Indian Journal of Chemical Technology
Vol. 32, September 2025, pp. 664-675
DOI: 10.56042/ijct.v32i5.11956

# Reaction optimization of biodiesel production from synthesized W/K/CaO catalyst using food waste: A sustainable waste to energy solution

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*Received 1 July 2024; accepted 11 August 2025*

The advancement of using food waste for energy conversion has attracted considerable attention among researchers. The present study investigates the sustainable way of biodiesel production using food waste as a green and innovative solution that aids in both the preservation of the environment and the efficiency of resource utilization. In this work, the sodium salt of tungstic acid and $K^+$ were coated over eggshells-derived CaO to convert the waste cooking oil (WCO) to biodiesel. The synthesized catalyst has been subjected to various characterization techinques such as XRD, FT-IR and SEM-EDX analysis. Response surface methodology approach is used to optimize the important parameters of transesterification reaction. The optimized conditions to transesterify waste cooking oil with synthesized W/K/CaO is found to be of 4 wt% of synthesized W/K/CaO catalyst, 13.7:1 ratio of methanol: oil, 90 min reaction duration and 60°C reaction temperature. The maximum biodiesel yield of 98.04% was obtained using the optimized conditions. Gas chromatography-mass spectroscopy (GC-MS) analysis and NMR studies were used to characterize the produced biodiesel. Finally, the reusability of the catalyst has also been discussed.

**Keywords:** Biodiesel, Egg shell, Food waste, Waste cooking oil, Waste to Energy, W/K/CaO catalyst

## Introduction

The demand for bioenergy is a challenge faced by the entire global community. So, the need for bioenergy is becoming increasingly important. A total of 557.10 exajoules (EJ) of energy were utilized worldwide across diverse fields in 2020[1]. Over 32,018.2 million tons of carbon pollutants were discharged into the atmosphere in 2020. Fig. 1 illustrates the three countries that primarily contribute to carbon pollution. In 2020, China came at the leading position, then the United States and lastly, India. As compared to 2019, the carbon release rate declined by 7.1% and 11.6% in India and the United States, respectively. Conversely, China exhibited a 0.6% rise in release rate. Therefore, adopting sustainable energy sources will be unavoidable in the upcoming days. The growing population and industrial sector have led to a high demand for energy, driving up fossil fuel consumption and their prices worldwide. Hydrocarbon-based fuels remain essential for meeting today's energy needs[2], yet, global demand particularly in countries like India is rising sharply. Modern societies rely heavily on affordable and sustainable energy sources, but reserves of fossil fuels such as petroleum and coal are shrinking rapidly due to intensive consumption.

Moreover, the growing number of vehicles has intensified environmental harm and contributed to public health issues through the release of greenhouse gases and other pollutants. India is predicted to manufacture 60 million tonnes of biodiesel annually by 2030. Fatty acid methyl esters (FAMEs) are considered among the most promising alternatives to conventional fossil fuels. They offer a cost-effective and sustainable energy option for the future, supported by their environmental benefits such as renewability, biodegradability, low flammability, high flash point, excellent combustion efficiency and non-toxic nature[3]. Biodiesel is obtained from various oils using transesterification, micro-emulsification and pyrolysis[4]. Biodiesel is typically produced through the transesterification reaction that involves a complex multi-stage reversible chemical transformation where triglycerides found in animal fat or vegetable oil

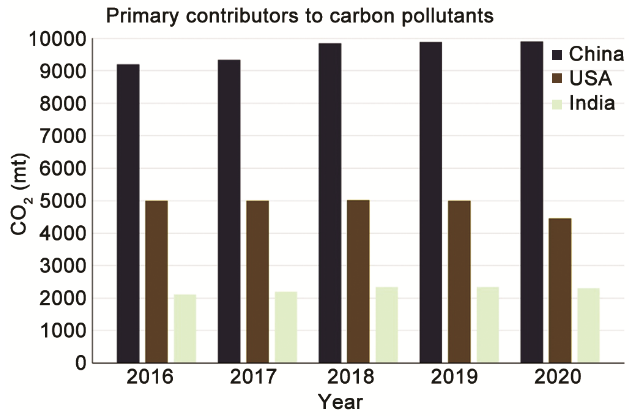


Fig. 1 — Overview of primary contributors to carbon pollutants

undergo a collision with methanol with the assistance of a catalyst, forming biodiesel and by-product glycerine. Triglycerides are first transformed into diglycerides and lower glycerides, and then converted into biodiesel and glycerol in the reaction process. Biodiesel is tested on safety and environmental pollution by standard methods, i.e., (ASTM D6751) or (EN 14214)[5].

A variety of feedstocks have been employed in biodiesel production including edible oils such as palm, sunflower, rapeseed, coconut and olive oil, as well as non-edible oils like jatropha, pongamia, karanja and castor oil[6]. Additionally, waste vegetable oil and oils extracted from sources like microalgae have been successfully utilized for biodiesel generation[7,8]. Used cooking oil (UCO), typically obtained from frying processes in restaurants, households and industrial kitchens, is another potential feedstock[9]. As a hazardous waste, UCO requires careful management since improper disposal can cause issues such as pipe blockages when the oil solidifies. Converting UCO into biodiesel helps to overcome the waste management challenges and also in addition reduces the environmental impact. However, the physicochemical properties of UCO differ significantly from crude vegetable oils[10]. While vegetable oils are readily available and commonly used for methyl ester production, their use can increase demand and market prices for edible oils, raising concerns over competition between fuel and food resources. To address cost and sustainability issues, research has increasingly focused on low-cost feedstocks and the application of heterogeneous catalysts in biodiesel production.

Heterogeneous catalysts offer several advantages such as high efficiency, reusability, low corrosion risk, minimal effluent production and simple purification processes. In contrast, homogeneous catalysts present challenges including difficult separation and longer reaction times. Consequently, recent developments prioritize inexpensive, eco-friendly methods that utilize economical feedstocks and recyclable heterogeneous catalysts for biodiesel production.

The RSM approach was utilized to optimize the parameters for maximum biodiesel yield. The experiments followed the CCD method using the Design Expert software. Key process variables included the methanol-to-oil (m/o) ratio (denoted as factor “A”), catalyst concentration (factor “B”), and reaction time (factor “C”). The objective was to evaluate the effects of these parameters on biodiesel production. The suitable properties and activity of Li/Mo nanocatalyst, along with the properties of CaO obtained from eggshells can pave the way to the synthesis of an efficient nanocatalyst to be used in the industrial scale biodiesel production which is assumed to be the core novelty of this study. Calcium oxide (CaO) is widely applied as a catalyst due to its low cost and strong alkaline properties, and it can be sourced from a variety of raw materials.

Nevertheless, certain challenges remain in improving its catalytic performance. The active sites of CaO can become deactivated or contaminated through carbon dioxide exposure or moisture absorption. Its alkaline reactivity is associated with surface ions of low coordination, which are sensitive to changes during the calcination process[11]. To enhance its basicity, CaO is typically calcined first at 900°C and then at 600°C to produce an active form. In this study, biodiesel was synthesized from waste cooking oil (WCO) using a combination of sodium tungstate and potassium-doped CaO derived from eggshells. Characterization techniques such as XRD, SEM-EDAX and FT-IR studies were used to study the morphology and chemical properties of the synthesized catalyst. Also, the produced biodiesel was characterized using GC-MS analysis along with spectroscopic techniques. The physico-chemical properties of the biodiesel have also been analyzed for the qualitative nature of produced biodiesel.

## Experimental Section

### Materials

Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), potassium hydroxide (KOH) and methanol (99.0%) were sourced from Rankem (India), while hexane (95%) was obtained from Sigma-Aldrich. All reagents and solvents were used as received, without prior

Table 1 — Characterization of the Collected Waste Cooking Oil: Physicochemical Properties

| Properties | Experiment value |
|---|---|
| Acid number (mg KOH/g) | 1.68 |
| Density at 15 °C (kg/m$^3$) | 0.86 |
| FFA (%) | 0.84 |
| Saponification value (mg KOH/g) | 227 |

purification or distillation. Waste cooking oil (WCO), collected from the Banasthali campus canteen, was served as the primary feedstock for methyl ester production. The WCO was first filtered to remove food residues and then heated to eliminate moisture content. The physicochemical characteristics of the WCO are presented in Table 1.

## **Preparation of W/K/CaO catalyst using *eggshells***

### ***Synthesis of calcium oxide from collected eggshells***

The collected waste eggshells were first washed thoroughly with water and then dried at 120°C for 24 h. The dried shells were ground into a fine powder using a mixer blender. This powder was subsequently calcined at 900°C for 3 h in a muffle furnace to obtain calcium oxide (CaO). The resulting CaO powder was stored for use in subsequent chemical processes[12].

### ***Preparation of W/K/CaO catalyst***

In the preparation process, 10 g of CaO obtained from waste eggshells was dispersed in 40 mL of distilled water. To this, 10 mL of an aqueous KOH solution (3.5 wt.%) was added. The resultant mixture was stirred for over 3 h and then heated in an oven at 180°C for 24 h. Subsequently, 10 g of the resulting K/CaO was combined with 40 mL of distilled water, proceeded with the addition of 10 mL of sodium tungstate solution (10–25 wt.%)[13]. This mixture was again subjected to stirring at room temperature for 5 h and then heated at 120°C for 24 h before undergoing calcination at 700°C for 3 h as depicted in Fig. 2.

Calcination temperature and duration play a critical role in heterogeneous catalytic systems, as they influence catalyst morphology and performance. Sufficient calcination time promotes uniform metal oxide distribution across active sites. During the calcination process, the compounds from the raw materials such as water and hydroxyl groups are removed. The exposed metal sites, being electron-deficient, strongly attract oxygen atoms with excess electrons. A calcination temperature of 700°C was selected because it favours the formation of $WO_3$. In literature, Wan *et al.* identified that biodiesel yield reduced beyond 50% when the tri-metallic oxide catalyst ($CrWMnO_2$) was calcinated at 800°C. The authors observed that the surface area of the catalyst reduced from 4.39 m$^2$/g to 2.46 m$^2$/g at calcined temperatures of 600 and 800°C, respectively. The porosity of the catalyst was also diminished upon calcination at 800°C[14].

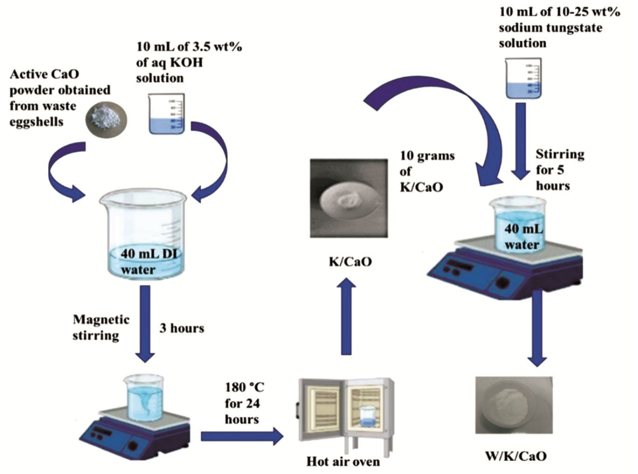


Fig. 2 — Flow on the preparation of W/K/CaO catalyst

## **Characterization of synthesized W/K/CaO catalyst from egg shells**

X-ray diffraction (XRD, PANalytical X'pert[3], Netherland) data was acquired employing copper K-alpha radiation. The measurements were observed over a 2θ range of 10 to 90° at a scanning rate of 2° per min. The phase identification was studied by comparing the obtained diffraction patterns with the standard data. The outer morphology and elements composition were studied using SEM instrument (JEOL JSM6510) coupled with EDX spectroscopy (AMETEK EDAX). The functional group analysis was carried out through FTIR instrument (Nicolet 6700, Thermo Scientific, USA). The spectra were gathered from 4000 to 400 cm$^{-1}$ to examine the chemical functionalities. KBr served as the matrix for the spectroscopic measurements.

## **Transesterification of waste cooking oil using synthesized W/K/CaO catalyst**

The transesterification reaction was done in a three-necked round-bottom flask fitted with a condenser, thermometer, oil bath and magnetic stirrer. The catalyst was first mixed with the measured volume of methanol and stirred continuously. Waste cooking oil (25 g) was then added to the mixture and reacted at the desired temperature. For optimization, the catalyst loading, methanol-to-oil (m/o) ratio and reaction time were varied to achieve maximum biodiesel yield. After the reaction, the catalyst was removed via filtration and excess methanol was recovered through heating. The filtrate was transferred into a separating funnel and allowed undisturbed for 24 h. The lower glycerol-rich layer, containing residual impurities, was drained while the upper biodiesel layer was subjected to warm water washing several times.

The conversion efficiency was calculated using the Kno the equation:

$$\text{FAMEs yield (\%)} = \{2I(\text{methoxy})/3I(\text{methylene})\} \times 100$$

The integration values for the methylene protons at 2.3 ppm and the methoxy protons at 3.6 ppm are denoted as I(methylene) and I(methoxy), respectively[15].

### Experimental design of biodiesel production from waste cooking oil

The combined effects of different process parameters on the transesterification reaction were evaluated, including reaction time (30–120 min), catalyst concentration (2–8 wt.%), and methanol-to-oil molar ratio (8.14–16.02 m/m). A statistical approach, the Central Composite Design (CCD) was utilized to optimize the reaction conditions for maximum biodiesel yield. The independent variables in the design were the molar ratio (factor "A"), catalyst loading (factor "B"), and reaction time (factor "C"). Design Expert software was used to define the experimental matrix, including two alpha levels representing the extreme values for each parameter, negative alpha ($-\alpha$) for the lowest level and positive alpha ($+\alpha$) for the highest. The software also facilitated regression analysis, and the model's validity was evaluated using analysis of variance (ANOVA). Residual analysis was performed by comparing observed and predicted values, with the expectation that the data points would align linearly on a normal probability plot.

## Results and Discussion

### Characterization of synthesized W/K/CaO catalyst

#### *XRD analysis*

X-ray diffraction (XRD) patterns for CaO derived from eggshells, K/CaO, and K/CaO impregnated with 10–25 wt.% tungsten are presented in Fig. 3. Distinct diffraction peaks at 2θ values of 34.74, 47.56, 51.56, 29.13, and 18.56° confirm the presence of CaO. Low-intensity peaks at 18.56, 34.74, 47.56, and 51.56° indicate successful potassium incorporation into the CaO structure. When tungsten loading reached 15 wt.%, faint $WO_3$ crystalline signals were detected, suggesting uniform dispersion of tungsten species across the K/CaO support. At 20 wt.%, prominent peaks appeared at 2θ values of 36.82°, 53.63°, and 31.7°, confirming tungsten phase formation. However, at 25 wt.% tungsten, a reduction in peak intensity was observed, indicating decreased catalytic activity in the transesterification reaction. Similar results were explored by Kumar and Ali[14] in the K/CaO catalyst. The bands at 2 θ values of 53.89, 37.37, and 32.18° indicated the presence of CaO at lattice spacings of 1.69, 2.39, and 2.78, respectively (JCPDS No. 821691). Likewise, Hossain *et al.* reported the 2θ values at 67.34, 53.82, 32.14, 64.18, and 37.30° that corresponds to the cubic phase of calcium oxide with miller indices of (222), (220), (111), (311), and (200), respectively (JCPDS No. 481467). The authors reported the decrease in strength of the most intense peak, indicating the deformation of the calcium oxide matrix by potassium ions[16]. In the W-Ti/$SiO_2$ catalyst, Kaur *et al.* observed the 2θ values at 23.71, 49.91, 50.55, 22.90, 34.21, 24.13, and 41.69° that corresponds to the tungsten oxide in monoclinic form (ICDD file No. 01-075-2072)[17]. Wan *et al.* observed the peaks at 2 theta values of 36.34° and 30.28°, indicating the presence of tungsten oxide ($WO_3$) in the tetragonal state[18].

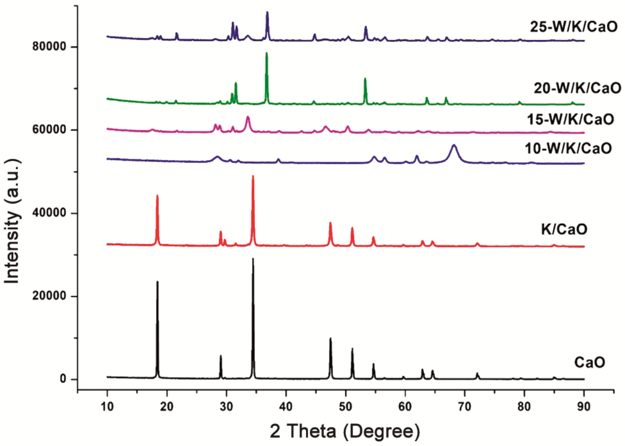


Fig. 3 — XRD patterns of CaO, K/CaO, and 10-25 wt % W/K/CaO

#### *FT-IR analysis*

The FT-IR spectroscopy method was analyzed to study the presence of different types of functional groups in the synthesized catalyst. The FTIR spectra for CaO, K/CaO, and 20-W/K/CaO are shown in Fig. 4. A characteristic band at 650 cm$^{-1}$ corresponds to

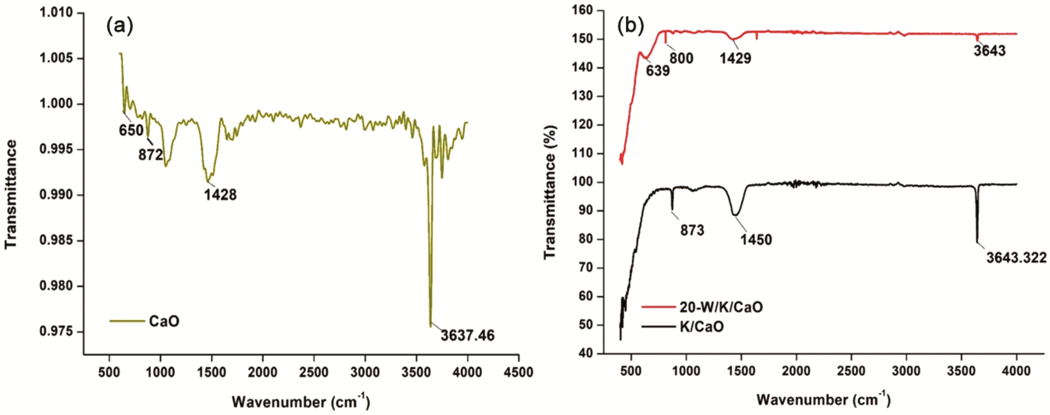


Fig. 4 — FT-IR spectra of (a) CaO and (b) modified CaO

the Ca–O bond. Absorption peaks at 872, 1450, and 1428 cm$^{-1}$ are attributed to the vibrations of carbonate ions ($CO_3^{2-}$). Broad peaks observed at 3637.46, 3643, and 3644.32 cm$^{-1}$ indicate water molecule absorption. Additionally, the peak near 800 cm$^{-1}$ confirms the successful incorporation of tungsten onto the K/CaO support.

Parallel findings were observed in past studies; Nassar and co-authors reported the presence of water molecules at a band value of 3637 cm$^{-1}$. The peak noticed at 650 cm$^{-1}$ was linked to the Ca–O–Ca vibration in eggshell-derived CaO. Likewise, Chaveanghong *et al*. reported the band value at 813 cm$^{-1}$ was ascribed to the presence of tungsten species in the W-CaO/hydroxyapatite catalyst. Furthermore, calcium carbonate was observed at band values of 875, 1417, and 1456 cm$^{-1}$ in the calcined samples[19]. As anticipated, the band intensity of carbonate was reported to decrease with the amount of tungsten impregnation and calcine temperature, owing to disintegration at a particular temperature. Aziz *et al*. said silica-loaded $WO_3$ for the transesterification of *Megalocarpus* oil, the band at 1542 and 1450 cm$^{-1}$ was identified due to the existence of pyridine molecules adhered to Bronsted acid and Lewis acid regions, respectively. It was also observed that the band moved to a higher band value of 1450 cm$^{-1}$ from 1447 cm$^{-1}$ upon impregnation of tungsten species into the silica structure, indicating an association between tungsten hexavalent ions and silicon atoms[20]. Likewise, in the present study, the band was observed at 1450 cm$^{-1}$, which moved to a higher band range of 1464.09 cm$^{-1}$. Wang *et al.* explored methyl ester synthesis utilising a heteropolyacid-based catalyst; they kept the peak values at 803, 888, and 982 cm$^{-1}$ for vibration associated with tungsten-oxygen bonds at the edge, within the bridging oxygen atoms and at terminal positions, respectively, in the heteropolyacid structure[21].

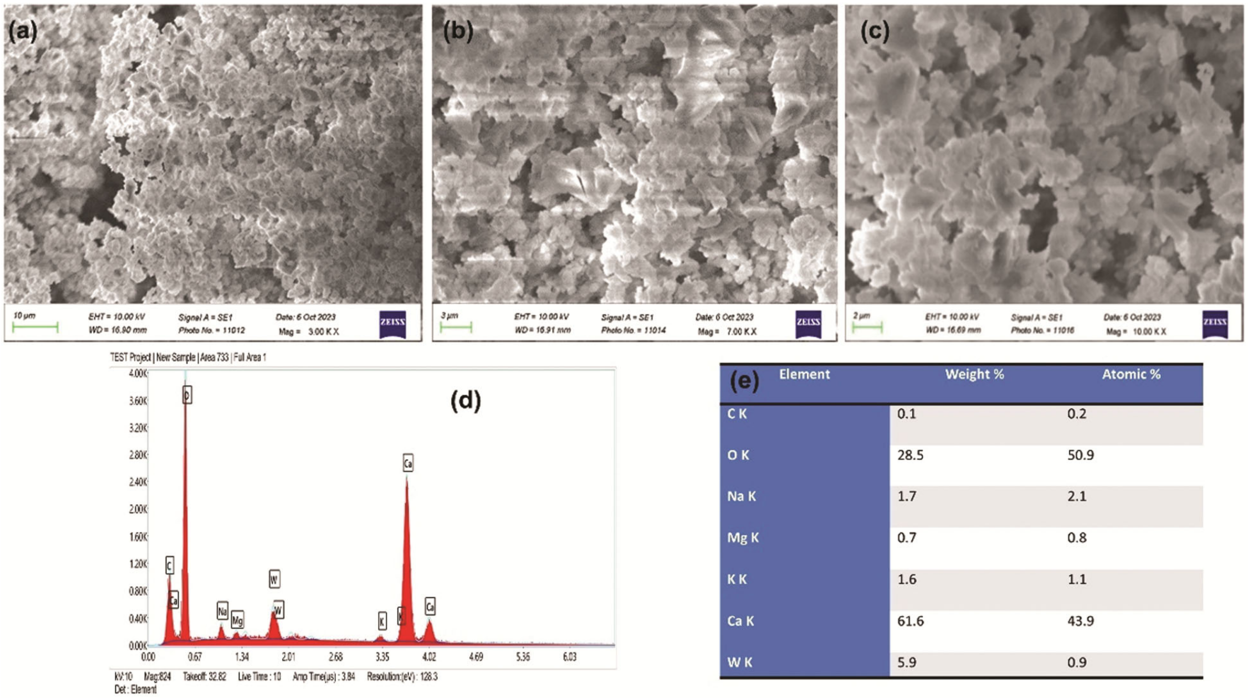
#### *SEM-EDX analysis*

The Fig. 5 (a, b, c) and (d, e) shows the SEM micrographs of the 20-W/K/CaO catalyst at various magnifications, along with its corresponding EDX elemental analysis. The prepared material showed the accumulations of non-regular crystal particles formed due to aggregation during the calcination process. The SEM image exposed the porous structure of the catalyst. The porosity was generated due to a high calcination temperature of 700°C, resulting in the catalyst's high chemical reactivity. The SEM-EDX characterisation showed that the catalyst contained 5.9 wt.% of tungsten species. The catalyst also validated the existence of calcium, potassium, and oxygen in the sample with weight percentages of 61.6, 28.5, and 1.6, respectively.

### Optimization of reaction parameters for biodiesel production from waste cooking oil

#### *Effect of impregnated tungsten species concentration*

Catalysts with tungsten loadings ranging from 10 to 25 wt.% were synthesized to determine the optimal W content for W/K/CaO activity. The catalytic performance improved as tungsten loading increased up to 20 wt.%, beyond which (at 25 wt.%) a decline in activity was observed. Thus, 20 wt.% was selected as the optimal tungsten loading. XRD analysis supported this finding, showing that tungsten levels above 20 wt.% reduced the peak intensity at a 2θ value of 36.82°, indicating diminished catalytic efficiency in transesterification. Excess tungsten at higher loadings likely blocked active sites on the



| Element | Weight % | Atomic % |
|---|---|---|
| C K | 0.1 | 0.2 |
| O K | 28.5 | 50.9 |
| Na K | 1.7 | 2.1 |
| Mg K | 0.7 | 0.8 |
| K K | 1.6 | 1.1 |
| Ca K | 61.6 | 43.9 |
| W K | 5.9 | 0.9 |

Fig. 5 — SEM-EDAX of the 20-W/K/CaO catalyst

K/CaO surface, significantly hindering the reaction. According to a previous study, the maximum efficiency of the catalyst was also achieved with 20 wt.% content of tungsten supported on Ti/$SiO_2$, calcined at 700°C[17]. Parallel results were likewise reported, where the highest efficiency of the catalyst was witnessed with a 20 wt.% content of 12-tungstophosphoric acid attached to the SBA-15 substrate used in the fatty acid esterification process.

### *Influence of catalyst concentration*

The optimal catalyst concentration was calculated by performing transesterification reactions at 60°C, using a m/o ratio of 13.70:1, time of 1.5 h, and a 0-W/K/CaO catalyst. The catalyst amount ranged from 2 to 8 wt.% (catalyst/oil). This study examined the relationship between catalyst dosage and biodiesel yield. The biodiesel output grew with the enhancement of the catalyst dosage, starting at 2.0 wt.%-4.0 wt.%. Continued elevation in the catalyst dose decreased the transesterification process's performance. Using more catalysts makes the reactor content more viscous, preventing reactants from reaching the catalyst's active surface and causing issues related to diffusion throughout the reaction. Therefore, higher catalyst dosage reduced biodiesel production because of increased viscosity and saponification reaction.

### *Influence of methanol: oil molar ratio*

The proportion of methanol to oil is significant in biodiesel production. This study examined how the molar ratio of m/o affects the production output of biodiesel. The biodiesel production increased with the rise in the m/o molar ratio. Subsequently, it declined after reaching an ideal ratio of 13.70:1. This discovery implies that the 13.70:1 m/o ratio influenced the reaction so that equilibrium shifts forward, resulting in the maximum biodiesel yield. Usually, an excess of methanol enhances the catalytic reaction. However, excess solvent prevents the isolating of biodiesel from glycerol, resulting in a reduced biodiesel output. The optimal m/o molar ratio was determined to be 13.70:1, which was then used in further experiments.

### *Influence of the reaction time*

The study examined how the duration of the reaction impacts the transformation rate of oil to biodiesel. The biodiesel production increased as the time extended but declined after reaching an optimal time of 90 min. Equilibrium shifts in a backward direction with the rise in temperature. This led to a reduction in biodiesel yield after 90 min of reaction. Fig. 6 illustrates the effects of tungsten loading, catalyst dosage, methanol-to-oil ratio, and reaction time on biodiesel production.

**Optimization of biodiesel production from waste cooking oil using synthesized W/K/CaO catalyst through RSM approach**

The RSM methodology consists of a set of computational and numeric methods derived from fitting experimental simulations to the data acquired in connection with the test plan. This can be achieved by employing straight or quadratic equations to characterize the system under investigation and subsequently to investigate empirical settings. Before implementing the RSM, select the empirical plan that details the no. of trials to be conducted within the explored practical area[22]. Empirical planning for primary-order models, such as two-level factorial design, can be applied when the data pool does not exhibit curving. If straight equations cannot represent the reaction characteristic, alternative schemes for polynomial response models should be employed[23].

The experiments were conducted using the Central Composite Design (CCD) approach in Design Expert software, with three independent variables: methanol-to-oil (m/o) ratio (factor "A"), catalyst loading (factor "B"), and reaction time (factor "C"). Temperature was kept constant at 60°C throughout all 15 experimental runs. The objective was to evaluate the influence of these parameters on biodiesel yield. Statistical analysis indicated that the model was highly significant (Table 2). Regression analysis established the relationship between the response variable and the

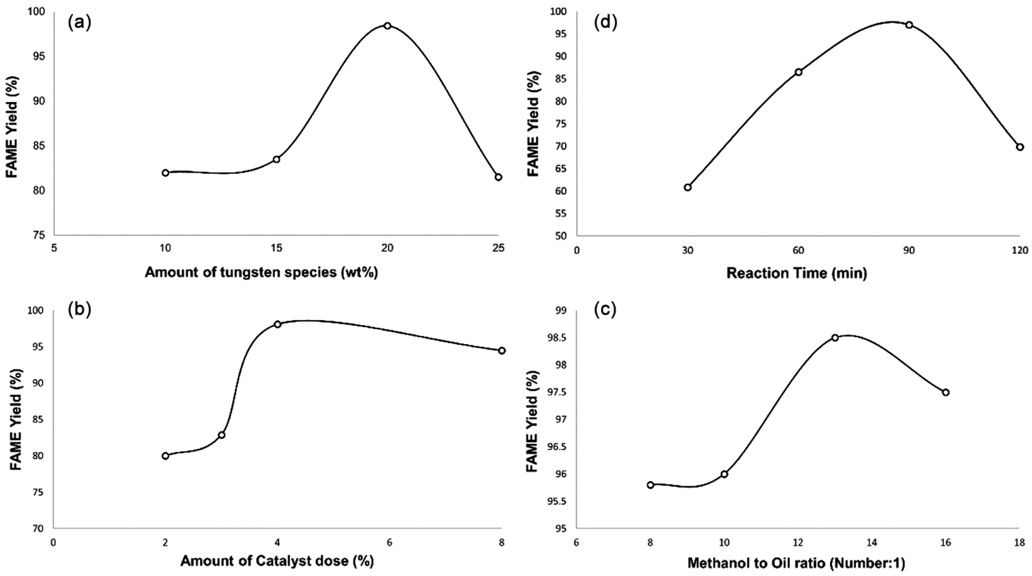


Fig. 6 — Impact of the amount of tungsten species, catalyst dose, methanol-to-oil molar ratio, and time on the yield of biodiesel

Table 2 — Model-predicted and observed biodiesel production

| Std | Run | A: molar ratio of m:o (m/m) | B: catalyst content (wt %) | C: time (min) | Experimental biodiesel yield (%) | Predicted biodiesel yield (%) |
|---|---|---|---|---|---|---|
| 7 | 1 | 8.14 | 8 | 120 | 77.94 | 76.14 |
| 4 | 2 | 16.02 | 8 | 30 | 96.35 | 96.96 |
| 2 | 3 | 16.02 | 2 | 30 | 90.28 | 89.25 |
| 6 | 4 | 16.02 | 2 | 120 | 70.96 | 66.31 |
| 12 | 5 | 12.08 | 8 | 75 | 92.74 | 90.65 |
| 14 | 6 | 12.08 | 5 | 120 | 50.53 | 56.40 |
| 10 | 7 | 16.02 | 5 | 75 | 80.06 | 82.73 |
| 5 | 8 | 8.14 | 2 | 120 | 50.86 | 47.44 |
| 3 | 9 | 8.14 | 8 | 30 | 96.62 | 98.26 |
| 8 | 10 | 16.02 | 8 | 120 | 70.49 | 66.43 |
| 11 | 11 | 12.08 | 2 | 75 | 62.73 | 63.33 |
| 1 | 12 | 8.14 | 2 | 30 | 60.34 | 61.97 |
| 13 | 13 | 12.08 | 5 | 30 | 98.08 | 95.48 |
| 9 | 14 | 8.14 | 5 | 75 | 70.45 | 67.96 |
| 15 | 15 | 12.08 | 5 | 75 | 67.98 | 75.35 |

explanatory factors, with empirical data subjected to multiple regression evaluations to ensure accurate yield predictions. This process resulted in a non-linear fitting equation (Eq. 1). The model's reliability was confirmed by a coefficient of determination ($R^2$) of 0.947 (Table 3).

$$Y = 75.35 + 4.39A + 9.10B - 11.27C + 2.82A^2 + 4.05B^2 + 2.29C^2 - 7.15AB - 2.10AC - 1.90BC \qquad \ldots(1)$$

In the regression model, Y denotes the biodiesel yield, while A, B, and C correspond to the methanol-to-oil molar ratio, catalyst loading, and reaction time, respectively. Interaction terms (AC, AB, and BC) represent the combined effects of two variables, whereas squared terms ($A^2$, $B^2$, and $C^2$) indicate second-order effects. The non-negative coefficient in the quadratic equation reflects a synergistic influence, meaning the response increases as the variable's value rises. For instance, $A^2$ describes the quadratic impact of the methanol-to-oil ratio, $B^2$ represents that of the catalyst dosage, and $C^2$ captures the effect of reaction time. Conversely, a negative coefficient indicates an opposite trend, where the response improves as the corresponding variable decreases.

Table 3 — Obtained and predicted $R^2$ values of the model

| | | | |
|---|---|---|---|
| Std. Dev. | 4.97 | $R^2$ | 0.947 |
| Mean | 75.35 | Adjusted $R^2$ | 0.908 |
| C.V. % | 6.60 | Predicted $R^2$ | 0.833 |

Fig. 7(a) presents the normal probability plot, where the residuals follow a near-linear trend,

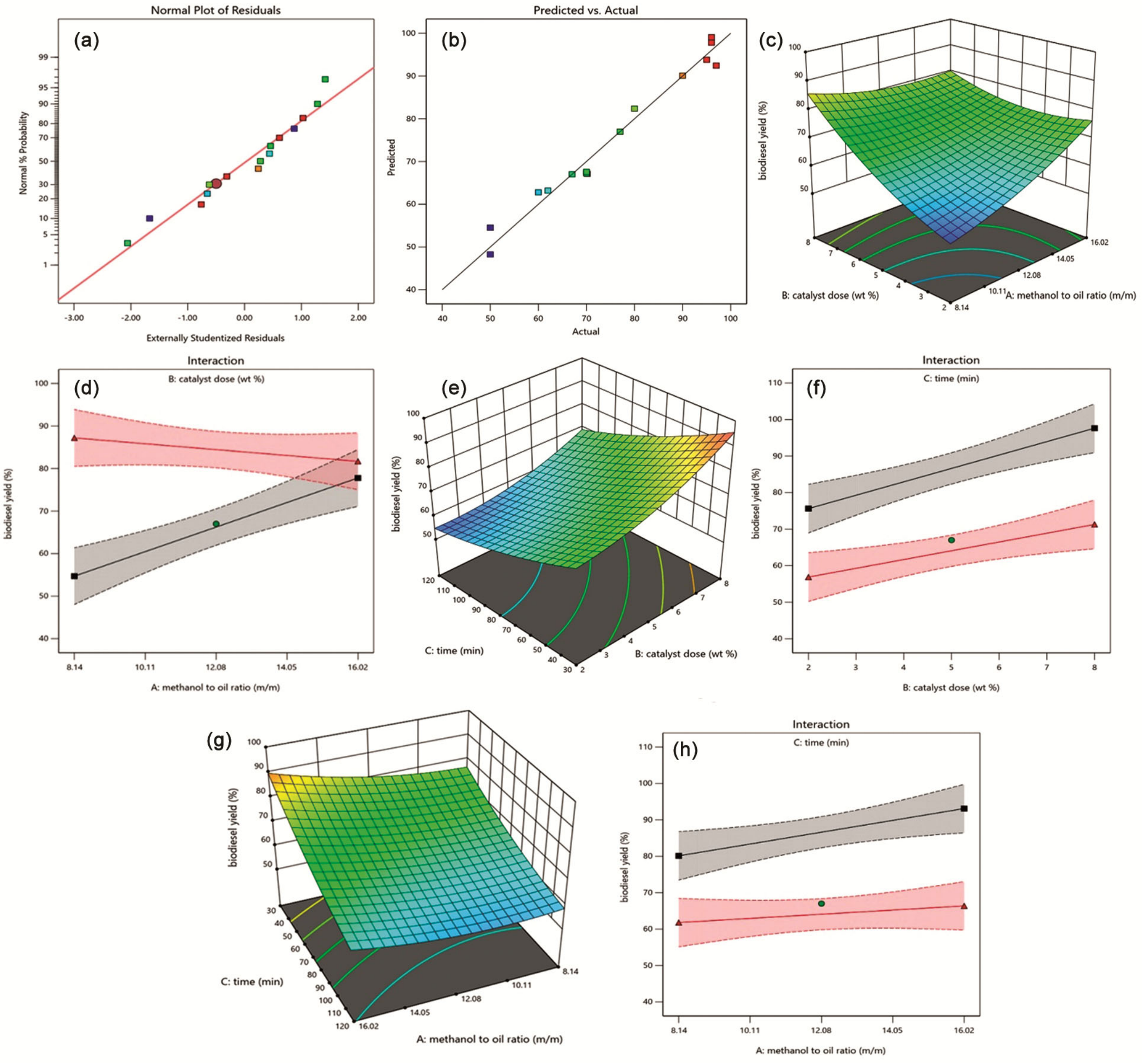


Fig. 7 — (a) Normal probability plot, (b) comparison of actual versus predicted biodiesel yields, (c) 3D surface plot, (d) interaction plot of yield as a function of catalyst loading and methanol-to-oil ratio, (e) 3D surface plot, (f) interaction plot of yield with catalyst loading and reaction time, (g) 3D surface plot and (h) an interaction plot of yield with methanol-to-oil ratio and reaction time

resembling that the found errors are normally distributed and confirming the appropriateness of the non-linear regression model. Fig. 7(b) compares the experimental biodiesel yields with the values predicted by the software. The close clustering of points along the diagonal line showed a strong correlation between observed and predicted results, reflecting a high level of agreement between the experimental results and predictions of the model.

Figs 7(c) and 7(d) display the 3D surface and interaction plots of biodiesel yield as a function of catalyst loading and methanol-to-oil ratio, generated using the Design Expert software. The alcohol-to-oil ratio is a key parameter affecting biodiesel production, as it enhances mixing efficiency and heat transfer. Yield increased with rising catalyst dosage and methanol-to-oil ratio due to their positive influence on the transesterification process. However, beyond certain threshold values, further increases in these parameters led to a slight decline in biodiesel yield. This decline is evident in Eq. (1), given that the square term bears a minus sign. Biodiesel production increased due to the rise in the number of reactive regions. However, a large amount of catalyst may disrupt the mixing of the reaction mixture containing methanol, oil, and catalyst, causing the partition of phase that hinders the reaction for scattering purposes. Given that the transesterification reaction is reversible, increasing the methanol concentration shifts the equilibrium toward greater biodiesel formation. However, excessive methanol can complicate the separation of biodiesel and glycerol from the reaction mixture.

The effect of catalyst loading and methanol-to-oil ratio was assessed while holding the reaction time constant at 75 min. Increasing catalyst concentration from 2 to 8 wt.% drastically improved biodiesel yield, with the highest production observed at 4 wt.% catalyst loading and an m/o ratio of 13.70:1. Beyond this point, surplus methanol hindered phase separation, thereby reducing yield[24]. Among the two variables, catalyst loading had a greater influence on biodiesel production than the methanol-to-oil ratio. When the m/o ratio was fixed at 12.08:1, increasing catalyst dosage enhanced biodiesel yield due to the higher number of active sites, which accelerated the reaction rate (Fig. 7 (e, f)). However, on increasing the time, the yield decreased, resulting in a reverse reaction. However, on loading excess of catalyst, the yield was reduced due to the high viscosity of the reactant species. An increase in both time and catalyst dose led to a reduction in yield at a constant m/o ratio. Comparable findings have been reported for a CaO–MgO catalyst used in biodiesel production from non-edible oil, where the highest FAME yield (93.55%) was achieved at 3.70 wt.% catalyst loading, a reaction temperature of 115.87 °C, a reaction time of 3.44 h, and a methanol-to-oil ratio of 38.67:1. The authors stated that biodiesel production was marginally impacted by the increase in the quantity of catalyst during extended reaction periods. The FAME response attained the highest value at a high value of time and catalyst amount. The study employed by Akshey *et al.*, with eggshell-derived CaO in the methyl ester synthesis from *Terminalia bellerica* oil[24]. The highest biodiesel yield obtained was 97.98% with optimised reaction conditions (temp: 62.5°C; catalyst dose: 2.25 wt.%; and the ratio of alcohol to oil: 9:1) using the RSM-CCD model.

Figs 7(g) and 7(h) illustrate the relationship between biodiesel yield, reaction time, and methanol-to-oil ratio, with catalyst loading fixed at 5 wt.%. Prolonged reaction times promoted the reverse transesterification reaction, leading to a decrease in oil-to-biodiesel conversion. Increasing the methanol-to-oil ratio enhanced FAME production, particularly when reaction time was short. At a reaction time of 30 min and an alcohol-to-oil ratio of 16.02:1, the biodiesel yield reached its highest level

### Characterization of produced biodiesel

#### *NMR analysis*

Fig. 8(a,b) represents the produced FAME's C-13 and proton NMR patterns. The proton NMR spectrum showed a characteristic signal at 3.59 ppm, confirming the formation of fatty acid methyl esters (FAME)[25]. A resonance at 2.25 ppm corresponded to methylene protons, while allylic protons appeared between 2.0–2.1 ppm. Signals in the range of 5.3–5.4 ppm were attributed to alkene protons, and diallyl carbons resonated between 2.7–2.8 ppm. Aliphatic methyl esters were further identified through the alkyl $CH_2$ proton signals observed at 1.2–1.4 ppm.

The $^{13}C$ NMR spectrum of WCO-derived biodiesel displayed a peak at 174.03 ppm, confirming the carbonyl carbon of methyl esters, and a peak at 129.97 ppm, indicating unsaturation within the ester chain. A resonance at 13.99 ppm represented the terminal methyl carbon[26,27]. Notably, the absence of any signal in the 3.9–4.5 ppm region confirmed the complete removal of glycerol.

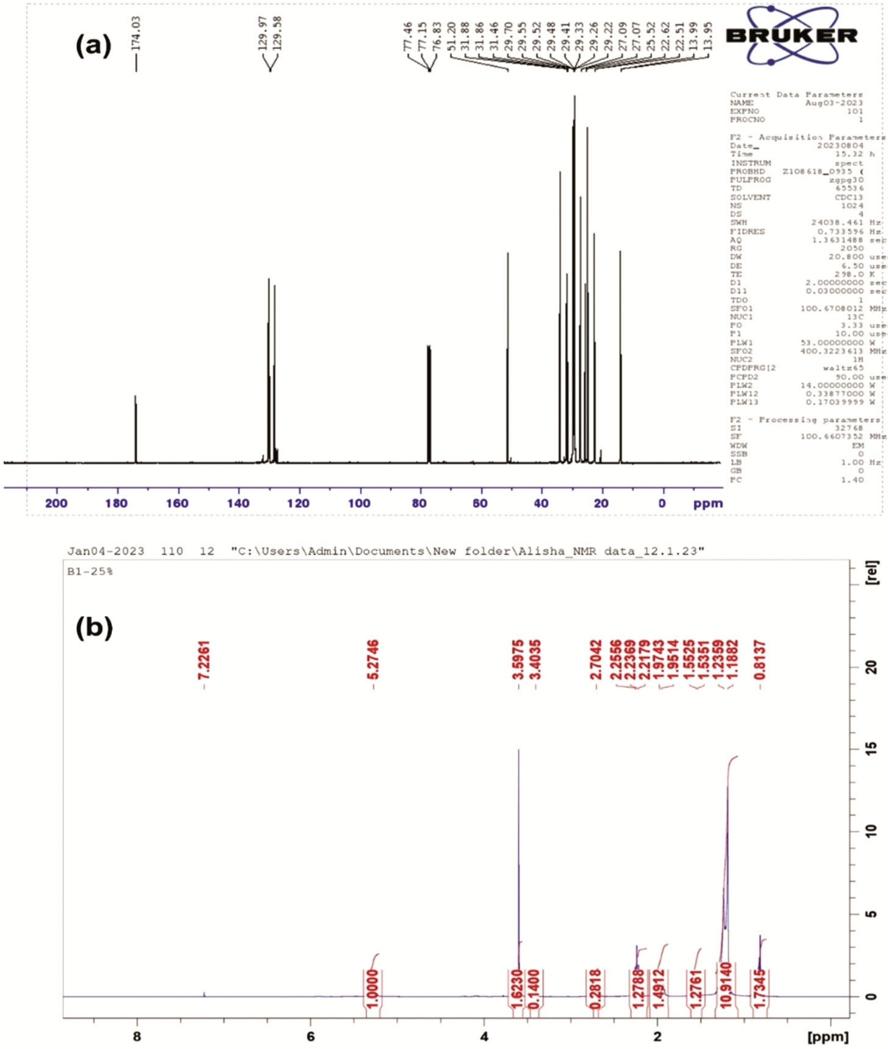


Fig. 8 — (a) C-13 and (b) proton NMR spectra of produced biodiesel from waste cooking oil using synthesized W/K/CaO catalyst

***GC-MS analysis***

Gas chromatography (GC) was utilized as an analytical technique to determine both the quantity and composition of the synthesized biodiesel. GC-MS analysis was performed to confirm the presence of methyl esters in the sample, with peak identification carried out using established reference data. Each measurement employed an inert 5975 mass-selective detector.

A capillary column composed of 95% dimethylpolysiloxane and 5% phenyl was utilized with helium used as the carrier gas. The oven temperature was programmed to start at 160°C with a 3-min isothermal hold, then ramped at 5°C per min until reaching 230°C. Results revealed that hexadecanoic acid methyl ester exhibited the highest peak area, accounting for 47.03% of the total composition (Table 4). Analysis of the table revealed that the major methyl esters present in the biodiesel were Methyl hexadecanoate, Methyl 9,12-octadecadienoate, Stearic acid methyl ester, Methyl 9-octadecenoate, Myristic acid methyl ester, Methyl eicosanoate, Methyl cis-11-eicosenoate, Methyl (3-octyl-2-oxiranyl)octanoate, Methyl docosanoate at retention time (RT) of 18.72, 20.36, 20.80, 20.69, 15.64, 22.93, 22.68, 23.44, and 22.98, respectively. Fig. 9 depicts how the relative presence of methyl esters changes over time.

**Reusability studies of the synthesized W/K/CaO catalyst for biodiesel production**

Using a heterogeneous catalyst in biodiesel synthesis provides the advantage of reusability, which helps lower overall production expenses[28]. Assessing catalyst reuse is essential for estimating the economic feasibility of large-scale methyl ester production. In

Table 4 — Composition of fatty acid methyl ester of waste cooking oil biodiesel

| S. No | RT | Name of the compound | Molecular formula | Molecular weight | Peak area (%) |
|---|---|---|---|---|---|
| 1 | 18.72 | Methyl hexadecanoate | $C_{17}H_{34}O_2$ | 270 | 47.03 |
| 2 | 20.36 | Methyl 9,12-octadecadienoate | $C_{19}H_{34}O_2$ | 294 | 19.58 |
| 3 | 20.80 | Stearic acid methyl ester | $C_{19}H_{36}O_2$ | 296 | 12.25 |
| 4 | 20.69 | Methyl 9-octadecenoate | $C_{19}H_{38}O_2$ | 298 | 5.25 |
| 5 | 15.64 | Myristic acid methyl ester | $C_{23}H_{46}O_2$ | 354 | 3.59 |
| 6 | 22.93 | Methyl eicosanoate | $C_{20}H_{40}O_2$ | 312 | 3.10 |
| 7 | 22.68 | Methyl cis-11-eicosenoate | $C_9H_{18}O_2$ | 158 | 2.49 |
| 8 | 23.44 | Methyl (3-octyl-2-oxiranyl)octanoate | $C_{22}H_{44}O_2$ | 340 | 2.30 |
| 9 | 22.98 | Methyl docosanoate | $C_{21}H_{40}O_2$ | 324 | 1.47 |

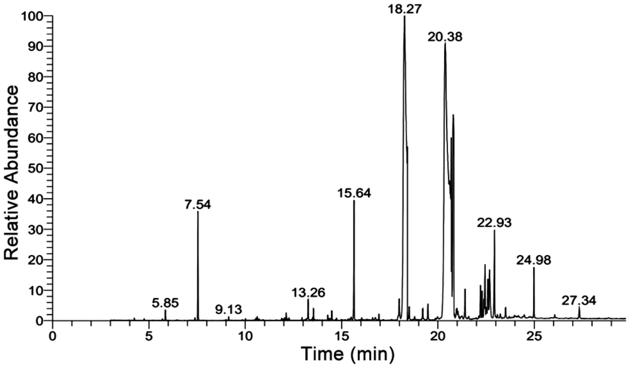


Fig. 9 — GC-MS chromatogram of produced biodiesel from waste cooking oil using synthesized W/K/CaO catalyst

general, catalysts supported on a solid substrate require regeneration of the active species before being used in successive reaction cycles. In the present study, the optimised 20-W/K/CaO catalyst was subjected to recycling tests under the established reaction conditions. After each run, the spent catalyst was washed three times with hexane to remove residual glycerol, methanol, and other impurities. It was then dried at 120°C and re-calcined at 700°C for three hours[29]. Results indicated that the regenerated catalyst could be effectively reused for biodiesel production at an industrial scale. However, the yield gradually decreased with each reuse cycle, primarily due to potassium leaching, minor tungsten dissolution from the K/CaO support, and physical loss of catalyst during recovery[17,30]. The catalyst was evaluated to be used upto 6 cycles of reuse.

## Conclusion

A 20-W/K/CaO catalyst was synthesized via the wet impregnation method for transesterifying waste cooking oil into biodiesel. Structural and morphological characterisation using XRD, SEM-EDX, and FT-IR confirmed the successful preparation and catalytic potential of the material. Tungsten loading was found to enhance activity up to 20 wt.%, beyond which performance declined. XRD analysis revealed that increasing tungsten content above 20 wt.% reduced the peak intensity at a 2θ value of 36.82°, indicating diminished catalyst activity due to partial blockage of active sites on the K/CaO support. Under optimised reaction conditions, 60°C, 4 wt.% catalyst, and a methanol-to-oil molar ratio of 13.70:1, the 20-W/K/CaO catalyst achieved biodiesel production in 1.5 h. Process optimisation using regression modelling considered reaction time (30–120 min), catalyst loading (2–8 wt.%), and methanol-to-oil ratios (8.14:1–16.02:1). The model exhibited strong predictive capability, with an $R^2$ value of 0.947, showing close agreement between experimental and predicted yields. The resulting biodiesel was further analysed using GC-MS, $^1H$ NMR, and $^{13}C$ NMR techniques.

## Acknowledgement

Department of Chemistry, Banasthali Vidyapith, Rajasthan is gratefully acknowledged for extending access to laboratory resources and internet facilities.

## Conflict of interest

The authors declare no conflict of interest.

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