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# Optimization of Biodiesel Production from Waste Vegetable Oil Using Crab Shell-Derived Calcium Oxide Catalyst

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## ABSTRACT

The growing demand for renewable and sustainable energy sources has prompted interest in producing biodiesel from used vegetable oils, yielding both environmental and economic benefits. This study investigated the production and optimization of biodiesel from waste vegetable oil, specifically Arachis oil, using a heterogeneous catalyst: Calcium oxide derived from crab shells. The calcium oxide catalyst used was derived from waste crab shells through calcination at 850 °C. Transesterification of waste vegetable oil was carried out by varying catalyst loading, methanol-to-oil ratio, reaction time, and temperature. Process optimization using Response Surface Methodology with Box-Behnken Design achieved a maximum biodiesel yield of 92.48% under optimum conditions. Optimum conditions included a catalyst loading of 5.5 wt%, a reaction time of 75 minutes, a reaction temperature of 60 °C, and a methanol-to-oil ratio of 7.5 wt%. The model developed for predicting biodiesel yield showed a high coefficient of determination ($R^2$) of 0.98, indicating strong alignment between experimental and predicted values. The use of a reusable heterogeneous catalyst minimizes waste and enhances process efficiency. These findings confirm that waste vegetable oil, particularly Arachis oil, offers a viable and sustainable feedstock for high-quality biodiesel production, contributing to waste valorization and providing a renewable energy source.

**Keywords:** Optimization, biodiesel, coefficient of determination, waste vegetable oil.

## INTRODUCTION

Environmental pollution, the depletion of non-renewable fossil fuels, and global warming are the world's present problems. Finding renewable, commercially viable, and ecologically-friendly alternative energy sources is necessary to solve these difficulties. A basic necessity for human existence is energy. Compared to other renewable energy sources (such as hydraulic, eolic, and wave energy), biomass has the advantage of being chemically modifiable, generating a product structurally similar to petroleum.

The use of biodiesel as an alternative fuel has enormous potential. Many countries in the world are resorting to biodiesel technology to solve the problem of the steady rising rate of requirement for fuel arising from the reduction of the world's non-renewable fossil fuels, and environmental pollution at large [1]. The fascinating biodiesel history that is entwined with the development of fuel sources indicates that biodiesel production has been around since the 1800s. Transesterification of vegetable oil was carried out in 1853 by researchers J. Patrick and E. Duffy, who did this before Rudolf Diesel invented the diesel engine. Diesel's engine, which was originally intended to run on mineral oil, was able to run on peanut oil at the 1900 Paris Exposition, demonstrating the viability of vegetable oils as an alternative fuel source. The current renaissance of biodiesel can be understood as a realization of Diesel's 1912 remark, in which Diesel noted that 'the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, over time, as important as petroleum and the coal-tar products of the present time' [2].

Biodiesel is usually produced by a transesterification reaction of vegetable or waste oil with a low-molecular-weight alcohol, such as ethanol or methanol [3]. Biodiesel, made from vegetable oils, is becoming more popular due to its lower pollution and renewable nature compared to traditional petroleum diesel [4]. The alternative fuel, known as "biodiesel," is made of methyl esters of fatty acids that are obtained by trans-esterifying vegetable oil with methanol. In the absence of a catalyst, the transesterification reaction proceeds relatively slowly. In order to increase the reaction rate and product yield, a catalyst is required. Catalysts for transesterification can be broadly categorized into three groups: biocatalysts, heterogeneous catalysts, and homogeneous catalysts.

Enzymatic transesterification represents a viable method for the production of biodiesel, wherein the conversion process involves the use of enzymes to catalyze the reaction between triglycerides and alcohol, yielding biodiesel and glycerol as the main products. Homogeneous catalysts, in which the catalysts and the reactants were in the same phase, were the first type of catalysts utilized in transesterification. Alkali catalysts (KOH and NaOH) and acid catalysts ($H_2SO_4$ and HCl) are two types of homogeneous catalysts. Homogeneous catalysts are preferred over other catalysts on account of their cost-effectiveness, high rate of activity, and capacity to carry out reactions under mild circumstances. However, there are significant difficulties connected with using these homogeneous catalysts The primary drawbacks of homogeneous catalysts in the transesterification process include the challenges associated with catalyst separation and recovery, potential contamination of the product by the catalyst, and difficulties in recycling the catalyst for multiple reaction cycles. To address these limitations, heterogeneous catalysts, which exist in a distinct phase than the reactants, are now used as the second type of catalyst in transesterification. Heterogeneous base catalysis is the most effective method for transesterifying triglycerides into biodiesels. Heterogeneous catalysts have advantages such as reusability, improved reaction speeds and selectivity, quicker product or catalyst separation, and low cost. Metal complexes, mixed metal oxides, transition metal oxides, boron group-based catalysts, and alkali metal oxides are examples of common base heterogeneous catalysts used in transesterification.

Vegetable oils from edible plants, including rapeseed, palm, soybean, sunflower, and other oleaginous crops, are commonly used as feedstock for biodiesel manufacturing [5]. Utilizing waste cooking vegetable oil (WVO) for biodiesel production poses challenges due to its high water content and elevated levels of free fatty acids (FFAs). Moisture retention during cooking and prolonged heat exposure increase FFAs, complicating the transesterification process. Effective removal methods for water and FFAs are essential to ensure the production of high-quality biodiesel fuel. Implementing such strategies is crucial for overcoming the challenges associated with WVO utilization in biodiesel production.

Many feed stocks can be used to make biodiesel, and each has benefits and drawbacks of its own. Typical feed stocks used in the manufacturing of biodiesel include:

- Vegetable oils: One of the most popular feed stocks for the manufacturing of biodiesel is vegetable oil, which includes canola, soybean, palm, sunflower, and corn oils. These oils are usually produced by solvent extraction or pressing from plants that are high in oil.
- Algae: Algae are photosynthetic creatures that develop rapidly and have the capacity to store large amounts of oil. There are several ways to extract algae oil and turn it into biodiesel. Because of their high oil yields and ability to be grown on non-arable soil, algae are thought to be a promising feedstock for the manufacturing of biodiesel.
- Animal fats: Tallow (rendered beef or mutton fat) and yellow grease (recycled cooking oil from animal sources) can both be utilized as feed stocks for biodiesel manufacturing. These fat are a

byproduct of the meat processing and food industries. In general, biodiesel made from animal fat has a higher percentage of saturated fatty acids, such as stearic and palmitic acids, than biodiesel derived from vegetable oil. The precise makeup can change based on the kind of animal and the sources of fat.

- Waste grease: Transesterification is a method that can be used to turn waste grease from industrial processes, such as industrial food processing or biodiesel glycerol by-product streams, into biodiesel.
- Waste Cooking Oil (WCO): After the proper pretreatment and purification, waste cooking oil obtained from food processing waste or post-consumer sources can be utilized as a feedstock for the manufacturing of biodiesel. Depending on the kinds of oils and fats used in cooking, the fatty acid composition of biodiesel made from waste cooking oil might vary significantly. Saturated and unsaturated fatty acids may be present in it, with oleic and linoleic acids typically predominating.

Biodiesel feed stocks are typically derived from agricultural crops, food processing waste, and industrial byproducts. This study aligns with previous findings by El-Mashad & Zhang [6], who reported acceptable viscosity and flash point values for biodiesel produced from WVO using calcium oxide catalysts. Similarly, Zabeti, et al [7] demonstrated the efficiency of CaO in yielding biodiesel with standard-compliant properties.

The aim of this project is to produce and optimize biodiesel from waste vegetable oil, using a heterogeneous catalyst (calcium oxide).

The objectives of the study are:

1. To use a heterogeneous catalyst to carry out the transesterification processes with waste vegetable oil and methanol.
2. To ensure that the reaction takes place under the desired operational conditions.
3. To evaluate the yield of the biodiesel and the reaction circumstances.
4. To optimize biodiesel production from waste vegetable oil with Response Surface Methodology (RSM) with Box Behnken Design.

## MATERIALS AND METHODS

The feedstock, waste vegetable oil used in this experiment was obtained from a local bean-cake frying spot in Warri, Delta state. Catalyst was processed from waste crab shells in Uselu, Benin city, Edo State, Nigeria. The waste crab shells were collected from a restaurant located around Jibale market, Warri, Delta State, Nigeria. The chemicals for this experiment were obtained in a high analytical grade form and are listed as follows:

- Sulphuric acid; 98% pure, produced by Fisons, Loughborough, England
- Phenolphthalein indicator; produced by Kermel Chemicals Reagent Company Ltd, Tianjin, China.
- Methanol; 99.7% pure, produced by JHD, Shatou, Guondghuo China.
- Potassium hydroxide; 96% pure, produced by CDH, New Delhi, India.
- Ethanol; 99.7% pure, produced by JHD, Shatou, Guondghuo China.
- Benzene; 98% pure, produced by BDH Chemicals Ltd, Poole, England.

Other instruments such as weighing balance, FTIR, Flash point tester, viscometer, pycnometer, a calorimeter were used for this experiment The specific instruments are presented below:

Table 1 : Instruments and Apparatus used during the course of this experiment;

| S/n | Property | Instrument and manufacturer |
|---|---|---|
| 1 | Weighing balance | AND (A&D) FX-3000i electronic balance, Hanoi, Vietnam. |
| 2 | Stirrer | Magnetic stirrer hot plate 85-2. Kentucky, USA. |
| 3 | Density | Glass JINOTECH 50 milliliter Pycnometer (Density bottles). SciLabware Ltd, Staffordshire, UK. |
| 4 | Functional groups | FTIR-8400S, Shimadzu, Japan |
| 5 | Calcination | VF-18M SS Body muffle furnace. Luoyang, China |
| 6 | Centrifuge | High speed centrifuge CFG-16D. Hong Kong, China. |
| 7 | Flash Point tester | SYD-261-1 PMCC Flash point tester, Nanbei , Instr. Company |
| 8 | Temperature | Digital thermometer MCM-M188, Microteknik, India. |
| 9 | Calorific value | C2000 Oxygen bomb calorimeter, IKA,UK |
| 10 | Structural morphology | Thermo Scientific, X-Ray Diffractometer (XRD), Shimadzu XRD-6000 Powder diffractometer, Thermo Fisher Scientific ,USA |
| 11 | Surface morphology | Scanning Electron Microscope (SEM). BC43 Benchtop Confocal Microscope. Oxford Instrument, England. |
| 12 | Drying | Vacutherm VT 6025 Air-Dry Vacuum Oven |
| 13 | Viscosity | Capillary viscometer AIVC series, Pennsylvania, USA. |
| 14 | Time | Black stopwatch racer, Ai-12 AMAZE Instruments, Uttar Pradesh, India. |

## Experimental design

Transesterification method was used for the production of biodiesel from used cooking oil (waste vegetable oil), with the aid of a heterogeneous catalyst (calcium oxide gotten from crab shells) and the optimization of biodiesel production yield using Response Surface Methodology.

Waste vegetable oil is a byproduct of the cooking process, primarily produced during deep frying and food preparation in industrial kitchens, restaurants, and residences. It is made up of used cooking oils such as soybean, canola, sunflower, and other vegetable oils that have previously served their purpose in food preparation. Improper disposal of waste vegetable oil can cause serious environmental issues. Pouring it down drains may lead to clogged pipes and sewer blockages. In landfills, the oil can seep into the soil, contaminating both the ground and nearby water sources. This contamination can harm local ecosystems and disrupt wildlife. Proper disposal and recycling of vegetable oil are essential to prevent these problems. WVO can be recycled and repurposed in a variety of ways, the most notable being as a feedstock for biodiesel production.

## Pre-treatment of waste vegetable oil

The purpose of pre-treatment is to eliminate impurities and pollutants that can interfere with the conversion process and lower the quality of the final product. Waste vegetable oil (Plate 1) must first be filtered in order to be used for other purposes, such as fuel in a modified diesel engine or the production of biodiesel. The procedure entails getting rid of solid particles that have accumulated in the oil during cooking, such as dirt, food residue, and other debris.

Plate 1: Waste vegetable oil

The oil is heated up to 27-38 ºC so as to make filtering easier, especially if it's solidified or contains congealed fats. Warming the oil helps to reduce its viscosity, which allows smaller particles to flow more freely during filtering. The WVO is filtered through a finer mesh filter, typically between 50 and 100 microns. Multiple stages of intermediate filtration may be employed to gradually reduce pore size to ensure thorough cleansing and removal of contaminants and pollutants. This filtration stage is particularly important if the WVO will be used in sensitive applications such as biodiesel synthesis or motor fuel. After the Filtration process, the WVO is left undisturbed for an extended period of time. The heavier particles and water will sink to the bottom, and the cleaner oil can be decanted from the top. Therefore, WVO is prepared for use as a raw material in the production of biodiesel after it has been cleansed and treated through filtration.

An essential stage in the manufacturing of biodiesel is the esterification of waste vegetable oil, especially for oils with high free fatty acid (FFA) content. Using an acid catalyst, esterification transforms FFAs into esters (biodiesel), which are then refined further using transesterification. The purpose of the esterification process is to produce esters by reacting an acid (usually a carboxylic acid) with an alcohol. This reaction typically occurs in the presence of an acid catalyst, like sulfuric acid, to speed up the process. If there is a significant FFA level in the WVO, then the acid esterification step is required. FFAs are reduced through this mechanism to a level appropriate for transesterification catalyzed by bases [8]. The following processes [9] were used for the esterification of the WVO used in these experiment:

- First, the waste vegetable oil was heated to around 50-60 °C, which is the optimal temperature for the esterification reaction.
- Sulfuric acid ($H_2SO_4$), at a concentration of roughly 1% to 2% of the oil volume (500ml), was utilized as a catalyst after the oil had been heated to the optimal temperature.
- The acid catalyst was mixed with an alcohol, methanol ($CH_3OH$), in a ratio of 2.5:0.1 (methanol to oil), that is 25% methanol and 1% sulfuric acid of the oil volume (500ml).
- The acid-alcohol mixture was added to the heated waste vegetable oil (WVO). To ensure thorough mixing a Magnetic stirrer hotplate was used to achieve uniform dispersion of the catalyst and methanol in the oil.
- The mixture was heated and regulated at 50-60 °C for about 2 hours. During this period, FFAs are transformed into methyl esters (FAME) and water.

$$\text{FFAs} + \text{Methanol } (CH_3OH) \rightarrow \text{Methyl Ester (FAME)} + \text{Water } (H_2O)$$

- Titration method was used to measure the FFA content and track the course of the esterification reaction. The objective was to lower the FFA content to less than 1% so that the oil can proceed to the next stage, base-catalyzed transesterification.
- After the esterification procedure is finished, the mixture of methyl esters (FAME) and water was separated using a separation funnel.
- The mixture was let to settle for a few hours following the reaction. The water in the mixture settled to the bottom of the container since it is denser than oil. The water at the bottom was carefully separated from the upper layer, which is made up of the methyl esters and oil.

With the esterification process completed and the free fatty acids minimized, the waste vegetable oil was now ready for the transesterification process, which will transform it into biodiesel.

### Preparation of heterogeneous catalyst

Preparation procedures can have a considerable impact on the catalyst's characteristics and performance. The heterogeneous catalyst used during this experiment is calcium oxide (CaO) after calcination process of crab shells in a muffle furnace.

### Pre-treatment of crab shell

The pre-treatment process is important for eliminating contaminants and preparing the crab shells (Plate 2) for subsequent processing. As it involves purifying the shells of contaminants and getting them ready for additional processing, the pre-treatment procedure is an essential part of the crab shell processing process. This phase entails washing to get rid of surface dirt and debris. After the crab shells are collected, the shells are sorted, non-shell components include residual crab flesh, various organic wastes, and non-crustacean debris. The crab shells are initially rinsed, the initial rinsing was brief, just enough to dislodge and remove surface debris, using clean water. The first stage in the rinsing process is to remove loose debris from the crab shells' surface, such as sand, mud, and any remaining organic material. This prevents contamination and makes future cleaning measures more effective. To clean the crab shells thoroughly, the shells are sprayed with water and the rinsing was done manually. Grease, proteins, and other organic materials can be eliminated from the water by adding detergents or surfactants. These disinfectants aid in the more efficient breakdown and dissolution of contaminants. After rinsing the crab shells, they are immersed in warm water which helps the effectiveness of cleaning agents and help dissolve organic residues. After properly washing the shells, the crab shells are dried before proceeding with the next steps in the pre-treatment procedure.

Plate 2: Crab shells

Drying reduces microbial development and makes the shells easier to handle. The pre-treatment of the crab shells is very important so as to make the shells ready for the next steps to efficiently convert the shells into the heterogeneous catalyst to be used for these experiment.

### Calcination of crab shells

Crab shells are high in calcium carbonate and organic material, particularly chitin (a biopolymer). Calcination is a high-temperature process that decomposes these materials, producing calcium oxide and other byproducts. Crab shells contain a substantial quantity of calcium carbonate, which gives them structural rigidity. A natural polymer, chitin is the second major component of crab shells, contributing to their flexibility. The following steps were followed in the calcination of the crab shells [10];

- Using a hammer, the dry crab shells are manually smashed into smaller pieces, increasing the surface area and to enable an effective calcination process.
- The broken crab shells are put into a muffle furnace and it was heated up at a temperature of 850 ºC for a period of 2 hours. At this temperature, the organic substance (chitin, proteins) in the shells has broken down and volatilized. When these materials break down, volatile organic molecules like $CO_2$, water vapor, and some gases are released.

$$CaCO_{3\,(s)} \xrightarrow{\text{Heat}} CaO_{(s)} + CO_{2\,(g)}$$

- After 2 hours, it was taken out and crushed using a laboratory pestle and mortar ( Plate 3) into small pieces and into granular form.

- The ground compound was sieved using a mesh (net wire mesh). For fine grain, the powderly components were sieved into a plate and ground once again.
- The grinding and sieving were done repeatedly to ensure the crab shell particles are ground into a fine powder form (Plate 4). The particles that did not pass through the mesh is ground repeatedly and sieved till a fine powder is achieved as the final product.
- This process was repeated 5-7 times to ensure all particles are grounded into a fine powder.

Plate 3: Pestle and Mortar

Plate 4: Ground powder

- The fine powder was put into a crucible and introduced to the muffle furnace for an hour.

The end product is calcium oxide, which served as the heterogeneous catalyst in this experiment in the transesterification of waste vegetable oil.

**Transesterification process**

The transesterification process is a chemical reaction that converts one ester into another by transferring the organic groups (R groups) of an alcohol and an ester. A triglyceride (fat/oil) and an alcohol (generally methanol or ethanol) react in the presence of a catalyst [11]. The steps and procedures [12] were followed during this experiment;

- Approximately 50 mL of oil sample was weighed using a weighing balance and a beaker,
- The oil sample was weighed into the beaker after it was cleaned, and also the scale was zeroed to avoid weighing errors.
- The allocated sample of heterogeneous catalyst (powdered CaO) for the first run (1wt% = 0.5g) was weighed using the weighing balance, after which the methanol (3 wt% = 5.9 g) is weighed into another beaker and covered so that it will not evaporate due to its volatility.

- The weighed oil sample (50 mL) was poured into a conical flask and placed on the magnetic stirrer hot plate to heat it up to the temperature allocated or specified for the first run, which is 60 ºC.
- After the oil sample has been heated up to the specified temperature of 60 ºC, the methanol and catalyst are mixed and poured into the heated oil sample and stirred effectively, allowed to react for a specified time of the first run (75 minutes), the experimental run is timed using a stop watch and was observed from time to time.
- After it has reacted for 75 minutes with the introduction of the heterogeneous catalyst, the mixture was separated using a centrifugal spin (Plate 5). The by-product gotten is glycerol and the main product is the biodiesel which floats on top and is poured into another beaker for storage.

Plate 5: Centrifugal spin

- The runs (Plate 6) are repeated 30 times with their allocated proportions of reacting materials. The experimental data (Table 2) for each run and with different factors taken into account which includes the catalyst ratio to the weighed oil sample of 50 mL, the reaction time, the temperature of the experiment, the methanol ratio so as to get the final biodiesel yield.

The data used were gotten from the design of the experiment which were inputted into a software called Design Expert, using BBD (Box Behnken Design) to optimize the biodiesel yield to know the best input variables that will lead to a maximum biodiesel yield.

Plate 6*:* Biodiesel experiment Set up.

## RESULTS AND DISCUSSION

The experimental steps and procedures were followed in order to achieve the results which show the experimental runs with combined effect of the four different variables (Temperature, Catalyst Load, Methanol ratio and the Time of Reaction) on amount of Biodiesel yield (wt %) using a model, a Box Behnken Design. In this study, 30 experimental runs were carried out. The experiments were conducted at random to prevent systematic errors. The experimental results are presented in Table 2.

Table 2: Experimental Design matrix and biodiesel yield results for optimization of waste vegetable oil transesterification using Box-Behnken Design (BBD);

| Std. | RUN | FACTOR 1 A: Catalyst (wt %) | FACTOR 2 B: Reaction time (min) | FACTOR 3 C:Temperature (ºC) | FACTOR 4 D: Methanol (wt %) | RESPONSE 1 BIODIESEL YIELD (wt %) |
|---|---|---|---|---|---|---|
| 9 | 1 | 1 | 75 | 60 | 3 | 22.47 |
| 14 | 2 | 5.5 | 120 | 40 | 7.5 | 37.23 |
| 2 | 3 | 10 | 30 | 60 | 7.5 | 33.02 |
| 5 | 4 | 5.5 | 75 | 40 | 3 | 47.83 |
| 29 | 5 | 5.5 | 75 | 60 | 7.5 | 92.48 |
| 25 | 6 | 5.5 | 75 | 60 | 7.5 | 85.48 |
| 22 | 7 | 5.5 | 120 | 60 | 3 | 37.61 |
| 18 | 8 | 10 | 75 | 40 | 7.5 | 35.34 |
| 11 | 9 | 1 | 75 | 60 | 12 | 45.62 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 28 | 10 | 5.5 | 75 | 60 | 7.5 | 92.48 |
| 20 | 11 | 10 | 75 | 80 | 7.5 | 35.46 |
| 23 | 12 | 5.5 | 30 | 60 | 12 | 47.41 |
| 15 | 13 | 5.5 | 30 | 80 | 7.5 | 21.04 |
| 8 | 14 | 5.5 | 75 | 80 | 12 | 54.36 |
| 16 | 15 | 5.5 | 120 | 80 | 7.5 | 44.57 |
| 4 | 16 | 10 | 120 | 60 | 7.5 | 34.04 |
| 12 | 17 | 10 | 75 | 60 | 12 | 43.41 |
| 17 | 18 | 1 | 75 | 40 | 7.5 | 23.09 |
| 1 | 19 | 1 | 30 | 60 | 7.5 | 13.42 |
| 26 | 20 | 5.5 | 75 | 60 | 7.5 | 92.48 |
| 7 | 21 | 5.5 | 75 | 40 | 12 | 49.69 |
| 3 | 22 | 1 | 120 | 60 | 7.5 | 32.84 |
| 27 | 23 | 5.5 | 75 | 60 | 7.5 | 92.48 |
| 6 | 24 | 5.5 | 75 | 80 | 3 | 30.34 |
| 13 | 25 | 5.5 | 30 | 40 | 7.5 | 34.72 |
| 21 | 26 | 5.5 | 30 | 60 | 3 | 34.71 |
| 24 | 27 | 5.5 | 120 | 60 | 12 | 57.89 |
| 30 | 28 | 5.5 | 75 | 60 | 7.5 | 92.48 |
| 10 | 29 | 10 | 75 | 60 | 3 | 46.06 |
| 19 | 30 | 1 | 75 | 80 | 7.5 | 25.57 |

### Optimization of the process parameters using RSM

This study's goal is to maximize the biodiesel yield through the use of a Box-Behnken Design together with Response Surface Methodology. Temperature, methanol to oil ratio, catalyst loading, and reaction duration are the four numerical parameters chosen for optimization. Biodiesel yield is the response that is being optimized. The study aimed to identify the optimal conditions for maximizing biodiesel yield using a Box-Behnken design. This design typically involves three levels for each factor and requires fewer experimental runs compared to full factorial designs. It consists of a combination of factorial points and center points, arranged to effectively evaluate the interactions between variables [13].

## Model fitting and Analysis of Variance (ANOVA) for biodiesel yield

The ANOVA results indicated the significance of the model in predicting biodiesel yield. The $R^2$ value was close to 1, indicating a good fit of the model to the experimental data. The ANOVA results is shown in Table 3.

Table 3: Response 1: Biodiesel Yield

| SOURCE | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Model | 16922.65 | 14 | 1208.76 | 163.32 | < 0.0001 | significant |
| A-Catalyst loading | 344.76 | 1 | 344.76 | 46.58 | < 0.0001 | |
| B-Reaction Time | 298.60 | 1 | 298.60 | 40.35 | < 0.0001 | |
| C-Temperature | 22.85 | 1 | 22.85 | 3.09 | 0.0993 | |
| D-Methanol : Oil | 524.83 | 1 | 524.83 | 70.91 | < 0.0001 | |
| AB | 84.64 | 1 | 84.64 | 11.44 | 0.0041 | |
| AC | 1.39 | 1 | 1.39 | 0.1881 | 0.6706 | |
| AD | 166.41 | 1 | 166.41 | 22.48 | 0.0003 | |
| BC | 110.46 | 1 | 110.46 | 14.93 | 0.0015 | |
| BD | 14.36 | 1 | 14.36 | 1.94 | 0.1839 | |
| CD | 122.77 | 1 | 122.77 | 16.59 | 0.0010 | |
| $A^2$ | 7858.62 | 1 | 7858.62 | 1061.83 | <0.0001 | |
| $B^2$ | 5800.05 | 1 | 5800.05 | 783.69 | <0.0001 | |
| $C^2$ | 5276.94 | 1 | 5276.94 | 713.00 | <0.0001 | |
| $D^2$ | 2214.52 | 1 | 2214.52 | 299.22 | <0.0001 | |
| **Residual** | 111.01 | 15 | 7.40 | | | |
| Lack of Fit | 70.18 | 10 | 7.02 | 0.8594 | 0.6095 | not significant |
| Pure Error | 40.83 | 5 | 8.17 | | | |
| **Cor Total** | 17033.67 | 29 | | | | |

Factor Coding is **coded**

Sum of Squares is **Type III**

Factors such as methanol to oil ratio, temperature, and reaction time were statistically significant.

## Fit summary

The fit summary describes how well the model explains the variation in the answer. Key measures including R-squared, Adjusted R-squared, and Predicted R-squared demonstrate the model's accuracy and predictive capabilities, with higher values indicating a better fit. Furthermore, p-values for each term show which factors and interactions have a substantial impact on the response, guiding improvements for better model accuracy and relevance. The Fit summary is shown in Table 4.

Table 4: Response 1: Biodiesel Yield

| Source | Sequential P-value | Lack of Fit p-value | Adjusted $R^2$ | Predicted $R^2$ | |
|---|---|---|---|---|---|
| Linear | 0.7573 | $< 0.0001$ | -0.0789 | -0.1245 | |
| 2FI | 0.9951 | $< 0.0001$ | -0.3748 | -0.4849 | |
| Quadratic | $< 0.0001$ | 0.6095 | 0.9874 | 0.9728 | Suggested |
| Cubic | 0.3067 | 0.9839 | 0.9900 | 0.9943 | Aliased |

The quadratic model is recommended for estimating biodiesel yield due to its great fit, significant terms, high adjusted and anticipated $R^2$ values, and non-significant lack of fit, preventing overfitting.

**The ANOVA result**

Table 4 shows the ANOVA findings, and all of the model variables are significant. The Model F-value of 163.32 indicates that the model is significant. There is just a 0.01% chance that an F-value this large will occur due to noise. The P-values served as a means to evaluate the significance of each coefficient, which was essential for understanding the interactions among the test variables [14]. P-values less than 0.0500 indicate model terms are significant. In this case A, B, D, AB, AD, BC, CD, $A^2$, $B^2$, $C^2$, $D^2$ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 0.86 implies the Lack of Fit is not significant relative to the pure error. There is a 60.95% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good, we want the model to fit.

Table 5: Fit Statistics

| | | | |
|---|---|---|---|
| Std. Dev. | 2.72 | $R^2$ | 0.9935 |
| Mean | 47.85 | Adjusted $R^2$ | 0.9874 |
| C.V % | 5.68 | Predicted $R^2$ | 0.9728 |
| | | Adeq Precision | 40.4878 |

The Predicted $R^2$ of 0.9728 is in reasonable agreement with the Adjusted $R^2$ of 0.9874; i.e. the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 40.488 indicates an adequate signal. This model can be used to navigate the design space.

**Model equation in terms of coded factors**

For the biodiesel optimization experiment using Box-Behnken Design (BBD), the model equation in terms of coded factors usually takes the form of a quadratic equation. In a second-order polynomial, it depicts the relationship between the independent variables and the response (biodiesel yield). The table showing the Coefficient of the Coded Factor is shown below;

Table 6: Coefficients in Terms of Coded Factor

| Factor | Coefficient Estimate | Df | Standard Error | 95% Cl Low | 95% Cl High | VIF |
|---|---|---|---|---|---|---|
| Intercept | 91.31 | 1 | 1.11 | 88.95 | 93.68 | |
| A-Catalyst loading | 5.36 | 1 | 0.7853 | 3.69 | 7.03 | 1.0000 |
| B-Reaction time | 4.99 | 1 | 0.7853 | 3.31 | 6.66 | 1.0000 |
| C-Temperature | -1.38 | 1 | 0.7853 | -3.05 | 0.2939 | 1.0000 |
| D-Methanol : Oil | 6.61 | 1 | 0.7853 | 4.94 | 8.29 | 1.0000 |
| AB | -4.60 | 1 | 1.36 | -7.50 | -1.70 | 1.0000 |
| AC | -0.5900 | 1 | 1.36 | -3.49 | 2.31 | 1.0000 |
| AD | -6.45 | 1 | 1.36 | -9.35 | -3.55 | 1.0000 |

| | | | | | | |
|---|---|---|---|---|---|---|
| BC | 5.25 | 1 | 1.36 | 2.36 | 8.15 | 1.0000 |
| BD | 1.90 | 1 | 1.36 | -1.00 | 4.79 | 1.0000 |
| CD | 5.54 | 1 | 1.36 | 2.64 | 8.44 | 1.0000 |
| $A^2$ | -33.85 | 1 | 1.04 | -36.07 | -31.64 | 1.05 |
| $B^2$ | -29.08 | 1 | 1.04 | -31.30 | -26.87 | 1.05 |
| $C^2$ | -27.74 | 1 | 1.04 | -29.96 | -25.53 | 1.05 |
| $D^2$ | -17.97 | 1 | 1.04 | -20.19 | -15.76 | 1.05 |

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. A variance inflation factor (VIF) measures the degree of multicollinearity in regression analysis. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-collinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable. The coding model equation for the biodiesel yield can be expressed as follows using the estimations of the coefficients for each element and interaction:

$$Y=91.313+5.36A+4.988B-1.38C+6.613D-4.6AB-0.59AC-6.45AD+5.255BC$$
$$+1.895BD+5.54CD-33.853A^2-29.083B^2-27.741C^2-17.971D^2.$$

Where

Y is the biodiesel yield,

A is the coded factor for catalyst loading,

B is the coded factor for reaction time,

C is the coded factor for temperature,

D is the coded factor for methanol-to-oil ratio,

AB, AC, AD, BC, BD, and CD represent interaction terms between respective factors,

$A^2$, $B^2$, $C^2$, and $D^2$ are the quadratic terms for each factor.

This equation predicts biodiesel yield based on the selected coded factors and their interactions. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

### Model graphs

Model graphs are essential visual tools in data analysis and optimization studies, such as those for biodiesel production. They display relationships between variables, helping to illustrate how different factors affect biodiesel yield and highlight optimal conditions for maximum efficiency.

### Perturbation plot for biodiesel yield sensitivity

The sensitivity of the biodiesel yield to various parameters, including catalyst concentration, reaction temperature, methanol-to-oil molar ratio, and reaction time, is displayed in this plot (Figure 1). A factor is represented by each line, and the slope shows how much of an impact it has on yield. Greater sensitivity is indicated by steeper slopes, which show which variables, when modified around the baseline, have the most effects on yield. The plot is shown below:

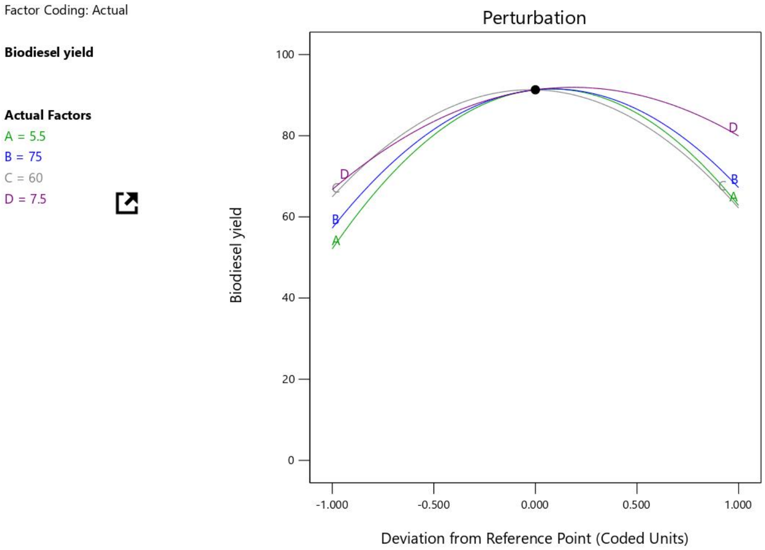

Figure 1: Perturbation plot of factors affecting biodiesel yield

### Effect of single process factor on the yield of biodiesel

This plot (Figure 2) shows how varying the catalyst load, represented as a weight percentage (wt %), affects biodiesel yield. The biodiesel yield initially rises as the catalyst load increases due to increased reaction speeds. However, beyond the optimal limit, increasing catalyst load may cause side reactions such as soap production, reducing yield.

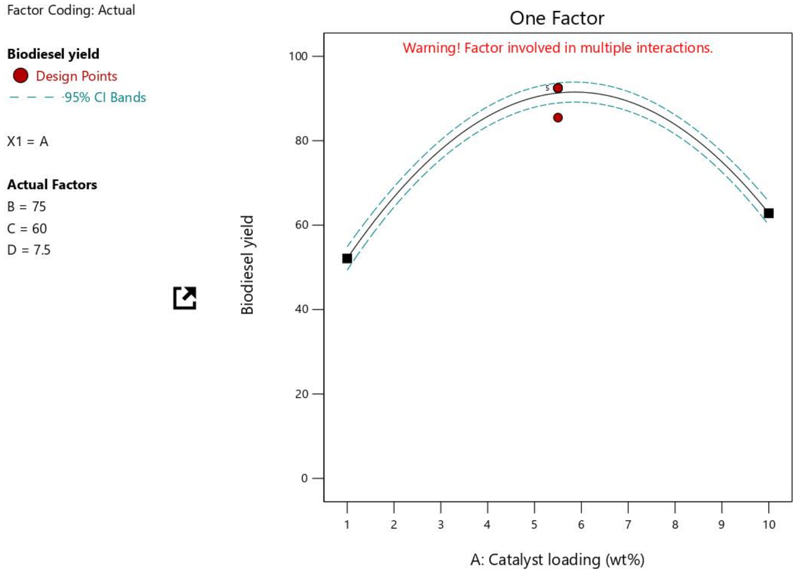

Figure 2 Effect of Catalyst Load (wt %) on Biodiesel Yield

## Contour plot for yield optimization

This contour plot (Figure 3) visualizes the interaction between two key factors, such as catalyst load and temperature, and their combined impact on biodiesel yield. The contour lines indicate yield levels, with the optimal region highlighted where maximum yield is achieved.

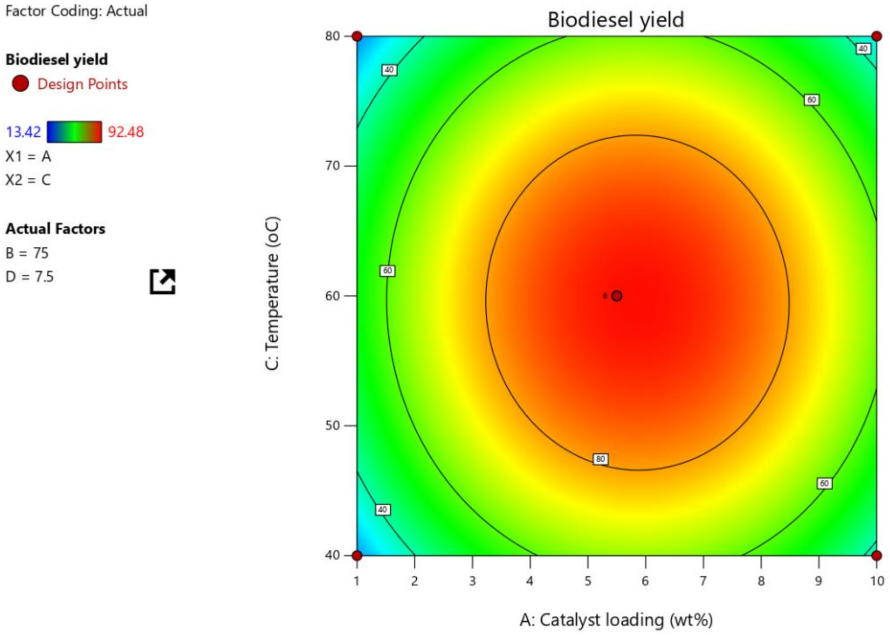

Figure 3: Contour plot of yield vs. Catalyst load and reaction temperature

## 3D Surface model for biodiesel yield

This 3D surface model visualizes the relationship between various reaction conditions (such as temperature, catalyst concentration, and reaction time) and the resulting biodiesel yield. Peaks and valleys on the surface illustrate optimal and suboptimal regions, helping identify the most favorable conditions for maximizing biodiesel production. Figures 4 and 5- are some of the 3D surface models:

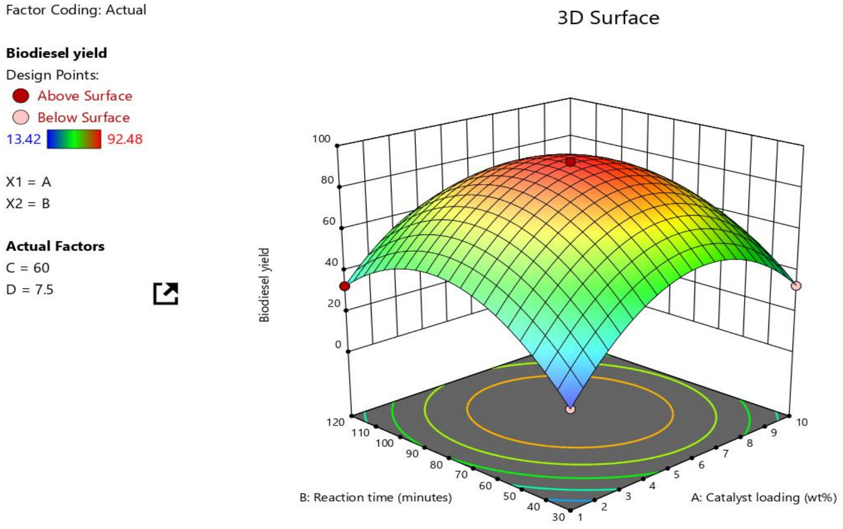

Figure 4: Impact of reaction time (minutes) and Catalyst load (wt %) on biodiesel yield

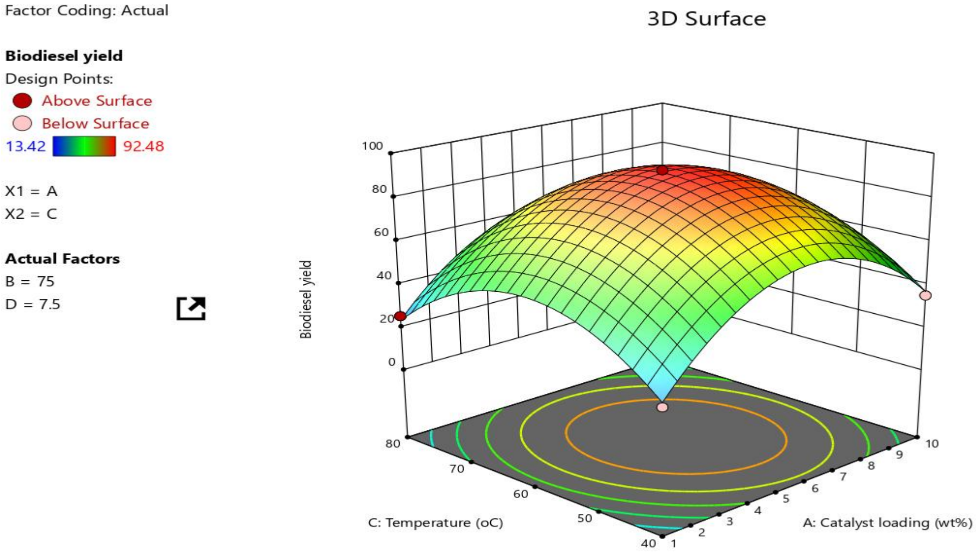

Figure 5: Impact of temperature (ºC) and Catalyst load (wt %) on biodiesel yield

## Model Diagnostics

| Run Order | Actual Value | Predicted Value | Residual | Leverage | Internally Studentized Residuals | Externally Studentized Residuals | Cook's Distance | Influence on Fitted Value DFFITS | Standard Order |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 22.47 | 21.07 | 1.40 | 0.583 | 0.800 | 0.790 | 0.060 | 0.934 | 9 |
| 2 | 37.23 | 35.60 | 1.63 | 0.583 | 0.927 | 0.922 | 0.080 | 1.091 | 14 |
| 3 | 33.02 | 33.35 | -0.3283 | 0.583 | -0.187 | -0.181 | 0.003 | -0.214 | 2 |
| 4 | 47.83 | 45.91 | 1.92 | 0.583 | 1.094 | 1.102 | 0.112 | 1.304 | 5 |
| 5 | 92.48 | 91.31 | 1.17 | 0.167 | 0.470 | 0.457 | 0.003 | 0.204 | 29 |
| 6 | 85.48 | 91.31 | -5.83 | 0.167 | -2.349 | -2.854 | 0.074 | -1.276 | 25 |
| 7 | 37.61 | 40.74 | -3.13 | 0.583 | -1.782 | -1.939 | 0.296 | -2.294(1) | 22 |
| 8 | 35.34 | 37.05 | -1.71 | 0.583 | -0.973 | -0.971 | 0.088 | -1.149 | 18 |
| 9 | 45.62 | 47.19 | -1.57 | 0.583 | -0.895 | -0.889 | 0.075 | -1.052 | 11 |
| 10 | 92.48 | 91.31 | 1.17 | 0.167 | 0.470 | 0.457 | 0.003 | 0.204 | 28 |
| 11 | 35.46 | 33.11 | 2.35 | 0.583 | 1.339 | 1.378 | 0.167 | 1.631 | 20 |
| 12 | 47.41 | 43.99 | 3.42 | 0.583 | 1.948 | 2.177 | 0.354 | 2.576(1) | 23 |
| 13 | 21.04 | 22.87 | -1.83 | 0.583 | -1.040 | -1.043 | 0.101 | -1.234 | 15 |
| 14 | 54.36 | 56.38 | -2.02 | 0.583 | -1.147 | -1.161 | 0.123 | -1.373 | 8 |
| 15 | 44.57 | 43.35 | 1.22 | 0.583 | 0.693 | 0.681 | 0.045 | 0.806 | 16 |
| 16 | 34.04 | 34.13 | -0.0850 | 0.583 | -0.048 | -0.047 | 0.000 | -0.055 | 4 |
| 17 | 43.41 | 45.01 | -1.60 | 0.583 | -0.913 | -0.907 | 0.078 | -1.073 | 12 |
| 18 | 23.09 | 25.15 | -2.06 | 0.583 | -1.173 | -1.189 | 0.128 | -1.406 | 17 |
| 19 | 13.42 | 13.43 | -0.0083 | 0.583 | -0.005 | -0.005 | 0.000 | -0.005 | 1 |
| 20 | 92.48 | 91.31 | 1.17 | 0.167 | 0.470 | 0.457 | 0.003 | 0.204 | 26 |
| 21 | 49.69 | 48.06 | 1.63 | 0.583 | 0.931 | 0.927 | 0.081 | 1.096 | 7 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 22 | 32.84 | 32.61 | 0.2350 | 0.583 | 0.134 | 0.129 | 0.002 | 0.153 | 3 |
| 23 | 92.48 | 91.31 | 1.17 | 0.167 | 0.470 | 0.457 | 0.003 | 0.204 | 27 |
| 24 | 30.34 | 32.07 | -1.73 | 0.583 | -0.984 | -0.983 | 0.090 | -1.163 | 6 |
| 25 | 34.72 | 36.14 | -1.42 | 0.583 | -0.806 | -0.796 | 0.061 | -0.942 | 13 |
| 26 | 34.71 | 34.55 | 0.1575 | 0.583 | 0.090 | 0.087 | 0.001 | 0.103 | 21 |
| 27 | 57.89 | 57.76 | 0.1342 | 0.583 | 0.076 | 0.074 | 0.001 | 0.087 | 24 |
| 28 | 92.48 | 91.31 | 1.17 | 0.167 | 0.470 | 0.457 | 0.003 | 0.204 | 30 |
| 29 | 46.06 | 44.69 | 1.37 | 0.583 | 0.783 | 0.772 | 0.057 | 0.913 | 10 |
| 30 | 25.57 | 23.57 | 2.00 | 0.583 | 1.139 | 1.152 | 0.121 | 1.363 | 19 |

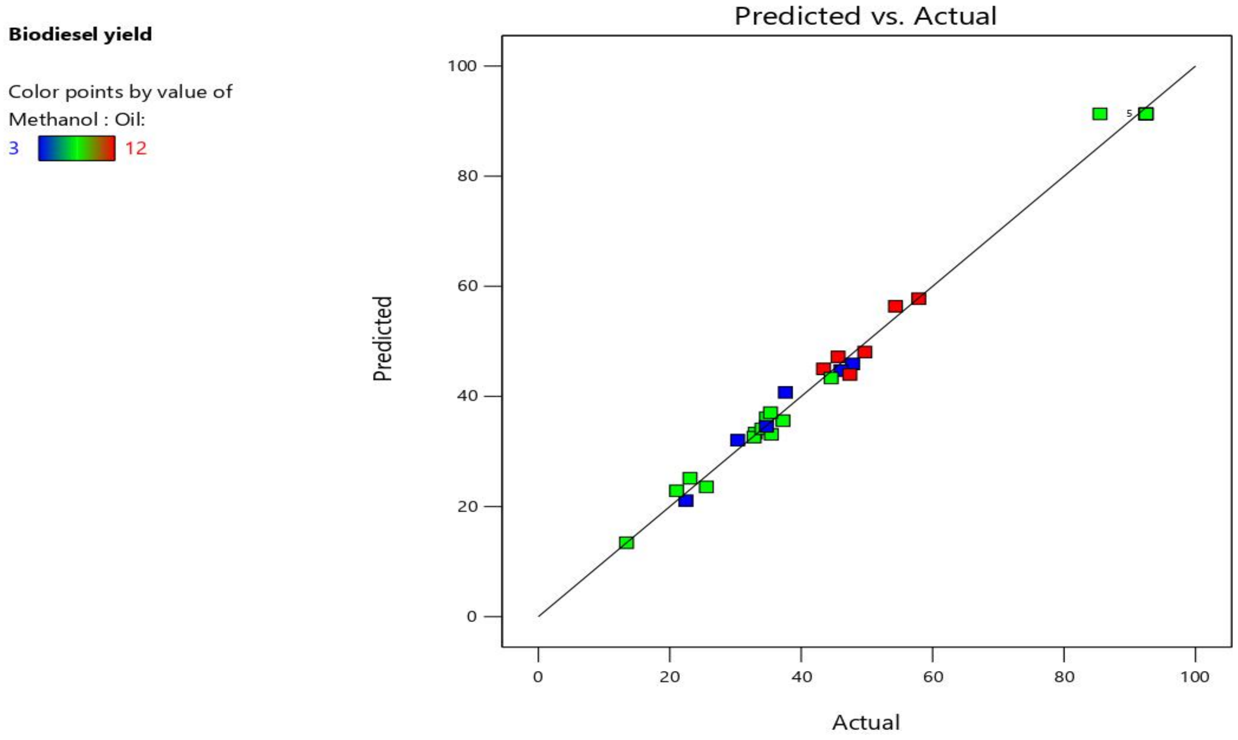

Figure 6: Graph of Predicted vs Actual

## Numerical optimization of reaction parameters for biodiesel yield

Using Box Behnken design in a response surface methodology, the numerical optimization yielded the optimal conditions for the input variables. Figure 7 shows the overall optimal setting for the FAME production process. The catalyst load of 5.5 wt %, the reaction temperature of 60°C, the reaction duration of 75 minutes, and the methanol to oil ratio of 7.5:1 were the ideal parameters. 91.3133wt% weight percent of WVO biodiesel could be produced in these conditions.

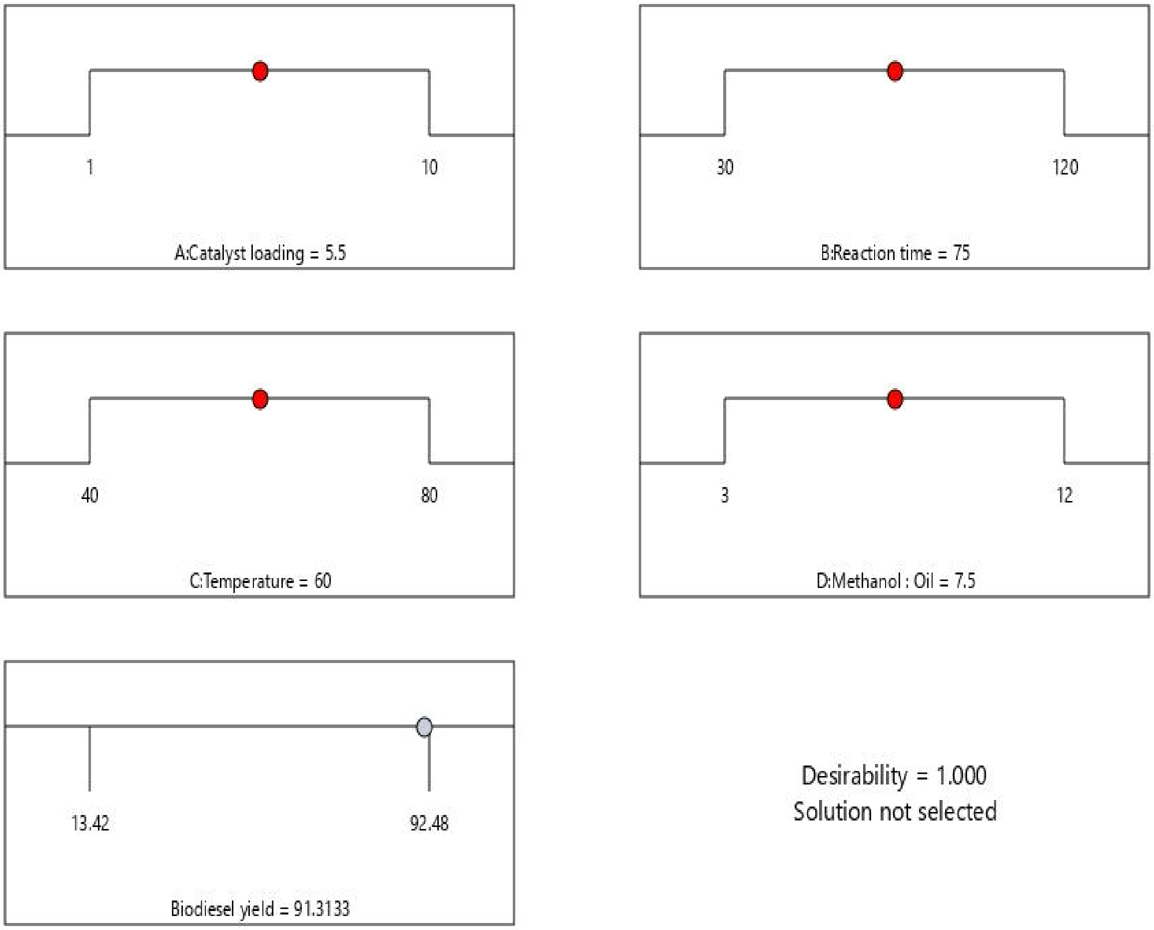

Figure 7: Optimization of the biodiesel process

### Box-Behnken optimization cube for biodiesel yield

This Box-Behnken Design explores the optimal conditions for biodiesel yield by testing different levels of catalyst loading, temperature, and methanol-to-oil ratio (with a constant factor held at 75), revealing that balanced, mid-range conditions maximize yield while extreme combinations can reduce efficiency (Figure 8). Each red dot represents a specific experimental condition with combinations of, Catalyst Loading (A): at levels 1% (A−) and 10% (A+), Temperature (C): at 40°C (C−) and 80°C (C+), Methanol-to-Oil Ratio (D): at ratios of 3 (D−) and 12 (D+). The anticipated biodiesel yield values are labeled at each corner, with the maximum yield (24.455) near the center, indicating that mid-range conditions boost efficiency, whilst extreme combinations (such as -0.345 yield) show lesser efficiency.

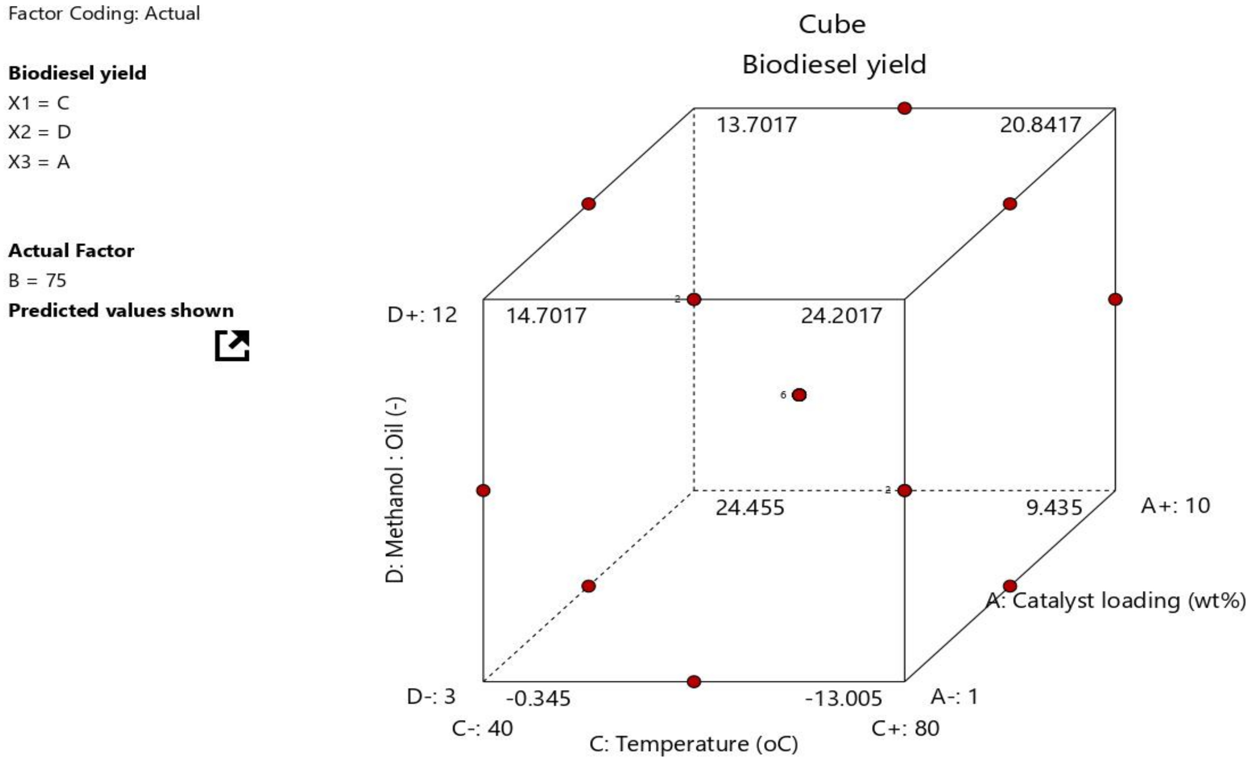

Figure 8: Box-Behnken optimization cube for biodiesel yield

## CONCLUSION AND RECOMMENDATION

This research successfully demonstrated the feasibility of biodiesel production from waste vegetable oil (Arachis oil) using calcium oxide derived from crab shells as a heterogeneous catalyst. The optimized biodiesel production in this study was achieved under specific conditions; a catalyst loading of 5.5 wt%, a reaction time of 75 minutes, a reaction temperature of 60 °C, and a methanol-to-oil ratio of 7.5 wt%. These parameters were carefully selected using Response Surface Methodology to maximize yield and ensure quality. Utilizing the Box-Behnken Design for optimization, a significant yield of 92.48% was achieved. The ANOVA results indicated that reaction temperature, reaction time, and methanol-to-oil ratio all have a significant influence on biodiesel yield.

This study not only emphasizes the environmental benefits of converting waste oil into renewable fuel, but it also shows the economic and practical feasibility of using a heterogeneous catalyst to improve process efficiency and reduce waste. This study provides a feasible route to cleaner, more sustainable energy solutions by addressing important facets of biodiesel synthesis, such as feedstock preparation, catalyst efficiency, and process optimization. The research highlights biodiesel's potential as a renewable, low-emission alternative to petroleum diesel, offering a viable solution for both waste management and sustainable fuel production. Unlike previous studies, this research utilizes calcium oxide derived from waste crab shells, offering a sustainable and low-cost alternative catalyst.

### Recommendations

The successful production and optimization of biodiesel from waste vegetable oil using a calcium oxide catalyst derived from crab shells has demonstrated both the feasibility and potential of this approach as a renewable energy source. However, to further enhance the efficiency, scalability, and environmental impact of biodiesel production, additional investigations are recommended. The following suggestions aim to improve biodiesel yield, reduce production costs, and ensure environmental sustainability:

- Feedstock variety and quality Control: The use of non-edible or other waste oils as substitute feed stocks. Examining the effects of pre-treatment procedures and oil quality can improve the production and stability of biodiesel. A systematic pre-treatment procedure for waste oils should be established in order to improve the uniformity of the quality of biodiesel.

- Catalyst reusability and efficiency Improvement: The calcium oxide catalyst used in these study was made from crab shells, future studies might look at the catalyst's lifetime and recyclability over a number of reaction cycles. This could assist in assessing calcium oxide's viability as an economical and sustainable choice for the large-scale manufacturing of biodiesel.
- Evaluation of byproducts: Glycerol, a byproduct of biodiesel synthesis, has potential applications in medicine and cosmetics. Future research should focus on the purification and marketing of glycerol, which would increase the economic sustainability of biodiesel manufacturing.

This study encourages the wider use of biodiesel as a low-emission fuel substitute, which helps with waste minimization and energy diversification. Its usefulness may be improved by further research into scaling this approach, which would make it a useful model for producing fuel sustainably and in line with both economic and environmental objectives.

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