response variable. They had an F-value of 0.4834 with a p-value of 0.5013, indicating that it is not statistically significant in predicting the yield. Temperature had an F-value of 1.4044 with a p-value of 0.2610, suggesting that it is also not statistically significant in predicting the yield. In contrast, dosage exhibited a high F-value of 11.1449 with a low p-value of 0.0066, indicating that it is statistically significant in predicting the yield. Table 3 shows the yield values obtained from biodiesel production from desert date seeds and the predicted yield values generated by the Design Expert.

It is important to note that the actual yield values vary across the different run orders, ranging from 20.8% to 98.1%. This indicates that various factors, such as temperature, time, catalyst dosage, etc., can influence the biodiesel yield of desert date seeds. The discrepancies between the actual and predicted values suggest that factors not accounted for in the prediction model or variations in the production process affect the yield.

Methanol Recovery Model and Analysis of Variance. The empirical model obtained for methanol recovery was as given in Equation 8.

$$R_1 = 53.30 + 4.85A - 2.28B + 4.36C - 5.36AB \quad (8)$$

In this equation, A, B, and C represent the predictor variables, the coefficients 4.85, -2.28, and 4.36 represent the impact of variables A, B, and C on the yield (R^2), respectively, and the coefficient -5.36 represents the interaction effect between variables time(A) and temperature(B).

This reduced 2-factor interaction equation represents the relationship between the yield (R2) and the predictor variables A, B, and C and the interaction term AB.

Table 4 shows that the model was significant, and Time (A) and the AB interaction were particularly impactful in predicting alcohol recovery, with their p-values being less than 0.05. However, the factors Temp (B) and Dosage(C) did not appear to have a significant impact on the alcohol recovery (R^2).

Table 4 – Predicted and Actual Yield of Biodiesel Obtained

Run Order	Time (min)	Temperature (° C)	Dosage (g)	Actual value (yield %)	Predicted Value (yield %)	Residual
1	60	55	1	24.8	13.14	11.66
2	60	55	2	20.8	44.12	-23.32
3	60	55	3	49.6	75.11	-25.51
4	40	50	3	80	77.31	2.69
5	80	50	3	95.2	80.51	14.69
6	120	50	3	98.1	83.7	14.40
7	160	50	3	95.1	86.9	8.20
8	40	60	3	80.4	69.71	10.69
9	80	60	3	64.6	72.9	-8.30
10	120	60	3	65	76.1	-11.10
11	160	60	3	63.8	79.3	-15.50
12	40	70	3	53.2	62.1	-8.90
13	80	70	3	83.5	65.3	18.20
14	120	70	3	95.5	68.5	27.00
15	160	70	3	56.8	71.7	-14.90

Table 5 – ANOVA for Methanol Recovery

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	689.02	4	172.25	5.98	0.0101	Significant
A-Time	241.47	1	241.47	8.39	0.0159	
B-Temp	40.22	1	40.22	1.4	0.2646	
C-dosage	73.27	1	73.27	2.54	0.1417	
AB	188.23	1	188.23	6.54	0.0285	
Residual	287.92	10	28.79			
Cor Total	976.93	14				

The 'Predicted versus Actual Response' plot is a graphical representation used to assess the performance of a predictive model. From the graph in Figure 6. It can be noted that points close to the diagonal line indicate good predictions, as the predicted values are close to the actual values. Points that are far from the diagonal line represent poor predictions. The spread of points around the diagonal line indicates the model's accuracy. While many points are reasonably close to the line in this plot, several are quite distant, indicating some prediction error. It can be concluded that, according to the plot, the model has varying levels of predictive accuracy across the dataset, with some predictions being quite accurate and others showing significant error.

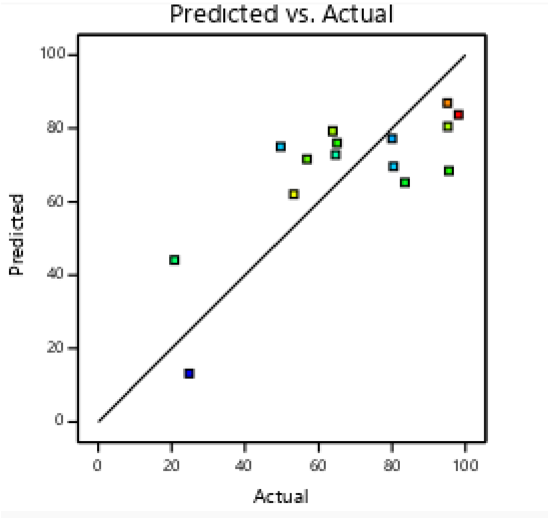

Figure 6 – Predicted versus Actual Value plot

Characterisation Results. The physicochemical properties of biodiesel play a crucial role in determining its quality and compatibility with established fuel standards. The table below shows the result of the physicochemical characterisation of biodiesel.

The relative density of biodiesel is an important parameter that indicates its mass per unit volume. The measured value of 0.8434 mg/ml for biodiesel falls within the acceptable range of 0.85-0.9. Specific Gravity: The specific Gravity of biodiesel measures its density relative to water. With a value of 0.8623, biodiesel conforms to the standard range of 0.8 to 0.94. Refractive Index: The refractive index of biodiesel determines how light bends as it passes through the fuel. A value of 1.485 indicates that biodiesel has a refractive index similar to the standard, ensuring optical compatibility. Viscosity measures the resistance of a fluid to flow. Biodiesel exhibits a viscosity of 3.7 mPas, within the acceptable range specified by standards. The ASTM standard specifies a viscosity of 1.9 to 6.0 mm^2/s at 40°C. Kinematic viscosity, measured in centistokes (Cp), accounts for the fluid's resistance to flow under gravitational force. Biodiesel has a kinematic viscosity of 4.387 Cp, meeting the standard requirements.

Table 6 – Physicochemical Properties of the Oil Sample

No	Parameters	Unit	Oil	ASTM D6751
1	Relative Density	mg/ml	0.8434	0.88
2	Specific Gravity	_	-0.8623	0.875-0.9
3	Refractive Index	_	-1.485	
4	Viscosity	mPas	3.7	
5	Kinematic Viscosity	Cp	4.387	1.9-6.0
6	Acid Value (Av)	mg KOH/g Oil	2.52	0.8 max
7	Free Fatty Acid (Ffa)	_	1.26	0.42 max
8	Saponification Value (Sv)	mg KOH/g Oil	220.193	
9	Iodine Value (Iv)	mg I/g Oil	100.76	120 max
10	Peroxide Value (Pv)	meq/kg	10	
11	Flash Point	OC	119.4	93 min
12	Pour Point	OC	-2.1	-15-10
13	Cloud Point	OC	1.7	3-12
14	Heating Value	MJ/kg	32.5237	
15	Cetane Number	_	50.3	47 min

The acid value of biodiesel represents the concentration of acidic compounds in the fuel. With an acid value of 2.52 mg KOH/g oil, biodiesel does not comply with the accepted limits specified by standards. Free Fatty Acid (FFA) content in biodiesel reflects the amount of unreacted fatty acids in the fuel. The free fatty acid (FFA) value of 1.26 was obtained, higher than the standard limit of 0.42. This elevated FFA level can adversely affect the quality and yield of biodiesel, as higher FFA contents can lead to lower conversion rates, resulting in a biodiesel product that may not meet industry standards. The saponification value indicates the average molecular weight of biodiesel. Biodiesel exhibits an SV of 220.193 mg KOH/g oil, aligning with the standards. The iodine value of biodiesel measures the degree of unsaturation in the fuel. Biodiesel meets the specified standards with an IV of 100.76 mg I/g oil. Peroxide value quantifies the level of peroxides, indicating the extent of oxidative degradation. Biodiesel's peroxide value of 10.0 meq/kg complies with the acceptable limits set by standards.

A flash point represents the lowest temperature at which a substance can ignite when exposed to an open flame or spark. Biodiesel exhibits a flash point of 119.4°C, conforming to the standard requirements. The pour point of biodiesel indicates the lowest temperature at which the fuel can still flow. Biodiesel meets the specified standards with a pour point of -2.1°C. Cloud point refers to the temperature at which the fuel begins to develop a cloudy appearance due to the formation of wax crystals. The ASTM standard does not specify a cloud point, but biodiesel generally has a higher cloud point than petroleum diesel. The cloud point of the oil sample (1.7°C) is relatively low, which is a positive sign for cold weather performance. The heating value of biodiesel measures its energy content. With a heating value of 32.5237 MJ/kg, biodiesel aligns with the standard requirements. The cetane number indicates the ignition quality of the fuel. The ASTM standard requires a minimum cetane number of 47. The cetane number of the oil sample (50.3) exceeds this minimum.

FT-IR Analysis (Fourier Transform Infrared Spectroscopy) of the Biodiesel. Infrared (IR) spectroscopy is a common method to know various functional groups in a substance. A typical IR spectrum of biodiesel exhibits characteristic absorption bands that indicate the presence of specific functional groups. Key absorption bands in a typical IR spectrum of biodiesel include bands in the region 1425-1447 cm^{-1} corresponding to CH3 asymmetric bending and bands in the 1188-1200 cm^{-1} range associated with O-CH_3 stretching [7]. From the IR spectrum, we can identify several of these features. A broad peak around 3360.16 cm^{-1}, could be due to O-H stretching, indicating the presence of alcohol or water. Peaks at 2922.72 cm^{-1} and 2850.84 cm^{-1} are consistent with the C-H stretching vibrations of the methyl and methylene groups. A sharp peak at 1740.89 cm^{-1} matches the expected C=O stretching vibration of the ester group. Peaks in the region of 1460 cm^{-1} could correspond to the C-H bending vibrations. A peak at 1145.83 cm^{-1} aligns with the C-O stretching vibration of the ester group. These observations suggest that the IR spectrum shows the characteristic peaks that one would expect from a biodiesel sample.

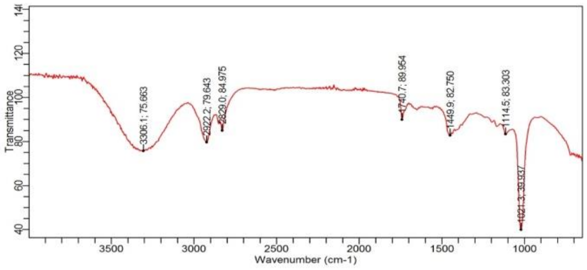

Figure 7 – FTIR of the Biodiesel

Proximate analysis of biodiesel. The table below shows the results from the proximate analysis of biodiesel.

Table 7 – Proximate Analysis of the Cake Sample

No	Parameter	Unit	Cake
1	Moisture Content	%	5.893
2	ASH Content	%	3.075
*	Nitrogen	%	1.04
3	Protein	%	6.531
4	Fat	%	38.432
5	Fibre	%	2.158
6	Carbohydrates	%	43.911

The moisture content of post-*in situ*- transesterification of desert date seeds was measured as 5.893 %. This parameter indicates the amount of water present in the biodiesel. The ash content of the biodiesel from the desert date was 3.075 %. Ash content represents the inorganic residue left after the complete combustion of the biodiesel. Higher ash content can indicate the presence of impurities or contaminants. The nitrogen content of the biodiesel from desert date seeds is measured at 1.04 %. Nitrogen is an important element present in organic compounds, such as proteins. The nitrogen content can provide insights into the protein content of the biodiesel. The protein content of the biodiesel from desert date cake was determined to be 6.531 %. Proteins are essential macronutrients, and their presence in biodiesel can affect their nutritional value. The fat content of the biodiesel from desert date seeds is measured at 38.432%. Fat content represents the lipid content in the biodiesel. The fibre content of the biodiesel from desert date seeds is determined to be 2.158 %. The carbohydrate content of the biodiesel from desert date seeds is measured at 43.911.

CONCLUSIONS

The conclusions drawn from the experimental and optimisation process are listed below.

1. The products from the experiment were found to have biodiesel properties within ASTM standards.

2. The optimum result from the optimisation process validates the experimental data. The values of the variables obtained as optimum are close.

3. The significance and adequacy of the models were confirmed by the F-value, coefficient of correlation (R^2), Adj-R^2, and lack of fit, which were shown to be statistically adequate.

4. 98.1% yield was achieved in 120 minutes at 50 °C using 3 grams of catalyst during the experimental process, and the optimisation result predicted an optimal biodiesel yield of 86.9% at a reaction temperature of 50 °C; a reaction time of 160 minutes, with 3g catalyst dosage.

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