Biogenic-Mediated Synthesis of the Cs₂O–MgO/MPC Nanocomposite for Biodiesel Production from Olive Oil

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ABSTRACT: In this work, a biogenic-mediated approach is successfully used to synthesize a novel heterogeneous Cs₂O–MgO/MPC basic nanocomposite. For the first time, the established technicality employs pomegranate seed extract that gives a green capping fuel and reducing mediators during an aqueous solution combustion process of metal ion precursors. The synthesized nanocomposites were identified by X-ray diffraction, Fourier transform infrared, N₂ isotherms, field emission scanning electron microscopy, and CO₂-TPD analyses. The transesterification process of olive oil was used to evaluate the catalytic performance. The nanocomposite displayed outstanding catalytic efficiency stemming from the boosting of the reactant and product diffusion. The transesterification activity and the optimization design were assessed by applying the response surface methodology. Based on the experimental tests, the finest experimental conditions with a biodiesel yield of 96.1% are 4 h, 4% catalyst amount, an oil/methanol ratio of 1:15, and a temperature of 65 °C. The predicted optimal conditions based on the statistical model are 6 h contact time, 5.2 % catalyst dose, 65 °C reaction temperature, and 1:15 oil/methanol molar ratio, attaining a biodiesel yield of 95.18%. The catalyst reusability has been performed almost continuously up to four cycles, with no loss of the active constituents. The obtained biodiesel demonstrated characteristics close to those of international standards of biodiesel. Besides, the process employed in this study demonstrated significant potential for further development and commercialization and is cheaper than the refined vegetable oil used in traditional approaches of biodiesel manufacturing.

1. INTRODUCTION

Economic and environmental accidents and subsequent impacts on human life were substantially affected nowadays.¹ The increasing reliance on life on energy is evident, but fossil fuel resources are scarce, and their use contributes to contamination of the environment.² Several researchers have attempted to explore a sustainable and environmentally friendly fuel comparable to the existing fossil fuels.³–⁶ The importance of biodiesel production is related to providing energy and preserving a clean and healthy climate. To date, several current research studies have oriented on sustainable and renewable fuels such as biodiesel.⁷–¹¹ Biodiesel is among the biodegradable fuels that result from an oil or fat and alcohol (methanol or ethanol) transesterification process in the existence of acidic or basic catalysts generating biodiesel and glycerin as a byproduct.¹² Biodiesel offers appealing features such as nontoxicity, renewability, environmentally friendliness, more magnificent flash, and cetane number. Biodiesel is associated with reduced carbon monoxide, hydrocarbon, and lower CO₂ emissions relative to traditional diesel, thus virtually removing sulfate. Biodiesel and fossil diesel are very identical to one another, so biodiesel in motors needs no significant maintenance costs to change engines with new fuel.¹³ Although biodiesel would be generated via un catalytic operations, the use of catalysts reduces costs. The commonly pure acids and bases with great reaction rates are homogeneous catalysts.¹⁴ While applying homogeneous catalysts, the steps of acid or base separation and recycling will be applied to the manufacturing process.¹⁵ Much research was outlined to find an appropriate heterogeneous catalyst to overcome these problems.¹⁶–¹⁸ The surface area provided using a support is one of the remarkable variables in tailoring the heterogeneous catalysts.¹⁹–²¹ Dispersing the active constituents on the support produces adequate molecular bonding relevant to the existence and kind of support, active...
site deposition, and several other working parameters.\textsuperscript{22} Therefore, various materials have various approaches to fabrication.\textsuperscript{23,24} Of these, carbon-based materials were used as a support for catalyst manufacture.\textsuperscript{25}

Heterogenic basic catalysts are categorized into metal oxides and their alternatives. Alkali earth metal oxides are commonly used as solid basic catalysts because of their minimal cost and strong basicity.\textsuperscript{26} The basicity of barium oxide and calcium oxide is typically greater than that of magnesium oxide.\textsuperscript{27} BaO, however, is poisonous and dissolves facilely in methanol or ethanol and has an undesirable environmental impact. CaO leaching was a significant problem, and Ca\textsuperscript{2+} leaching resulted in a rapid catalyst deactivation and the development of free fatty acid soap.\textsuperscript{28} In contrast, MgO has not been readily detached from the reaction process and retains significant performance when reacted with raw materials with a higher content of water.\textsuperscript{29} However, owing to its low surface area and catalytic performance, there is no economic value for the direct need for pure MgO as a catalyst. Hence, fabrication of MgO with great surface area and catalytic performance is vital.

Among the most potential applications of transesterification is the development of biodiesel from vegetable oils. Still, if vegetable oils of edible quality are considered, this process is not economical because raw materials are key factors contributing to biodiesel cost. Through the process of producing olive oil, however, it often tends to happen that the free fatty acid content of the olive oil meets nonstandard high quantities, which effectively make the oil inedible. The olive oils refining with a high concentration of free fatty acids is vulnerable to refining loss, and their processing is usually not affordable to the industrial food sector. The Al-Jouf region in the Kingdom of Saudi Arabia is famous for olive agriculture and abundance of water. Because of the difference in the quality of both groundwater and the nature of the soil, two types of olive oil with different qualities were produced. One is suitable for human (edible quality) use because of its distinctive taste and high quality and the other type is inedible. Consequently, the use of this inedible olive oil is of commercial benefit to biodiesel development through transesterification. The impact of the competitive nature of the suggested approach on the market because biodiesel production from olive oil is economically feasible without government assistance or tax benefits even under the commercialization trend of significant increases in raw material prices. Besides, if cheaper feed as inedible olive oil could be used in the suggested approach, its productivity is expected to be further enhanced, and industrial availability could be considerably increased.

In this paper, Cs\textsubscript{2}O–MgO/mesoporous carbon (MPC) as a basic nanocatalyst is practiced for biodiesel development from olive oil via the transesterification reaction. The nanocatalyst was fabricated by a one-pot aqueous solution combustion process in the presence of pomegranate seed extract (PMSSE) as the capping reducing/stabilizer agent. Different parameters influencing the biodiesel production efficiency from olive oil, comprising methanol/olive oil molar ratio, contact time, temperature, and catalyst dose, were further examined. The response surface methodology (RSM) was utilized to optimize the biodiesel process and evaluate the influence of the variable connections.

2. RESULTS AND DISCUSSION

2.1. Nanocomposite Characterizations. 2.1.1. X-ray Diffraction Assessment. Figure 1 reveals the X-ray diffraction (XRD) patterns of MPCs and Cs\textsubscript{2}O–MgO/MPC nanocomposite with various Cs\textsubscript{2}O contents. The pristine MPCs offer two sharp and strong peaks allocated at 25.5 and 44.2° corresponding to the (002) and (101) facets, which can be related to the graphite nature of MPCs.\textsuperscript{30} The diffraction pattern for MgO/MPC shows characteristics peaks at 36.8, 42.7, 62.3, and 74.6, assigned to the (111), (200), (220), and (311) facets, respectively, suggesting the development of a cubic MgO.\textsuperscript{31} It is also worth mentioning that the XRD patterns of Cs\textsubscript{2}O–MgO/MPCs are closely similar to that of the MgO/MPCs. However, the intensity of the diffraction peak of MgO (PDF#45-0946) became slightly broader and weaker, indicating that the crystal structure of the MgO remained unchanged in the presence of Cs\textsubscript{2}O. Also, The MPC diffraction peaks were not observed because Cs\textsubscript{2}O–MgO was incorporated within the MPCs. These findings show that the Cs\textsubscript{2}O–MgO, as the primary components, would have a strong relationship with the prior synthesizing features. The diffraction peak for Cs\textsubscript{2}O–MgO was observed at 19.7 and 28.1° even in the sample (MgO with 5 mol % Cs\textsubscript{2}O). It is worth noting that with increasing Cs\textsubscript{2}O content, the intensity of the diffraction peaks of MgO markedly decreased. Furthermore, the particle size of the Cs\textsubscript{2}O–MgO/MPC nanocomposite with different Cs\textsubscript{2}O contents was calculated using Debye–Scherrer eq 1

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

where the wavelengths \(\lambda\) and \(\beta\) are related to the line broadening at half the maximum intensity in radian and \(\theta\) is assigned to the Bragg angle. The average particle size for MgO/MPCs was estimated to be 11.3 nm. The incorporation of Cs\textsubscript{2}O resulted in an increase in the particle size to 13.1 and 14.6 nm because of the presence of 5 and 20 mol % Cs\textsubscript{2}O, respectively (Table 1).

2.1.2. Fourier Transform Infrared Analysis. Fourier transform infrared (FTIR) study was performed to evaluate the functional moieties in the MPC, and the connections between them follow the inclusion of MgO and Cs\textsubscript{2}O in the MPC structure. FTIR spectra of the fabricated nanocomposite are displayed in Figure 2. The results revealed similar bands for all samples. No band designated to NO\textsubscript{3}\textsuperscript{−} (at 1380 cm\textsuperscript{−1}) was

![Figure 1](https://dx.doi.org/10.1021/acs.omega.9b03814)

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identified in the spectra because the full decomposition of nitrates into the corresponding metal oxides occurs during the solution combustion reaction. The absorption bands centered at 3200 cm\(^{-1}\) correspond to the stretching vibrations of O–H groups because of the physisorption of water molecules.\(^32\) The weak band at 2980 cm\(^{-1}\) is related to stretching vibration of C–H aliphatic, and the peaks are allocated at 1680 cm\(^{-1}\) assigned to the C=C group of the unsaturated structure. Besides, the sharp band at 1340 cm\(^{-1}\) can be ascribed to the Mg–O stretching mode. The peaks at 800–1050 cm\(^{-1}\) for the Mg–O bond result in the fruitful fabrication of MgO.\(^33\) The intensity of the bands increased, which could be attributed to the promotion of sintering by adding cesium on MgO that eventually declined the hydroxyl surface moieties. Besides, all the fabricated composites display further desorption peak within the temperature range of 350–800 °C, which is associated with the forceful CO\(_2\) interaction with influential basic sites.\(^34\) Although all the composites demonstrated the existence of super basic sites, their intensity varies with the incorporation of Cs\(_2\)O. The quantification results of the desorption region indicate that Cs\(_2\)O–MgO/MPCs exhibit the highest basic strength than the MgO/MPC composite. The overall basicity, along with the dispersion of the basic centers in TPD profiles, increased with the incorporation of Cs\(_2\)O (Figure 3). The quantity of the overall basicity is evaluated and displayed in Table 1. The robust basicity of Cs\(_2\)O–MgO/MPCs is attributed mainly to (i) the presence of Cs\(_2\)O species in close vicinity of MgO, (ii) the boosted surface electron density of actively distributed monovalent Cs by creating a Cs\(^+\)O\(^2−\) ion pair, stemming from the variation in charge of Mg\(^2+\) and Cs\(^+\) ions, and (iii) the presence of surface defects owing to the incorporation of Cs\(_2\)O.\(^35\)

2.1.3. Basicity Assessment. The TPD assessment is performed to examine the impact of the incorporation of Cs\(_2\)O–MgO on the porosity of the MPCs. The BET surface area, pore width, and pore volume of the synthesized materials are displayed in Table 1. Figure 4 displays the N\(_2\) adsorption–desorption isotherms of the synthesized composites. It can be shown that all fabricated composites exhibit type IV isotherm, with an H1-type hysteresis loop based on IUPAC classification. The pores formed in the fabricated composites were cylindrical, that is, a reasonable shape for the diffusion of large triglyceride molecules as a fuel source in the biodiesel-manufacturing processes. The influence of Cs\(_2\)O incorporation on the BET surface area, pore volume, and pore size of all composites is displayed in Table 1. Both 5Cs\(_2\)O–MgO/MPC and 20Cs\(_2\)O–MgO/MPC nanocomposites exhibit lower BET surface areas and pore volumes compared with MgO/MPCs;...
the alcohol/oil ratio, catalyst dose, contact time, and temperature.

2.2.1. Influence of the Methanol/Oil Molar Ratio. A small volume of methanol could not fulfill the transesterification process. Excessive methanol will increase the expense of the recovery of alcohol. Besides, glycerol becomes harder to isolate from biodiesel when a higher volume of methanol is used.37 Figure 6 presents the influence of different parameters on the biodiesel development. Figure 6a examines the impact of varying methanol/olive oil molar ratio (3, 6, 9, 12, 15, and 18) on the biodiesel development applying the prepared 20Cs2O–MgO/MPC nanocomposite. Experimental findings revealed that with increasing methanol/olive oil ratio from 3 to 15, the yield of biodiesel increased from 71.6 to 96.1%, as an increase in the ratio at the beginning of the process could cause the creation of methoxy over the 20Cs2O–MgO/MPC nanocomposite surface, consequently, increasing the biodiesel development performances. However, an additional increase in the methanol/olive oil ratio to 18 resulted in a slight improvement in the biodiesel yield (95.7%). This was due to the difficulty of removing the excess glycerol content in methanol. The excess glycerol prevents the interaction between methanol, 20Cs2O–MgO/MPC nanocomposite, and the reactant, shifting the equilibrium into the backward direction leading to a decrease in the development of biodiesel. Consequently, based on this study, optimum biodiesel yield (96.1%) was gained at the methanol/olive oil molar ratio of 15.

2.2.2. Effect of Transesterification Time. Figure 6b contributes to the impact of contact time from 1 to 6 h on biodiesel development at different parameters according to the RSM design. The yield followed a growing trend with time. The performance after 4 h was obtained as 96.1%; after that, the activity slightly declined. A rapid increase in the yield (79.2%) is observed after 1 h. This could be attributed to the existence of a large quantity of ester in the system. Then, after 4 h, the yield increased. Accordingly, an increase in the contact time may assign to ester hydrolysis, thereby increasing the amount of available fatty acids for soap development. Therefore, the contact time of 4 h was stated as the appropriate contact time.

2.2.3. Influence of Temperature. The reaction temperature is a critical factor that drastically alters the transesterification process. The influence of this variable was assessed for the transesterification of olive oil to an ester at 40, 50, 55, 60, 65, 70, and 75 °C at different parameters according to the RSM design. Figure 6c reflects the influence of temperature on the reaction performance. Inspection of Figure 6c disclosed that increase in the transesterification temperature from 40 to 65 °C resulted in a remarkable increase in the yield from 65 to 96.1%. This could be attributed to high temperatures that appeared to enhance the dissolution of glycerin. On the other hand, a further increase in temperature greater than 65 °C decreased the performance because of the evaporation of methanol, thereby decreasing biodiesel generation performance. Therefore, 65 °C is the optimum transesterification temperature. The same trend was observed in the impact of the temperature on the biodiesel production.38,39

2.2.4. Effect of the Catalyst Dose. To emphasize the impact of the catalyst dose on the transesterification yield, a series of experiments with different catalyst dose percents (2, 4, 6, and 7%) were performed at different parameters according to the RSM design. The transesterification yield percent as a function of the amount (%) of catalyst is depicted in Figure 6d. It was

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Figure 4. Nitrogen sorption isotherms at 77 K for the MgO/MPC nanocomposite containing various contents of Cs2O (inset represents the pore size distribution).

Figure 5. FESEM images of (A,B) 20Cs2O–MgO/MPC nanocomposite prepared by an aqueous solution combustion approach.
found that the yield was increased with an increase in the dose of the catalyst up to 4%. This could be attributed to the increase in the dose that improved the interaction between the nanocomposite and the reactant. Besides, the number of the basic centers steaming from MgO and Cs₂O was increased. An additional increase in the catalyst dose up to 7% caused a decrease in transesterification yield to 83%. Therefore, 4% is the optimum dose for transesterification of olive oil.

2.2.5. Effect of the Catalyst Composition. The variation in the biodiesel yield percent as a function of Cs₂O content was investigated and is graphically represented in Figure 7. The reaction was performed under the optimum conditions according to different parameters according to the RSM design. As shown in Figure 7, MgO/MPCs containing different mol % of Cs₂O showed a significant increase in biodiesel and attained the maximum yield of 96.1% for 20Cs₂O–MgO/MPCs. This could be ascribed to the existence of many influential basic sites in 20Cs₂O–MgO/MPCs that contribute to the process toward more yield of ester. There is a linear relationship between the biodiesel yields and the basicity of the composites. The CO₂-TPD of this composite indicates the existence of extremely basic centers with a considerable quantity of total basicity.

For further understandable comparison, the process parameters and biodiesel yields attained by different MgO containing catalysts for the biodiesel process are presented in Table 2. As displayed in this table, the developed biodiesel in the current investigation has a significant performance compared to other catalysts.

2.3. Biodiesel Features. The features of the biodiesel such as flashpoint, kinematic viscosity, density, pour point, and acid value were estimated and matched with the respective United States standard (ASTM D6751) and Europe standard (EN14214) (Table 3). The obtained characteristics of the produced biodiesel perfectly coincide with universal standard specifications. However, the observed high viscosity could be related to the presence of large amounts of fatty acid-containing lower numbers of the double bond (C18:1). The viscosity of FAMEs increased with decreasing number of double bonds $\mu_{C_{18:3}} < \mu_{C_{18:2}} < \mu_{C_{18:1}} < \mu_{C_{18:0}}$. Besides, the FTIR spectra of the biodiesel are provided in Figure 8. The FTIR peak at 3300 cm⁻¹ for carboxylic acid (O–H stretching) is very weak, indicating that most free fatty acids have been converted to their corresponding ester. The FTIR bands at

![Figure 6. Impact of (a) methanol/olive oil ratio, (b) time, (c) temperature, and (d) catalyst dose (%) on biodiesel yield (%) from olive oil using the 20Cs₂O–MgO/MPC nanocomposite.](image)

![Figure 7. Influence of the catalyst composition on biodiesel yield (%) from olive oil.](image)
2953 and 2870 cm$^{-1}$ are ascribed to asymmetric and symmetric starching vibrations of the sp$^3$ C–H bond, respectively. As for the FTIR peak of ester, the obtained intense peak at 1769 cm$^{-1}$ is consistent with the publication of Rabelo et al.,$^{51}$ where the carbonyl group of free fatty acid and its corresponding ester was noted in the region 1800–1700 cm$^{-1}$. The significant spectral area enabling to confirm the formation of biodiesel is 900–1500 cm$^{-1}$ that corresponds to a fingerprint zone. The peak at 1446 cm$^{-1}$ is assigned to the asymmetric stretch of $-\text{CH}_3$ which is only found in biodiesel, while the peak at 1183 cm$^{-1}$ is ascribed to the stretching of O–C–H$_3$ which is typically biodiesel. The weak band at 973 cm$^{-1}$ is assigned to the olefin moieties in the alkyl chains. The peak at 738 cm$^{-1}$ is ascribed to the rocking C–H bond. This finding is in line with the literature.

2.4. Reusability Assessment. The reusability was performed using the 20CaO–MgO/MPC nanocomposite for four cycles under optimal conditions according to the RSM design. Recycled run findings indicate that the transesterification performance of the nanocomposite demonstrated stable catalytic performance up to four cycles with a small conversion variance of up to 3% (Figure 9).

Table 2. Comparison of the Transesterification Performance Process of Different Catalysts Containing MgO

| catalysts       | oil           | temperature (°C) | time (h) | MeOH/oil (molar ratio) | yield (%) | reference  |
|------------------|---------------|------------------|----------|------------------------|-----------|------------|
| CaO–MgO         | Jatropha      | 120              | 3        | 25:1                   | 90        | 40         |
| MgAL-LDH        | West sunflower| 120              | 4        | 15:1                   | 94.6      | 41         |
| MgO/ZSM-5       | spirulina oil | 75               | 1        | 15:1                   | 92.1      | 42         |
| MgO             | triacetin     | 60               | 9        | 6:1                    | 18        | 43         |
| MgO/MCM-41      | soybean frying oil | 60    | 24       | 85                    |           |           |
| Sr/MgO          | soybean oil   | 65               | 0.5      | 12:1                   | 93        | 45         |
| Li2–MgO         | soybean oil   | 60               | 2        | 12:1                   | 93.9      | 46         |
| MgO/CeM(Si/Ce = 10) | waste cooking oil | 70  | 6        | 9:1                    | 94.3      | 47         |
| 20CaO–MgO/MPCs  | olive oil     | 60               | 6        | 15:1                   | 96.1      | this work  |

Table 3. Biodiesel Features Obtained for Biodiesel Stemmed from Olive Oil

| property                      | EN14214 | ASTM D-6751 | biodiesel |
|-------------------------------|---------|-------------|-----------|
| flash point (°C)              | ≥101    | ≥130        | 139       |
| kinematic viscosity at 40 °C  | 3.5–5.0 | 1.9–6.0     | 5.2       |
| density at 15 °C (kg/m$^3$)   | 860–900 | 860–894     | 871       |
| pour point (°C)               | –24     |             |           |
| acid value (mg KOH/g)         | max. 0.5| max. 0.5    | 0.31      |

2.5. Optimization of the Transesterification Process by RSM. 2.5.1. Fitting Model. The analysis of the variance model (ANOVA), the most reliable approach for assessing the precision of the experiments, has been used. The method also enables the variation of the relationship between the evaluators and the parts to be calculated. RSM explores the relation between the transesterification yield percent and four independent variables of methanol/oil molar ratio ($A$), contact time ($B$), temperature ($C$), and catalyst dose ($D$). It is worth noting that the model’s predicted values were inconsistent with the actual experimental results for each run, and the quadratic relation is defined in eq 2 with respect to the coded variables.

\[
\text{Biodiesel yield} = 92.61 + 5.03A + 0.2036B - 4.20C + 2.38D + 0.93S1AB + 5.65AC + 0.9481AD + 1.27BC + 0.0640BD + 0.3208CD - 5.30A^2 + 0.0635B^2 - 17.54C^2 - 3.60D^2
\]  

(2)

Figure 9. Reusability of the 20CaO–MgO/MPC nanocomposite toward biodiesel development from olive oil.

Figure 8. FTIR spectrum for biodiesel developed from olive oil using the 20CaO–MgO/MPC nanocomposite under optimum conditions.

Figure 10. Linear regression analysis was utilized to evaluate the degree of consistency between the experimental results and the predicted findings stemmed from the statistical model (Figure 10). The acquired regression coefficient ($R^2 > 0.98$)
demonstrated robust fit with the theoretical findings and the significance of the model to illustrate the method.

![Figure 10. Relation between the predicted and the actual biodiesel yield (%).](image)

The feasibility of the regression model was analyzed on the basis of the variable stemmed from ANOVA. Table 4 displays the variables of the \( p \) value, lack of fit, \( R^2 \), predicted \( R^2 \), and adequate precision to estimate the fitness of the model. The pattern is essential for predicting the yield with the \( p \) value less than 0.0001. The model \( F \) value is 20.94, which showed an incredibly important model with just about 0.0001% probability to the noise impact of this value. The \( p \) values of \( A, B, C, D, AB, AC, AD, BC, CD, A^2, B^2, C^2, \) and \( D^2 \) are less than 0.05, demonstrating the significance of these terms (Table 4). Besides, the estimated value of \( R^2 \) is 0.8991 that is somewhat in line with the Adj \( R^2 \) (0.9321), and the amount of Adeq Precision (19.32) implies an appropriate signal and the design could be used to adjust the design space. Thus, the trend in eq 2 is in well-consistent with the experimental results.

### 2.5.2. Interaction Impact between Transesterification Parameters

The 3D response graphs were developed to demonstrate the impacts of the independent variables on the dependent one (Figure 11). The surface enclosed in the smallest ellipse in the contour diagram had indicated the maximum predicted values. Elliptical contours were achieved when the independent parameters were in a complete interaction. A correlation between every two parameters and the highest predicted yield is emphasized by the surface confined in the smallest ellipse in the contour graphs.

#### 2.5.2.1. Interaction Impact between Reaction Time and Temperature

The interaction impact showed enhancing biodiesel yield with the incremental increase in reaction time for the selected temperatures (Figure 11a). The yield increased from 50 to around 60.4% for the transesterification temperature of 40 °C, with contact time increasing from 2 to 6 h. The biodiesel yield increased at 60 °C from 81 to around 92.4%, with increasing the time from 2 to 6 h (Figure 11a). The interaction impact of time on the role of temperature also revealed a major effect on the biodiesel yield obtained (Figure 11a). The biodiesel yield enhanced from 50 to 73% at a lower time (2 h), with temperature changes from 40 to 50 °C. Besides, the values increased from 78 to around 95% at the maximum time limit (6 h), with a temperature increase from 40 to 65 °C. The results obtained showed the potential to enhance the influence of time by increasing the temperature and the subsequent evaluation of the impact of temperature by increasing the temperature, which indicated a substantial improvement in the biodiesel yield by increasing the reaction time. The reaction’s temperature has a favorable effect on the yield of 65 °C, after which there is a substantial decrease in yield because of the boiling of methanol.57,58 The process temperature and composite dose effects on yield have interacted. One possible justification is that the reaction’s temperature is the restricted transesterification parameter. It is the little mass transfer resistance with the low catalyst dose, leading to a high yield at 65 °C. However, the resistance to

| Table 4. ANOVA Data for the Response Surface Quadratic Model |
|-----------------|----------------|-----------------|----------------|-----------------|----------------|
| source          | sum of squares | degree of freedom | mean square | \( F \)-value | \( p \)-value |
| model           | 2632.7         | 14              | 188.05       | 20.94          | <0.0001        |
| \( A \)=methanol/oil ratio | 44.25         | 1              | 44.25        | 4.93           | 0.0422         |
| \( B \)=time    | 0.1068         | 1              | 0.1068       | 0.0119         | 0.0146         |
| \( C \)=temperature | 2.39          | 1              | 2.39         | 0.2662         | 0.0134         |
| \( D \)=catalyst dose | 13.63         | 1              | 13.63        | 1.52           | 0.0369         |
| \( AB \)| 7.91              | 1              | 7.91         | 0.8811         | 0.0628         |
| \( AC \)| 34.41              | 1              | 34.41        | 3.83           | 0.0691         |
| \( AD \)| 8.38               | 1              | 8.38         | 0.9338         | 0.0492         |
| \( BC \)| 2.47               | 1              | 2.47         | 0.2749         | 0.0307         |
| \( BD \)| 0.0548             | 1              | 0.0548       | 0.0061         | 0.0387         |
| \( CD \)| 0.1286             | 1              | 0.1286       | 0.0143         | 0.0263         |
| \( A^2 \)| 35.44              | 1              | 35.44        | 3.95           | 0.0355         |
| \( B^2 \)| 0.0401             | 1              | 0.0401       | 0.0045         | 0.0476         |
| \( C^2 \)| 53.73              | 1              | 53.73        | 5.98           | 0.0272         |
| \( D^2 \)| 16.06              | 1              | 16.06        | 1.79           | 0.0200         |
| residual        | 134.68          | 15             | 8.98         |                |                |

\(^{\text{Model: significant. Lack of fit: not significant. R-squared: 0.9811. Adj R-squared: 0.9321. Pred R-squared: .8991. Adeq precision: 19.32.}}\)
mass transfer is rapidly increased owing to the increased catalyst dose, and the high-temperature methanol evaporation aggravates the tolerance to mass transfer. Time has a proportional impact on biodiesel yield. The yield increases because of the availability of sufficient time to complete the reaction, but afterward, the biodiesel yield began to decline because of the reverse reaction. Such findings also agree with the literature.

2.5.2.2. Interaction Impact Between Reaction Time and Catalyst Dose. The produced biodiesel increased from 55.6 to 87.2% at the lower catalyst dose (2%), as the transesterification time increased from 2 to 6 h. Increasing the catalyst dose to 5%, the yield increased from 83.2 to approximately 94.3% as the reaction time changed from 2 to 6 h (Figure 11b). Therefore, the superior influence of time could be achieved using 5% of 20Cs₂O−MgO/MPCs as catalyst dose and the more increase in the catalyst amount has a reverse impact.

2.5.2.3. Interaction Impact between Reaction Time and Methanol-to-Oil Ratio. Realistically, transesterification needs triglyceride/methanol (1:3) to produce 3 mol of ester along with 1 mol of glycerol, while the transesterification process is thus reversible, more methanol is commonly required to transfer the equilibrium to the final product. The interaction influence between methanol/oil ratio and transesterification time was investigated at 5% catalyst dose and 65 °C (Figure 11c). The biodiesel yield enhanced at a transesterification time (2 h) from 50 to 70%, with the methanol/oil ratio increasing from 3 to 15. The yield increased from 84.1 to

Table 5. Manufacturing Cost of Producing 1 ton of Biodiesel Using the 20Cs₂O−MgO/MPC Catalyst

| no. | cost item     | components          | price ($) | quantity | cost ($) |
|-----|---------------|---------------------|-----------|----------|----------|
| 1   | raw material  | edible olive oil    | 2.5/kg    | 1100     | 2750     |
|     |               | inedible olive oil  | 0.81/kg   | 1100     | 891      |
|     |               | methanol            | 0.44/kg   | 300      | 132      |
| 2   | catalyst      | mesopores carbon    | 1.5/kg    | 6        | 18       |
|     |               | MgO−Cs₂O            | 1.4/kg    |          |          |
|     |               | PSE                 | 0.1/kg    |          |          |
| 3   | utility       | tap water           | 0.33/t    | 1'       | 0.33     |
|     |               | electricity         | 0.12 kw/h | 8        | 0.96     |

Therefore, the superior influence of time could be achieved using 5% of 20Cs₂O−MgO/MPCs as catalyst dose and the more increase in the catalyst amount has a reverse impact.

Figure 11. Response 3D surface plots displaying the combination effect of (a) temperature and methanol-to-oil ratio, (b) time and methanol-to-oil ratio, and (c) catalyst dose and temperature.
around 93% at the transesterification time (6 h), with the methanol/oil ratio increasing from 3 to 15. Besides, at a constant methanol/oil ratio of 10, the yield increased from 66.5 to around 83% with increasing reaction time from 2 to 6 h. At higher methanol/oil ratio (15:1), the attained yield increased from 70.1 to 93.6%, increasing the transesterification time from 2 to 6 h (Figure 11C). This suggested that at all the transesterification time intervals, the methanol/oil ratio of (15:1) is the exceptional value for the full yield, and increasing the ratio above this ratio is of adverse influence. Summing up, the obtained results do reflect a feasible improvement in the 20Cs2O–MgO/MPC catalyst to attain a yield of 96.1% by tuning the conditions at 6 h, 65 °C, 5.2 wt % as 20Cs2O–MgO/MPC dose, and 1:15 as an oil/methanol ratio.

3. TECHNOECONOMIC ASSESSMENT

Evaluation of economic viability is an essential predictor for impacting sustainable biodiesel development. Accordingly, by taking into account the Saudi Arabia market price of all components, we evaluate the production cost of 1 ton of biodiesel from inedible olive oil, as shown in Table 5. The cost of raw materials constitutes 60–80% of biodiesel production’s overall cost.39,40 Applying lower-cost raw materials is a significant factor in reducing biodiesel costs. The price of edible and inedible olive oil is enormously different. The cost of biodiesel is predicted to decrease with the success of using waste olive oil. In this work, in the case of using inedible olive oil, the cost of biodiesel production is estimated to be $1.04 kg⁻¹, which is lower than that in the case of edible olive oil ($2.9 kg⁻¹). Future research will concentrate on the possibility of sustainable development and growth in minimizing production costs and, in the meantime, generate more biodiesel, fulfilling the requirements.

4. CONCLUSIONS

Biogenic-mediated synthesis of the Cs₂O–MgO/MPC nanocomposite as a powerful catalyst for the generation of biodiesel from olive oil with outstanding durability was successfully fabricated. The transesterification performance and the optimization design were estimated by utilizing the RSM. Based on the experimental tests, the finest experimental circumstances with a biodiesel yield of 96.1% are 4 h, 4% catalyst, an oil/methanol of 1:15, and a temperature of 65 °C. The predicted optimal conditions based on the statistical model are a contact time of 6 h, a catalyst dose of 5.2%, a reaction temperature of 65 °C, and an oil/methanol molar ratio of 1:15 attaining a biodiesel yield of 95.18%. The various physicochemical features emphasized the good quality of the biodiesel achieved according to the international biodiesel standards ASTM D-6571 and EN 14214. Therefore, utilizing 20Cs₂O–MgO/MPCs for transesterification of olive oil using methanol as a short-chain alcohol in the absence of any other organic solvent could be desirable in the production of biodiesel with high quality from waste olive oil as a raw material which can be used as an alternative rather than conventional petrochemicals. Besides, the results of technoeconomic assessment display that the inedible olive oil is efficient in the low-cost biodiesel production ($1.04 kg⁻¹) and offers desirable support for a progressively developing industry compared to edible olive oil ($2.9 kg⁻¹). This study may serve the baseline for further development in heterogeneous catalysis for biodiesel production from waste olive oil on a larger scale at the Al-Jouf region in the Kingdom of Saudi Arabia.

5. MATERIALS AND METHODS

5.1. Materials and Chemicals. Olive oil was derived from olive milling at the city of Sakaka (Jouf, SA). Cesium nitrate (CsNO₃), magnesium nitrate (Mg(NO₃)₂·6H₂O), and MPCs were obtained from Sigma-Aldrich. PMSE was obtained from fresh pomegranate fruits. Other solvents are of analytical quality and used with no more treatment.

5.2. Gas Chromatography (GC/MS) of Olive Oil. The gas chromatography (GC) equipment (Shimadzu-QP2020) was utilized to assess the contents of the fatty acid of the applied olive oil. The equipment was fitted with a flame ionization detector (FID) in the presence of helium as the carrier gas. Specifications of the composition of the fatty acid of the olive oil are cited in Table 6.

| molecular formula | fatty acid     | amount (%) |
|-------------------|---------------|------------|
| C16:0             | palmitic acid | 17.2       |
| C16:1             | palmitoleic   | 1.3        |
| C18:0             | stearic acid  | 4.8        |
| C18:1-trans       | oleic acid    | 59.1       |
| C18:1-cis         | elaidic acid  | 2.2        |
| C18:2             | linoleic acid | 13.7       |
| C18:3             | c-linolenic   | 0.674      |
| C20:0             | arachidic acid| 0.46       |
| C20:1             | palminic acid | 0.46       |

5.3. Catalyst Fabrication. 5.3.1. Preparation of the Cs₂O–MgO/MPC Nanocatalyst. Typically, 50 mg of PMSE is placed in a beaker (≈100 mL capacity) and then precisely 40.0 mL of DI water has been added to dissolve the extract. A certain quantity of cesium nitrate (CsNO₃), magnesium nitrate (Mg(NO₃)₂·6H₂O), and MPC were then added to the mixture with continuous stirring overnight. A significant darkness of the pink color of PSE solution was found by adding the metal nitrate salts that suggest a characteristic of interaction between PSE and Mg²⁺ and Cs⁺ ions. Upon complete dissolution, the mixture was transferred to the crucible. The crucible was then placed in a preheated muffle furnace at 300 °C, starting a 2 h solution combustion reaction. After the combustion process, the Cs₂O–MgO/MPC nanocatalyst is fabricated.

5.4. Nanocatalyst Characterization. For recording FTIR readings, a Shimadzu IR Tracer-100 FTIR spectrophotometer has been applied. Powder XRD profiles have been recorded using the X-ray diffractometer Maxima—X (D/MAX2500VB2+/Pc, Shimadzu Company, Japan) with an X-ray wavelength Cu detector. Raman spectroscopic analysis was conducted. The developed materials’ morphological features were examined applying FESEM (Zeiss FESEM Ultra 60). A NOVA 4200e (Quantachrome Instruments) surface area and pore size analyzer collected the nitrogen adsorption–desorption isotherms at 77 K. FESEM investigation using Zeiss FESEM Ultra 60 was conducted to investigate the morphology of the nanocomposite. CO₂ desorption (CO₂-TPD) assessment was performed on a Quantachrom Nova Sorbimetric system.

5.5. Biodiesel Production Procedure. The transesterification approach was chosen to produce biodiesel from the.
olive oil. The oil was commercially obtainable and was purchased from local distributors (Jouf, Saudi Arabia). A reflux system equipped with a closed upper part condenser was used to prevent methanol evaporation while better attempting to control the temperature of the process. Typically, a certain amount of the catalyst has been introduced to the oil and methanol mixture. At the reflux temperature, the blend was agitated. Biodiesel and glycerol were obtained after the stipulated contact time, and the mix was allowed to isolate overnight. The catalyst was separated from the mix by filtration. The final product after isolating the catalysts was rinsed with water to remove glycerol. Through filtration, the catalyst was isolated from the mixture. The product had been rinsed with water after removing the catalysts to isolate glycerol. The biodiesel collected was retained for the physicochemical investigations. The yield of biodiesel was evaluated from eq 3.  

\[ \text{yield} \% = \frac{\text{weight of biodiesel}}{\text{weight of olive oil used in reaction}} \times 100 \]  

(3)

5.6. Optimum Conditions for Biodiesel Production.

The impacts of variable settings on biodiesel development, such as reaction time (1, 2, 3, 4, 5, and 6 h), temperature (40, 50, 55, 60, 65, 70, and 75 °C), catalyst dose (2, 4, 6, and 7%), and methanol/olive oil molar ratio (3, 6, 9, 12, 15, and 18), were addressed.

5.7. Biodiesel Characteristics. After the biodiesel was prepared, biodiesel features such as kinematic viscosity, density, flash point, cloud point, pour point, acid number, and oxidation stability were assessed based on global standards.  

5.8. Reusability Experiment. The 20Ca2O−MgO/MPC nanocomposite was separated from the mixture by filtration, rinsed several times with methanol to eliminate any organic traces on the catalyst surface, and dried in an oven for 4 h at 120 °C. This was recycled for subsequent transesterification reactions. A similar approach is adopted for all recycled experiments.

5.9. Optimization Assessment. Optimization of the transesterification process was performed through a three-factor experiment to investigate the impacts of the independent variables including methanol/oil molar ratio (A), contact time (B), temperature (C), and catalyst dose (D) on the ester yield applying the RSM of the experiments. The RSM is designed and performed by the regression and graphical analysis of the data pertaining Design-Expert software (state Ease Inc., Minneapolis, MN, USA). The coded and uncoded levels of the independent variables used for the transesterification of olive oil are given in Table 7. Consequently, the entire sets of 30 experiments were conducted separately for getting the experimental response of yield. The data were analyzed by adopting the second-order polynomial in eq 4.

\[ Y = a_0 + \sum_{i=1}^{n} a_i X_i + \sum_{i=1}^{n} a_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij} X_i X_j \]  

(4)

where \( Y \) is the predicted response of the yield, \( X_i \) and \( X_j \) are the independent parameters, \( a_0, a_i, a_{ii}, \) and \( a_{ij} \) are the constant, linear, quadratic, and interactive coefficients, respectively.

### Table 7. RSM-CCD for Transesterification

| factor | name              | units | minimum | maximum | low   | high   |
|--------|-------------------|-------|---------|---------|-------|--------|
| A      | CH3OH:Oil         |       | 3.00    | 18.00   | −1 ↔ 3.00 | +1 ↔ 18.00 |
| B      | time              | h     | 1.0000  | 6       | −1 ↔ 1.00 | +1 ↔ 6.00 |
| C      | temperature       | °C    | 40.00   | 65.00   | −1 ↔ 40.00 | +1 ↔ 65.00 |
| D      | catalyst dose     | %     | 2.0000  | 7.00    | −1 ↔ 1.00 | +1 ↔ 7.00 |

Note the authors declare no competing financial interest.

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