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Enhancing the Catalytic Activity of Eggshell-Derived CaO Catalyst and Its Application in Biodiesel Production from Waste Chicken Fat

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Abstract: The comparatively greater cost of producing biodiesel in comparison to petroleum diesel is one of the key drawbacks. Eggshells and leftover chicken fat are examples of poultry wastes that can be used to produce biodiesel at a low cost as catalysts and oil, respectively. In this study, eggshell-derived CaO and its doping with sodium methoxide catalyst for enhancing catalytic activity was synthesized for the transesterification of waste chicken fat and characterized by FT-IR and XRD analyses. XRD studies confirmed the crystalline structure of the developed catalyst and doping of sodium with eggshell-derived CaO. The transesterification reaction was performed at different reaction parameters such as the catalyst loading, the methanol to oil ratio, the reaction temperature, and the reaction time. The biodiesel produced at the maximum yield was evaluated by gas chromatography mass spectrometry analysis. A maximum yield of 96% biodiesel was obtained with catalyst loading of 2 wt% of oil, as well as a methanol to oil ratio of 13:1 at 60 °C in 1 h. The output demonstrates that eggshell waste is a potentially accessible source of biomass-derived nano catalyst for the synthesis of biodiesel using chicken fat as a feedstock.

Keywords: eggshells; catalysts; biofuel; renewable; sustainable

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1. Introduction

From the last decade, there has been a continuous growing trend in producing and consuming biofuels in transportation and energy sectors [1–3]. Because of the problems and limitations associated with the use of fossil fuels, there will be a significant rise in the demand for biofuels in near future [4–6]. Biodiesel is one of the important biofuels and an alternative energy source because it possesses similar properties, such as a high flash point, a high cetane number, good lubricity, non-toxicity, low sulfur contamination, etc., compared to conventional fossil fuels [7,8]. Biodiesel is a mono alkyl ester of long-chain fatty acids produced from a range of feedstocks, e.g., edible and non-edible oils. Moreover, non-edible oils are in forefront of this field as these overcome the food vs. fuel debate caused by edible oils [9,10]. In the last few years, biodiesel has been produced and is being consumed as an alternative to fossil fuel on a commercial scale, and it is available in fuel markets [11,12]. The type of feedstock used is the main economic contributor, which can have a remarkable effect on biodiesel production costs [13,14]. Therefore, using non-edible

oils can reduce biodiesel production costs and biomass-derived feedstock costs. Hence, the choice of feedstock is very important in biodiesel production [15,16].

Animal fat wastes (AFWs) are easily available in slaughterhouses, farms, and restaurants in almost every region of the world. AFWs are not consumed by human beings directly and are disposed of in an open environment, which causes several health and environmental problems [17]. That is why the valorization of such wastes to derive different valuable products is more desirable to address these concerns. Numerous reports in the literature indicate that AFWs are composed of free fatty acids and triglycerides as major constituents [18]. Hence, AFWs such as tallow, lard, and chicken fats are considered as more promising candidates for producing biodiesel [19]. The biodiesel produced from using AFWs has number of advantages such as lower emissions and a higher cetane number due to the high ratio of free fatty acids in AFWs. Moreover, the biodiesel obtained from AFWs exhibits oxidative stable characteristics [20]. The transesterification of the oil extracted from AFWs is an obvious and affordable way to produce biodiesel from AFWs feedstock [21,22]. Transesterification is the reaction of triglycerides with methanol in presence of suitable catalyst and operating conditions. The reaction rate of transesterification can be faster when using different catalysts [23,24]. Different homogeneous and heterogeneous catalysts have been developed for optimum biodiesel production. Among these, heterogeneous catalysts are superior due to their ease of separation from the final products [25]. However, the synthesis of chemical and biological heterogeneous catalysts is a challenging task from an industrial point of view [26]. To cope with this problem, biomass-derived nano catalysts are intriguing due to their cost effective synthesis [27].

Waste eggshells are easily accessible as chicken eggs are commonly consumed on a regular basis by humans. Waste eggshells are recognized as one of the suitable precursors of CaO, an active catalyst in biodiesel production [28]. However, the lone CaO is not stable and active as it requires a long period of time to achieve equilibrium conversion [29]. Therefore, it has been attempted here to develop a CaO-based catalyst to overcome the mentioned problem. Various reports are available in the literature, which focus on enhancing the properties of CaO by using different chemical and physical ways [30–33]. It can also be concluded that the activity and stability of CaO can be improved by doping with a suitable dopant [34–36]. It has been reported that the employment of CaO as a catalyst resulted in an 80% increase in the amount of biodiesel produced. The yield with tungsten- and molybdenum-doped CaO, on the other hand, was roughly 96% [37,38]. The generation of biodiesel from Nahor oil (Mesua ferrea Linn) with lithium-doped CaO achieves an efficiency of approximately 94% [39]. In the process of producing methyl esters, the methoxide ions function as an active catalyst. This chemical unit is responsible for attacking the triglyceride molecules and resulting in the production of methyl esters. It is regenerated at the end of each reaction step when a hydrogen ion is stripped from a nearby methanol molecule. To the best of the authors' knowledge, there has been no report in the literature indicating a CaO-based catalyst with sodium methoxide as an active species. Hence, herein, a CaO-based catalyst with enhanced activity due to incorporation with sodium methoxide (CH_3NaO) as an active species is reported. Further, the designed catalyst CaO-CH_3NaO was used in the transesterification reaction of oil obtained from chicken fat. Additionally, this work also emphasizes the optimization of catalyst loading and reacting conditions for transesterification to produce biodiesel from chicken fat oil.

2. Result and Discussions

2.1. FTIR Analysis

Figure 1 shows the FTIR analysis CaO-CH_3NaO catalysts with different loadings and the uncalcined CaO-CH_3NaO catalyst. The band of CaO appeared at around 649 $cm^{-1,}$ which indicates the presence of Ca-O vibration [40]. The area looked different in uncalcined and calcined CaO at 649 cm^{-1}. The single bond region includes 1500–500 $cm^{-1,}$ and CaO peaks observed at 649 $cm^{-1,}$ which are a strong indication of its presence. NaO stretching was observed at 719 cm^{-1} in calcined and un-calcined groups. As concentration increases,

the broader and strong peak observed shows stretching and an absorbance band of NaO. At 1090 $cm^{-1,}$ the C-OH stretching is observed in that region. At 1390$cm^{-1,}$ the broader peak is shown due to the presence of CH_3. As concentration increases and after calcination at 700 °C, the CH_3 has a strong broader peak, indicating its confirmation. The presence of a peak for the produced catalyst at 3680 cm^{-1} is due to the formation of OH in $Ca(OH)_2$ during H_2O adsorption by calcium oxide [40].

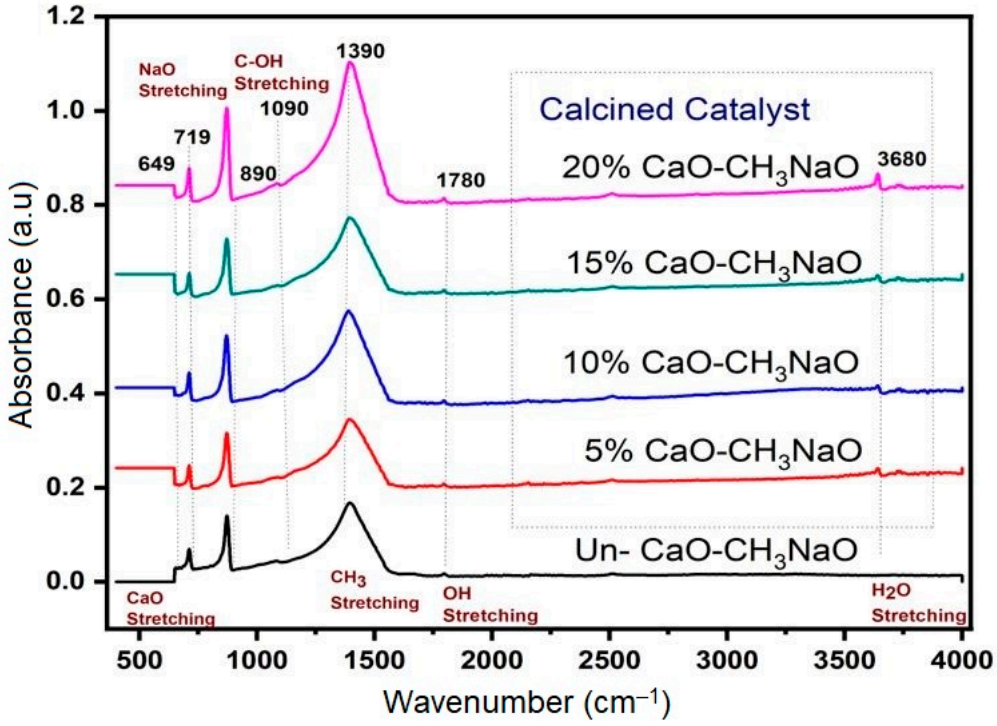

Figure 1. FTIR analysis of uncalcined and calcined CH_3NaO-doped CaO catalyst with different doping ratios.

2.2. XRD Characterization

XRD studies confirmed the crystalline structure of CH_3NaO-doped CaO catalyst using different doping ratios of dopant, as is shown in Figure 2. For the 5% CaO-CH_3NaO catalyst, the peaks at 31.66°, 36.72°, and 52.92° correspond to CaO (COD entry no. 96-900-6706) [41], while the peaks at 29.84 °, 42.70°, and 52.96° were found regarding sodium (COD entry no. 96-901-1003) [42]. The peaks at 31.78, 36.86, and 53.12 are CaO peaks (COD entry no. 96-900-6703) [41], and the peaks at 29.84°, 42.70°, and 52.96° are sodium peaks (COD entry no. 96-901-1003) [42] in 10% CaO-CH_3NaO catalyst. As far 15% CaO-CH_3NaO catalyst is concerned, the angles 32.24°, 37.38°, and 53.90° correspond to CaO (COD entry no. 96-720-0687) [43], and 29.90°, 42.80°, and 53.08° correspond to sodium (COD entry no. 96-900-8545) [44]. In 20% CaO-CH_3NaO catalyst, CaO peaks (COD entry no. 96-900-6746) were found at 30.82°, 35.74°, and 51.44° [41], while sodium peaks were found at 29.84°, 42.70°, and 52.96° (COD entry no. 96-901-1003) [42]. In summary, it is clear from XRD studies that the calcined CaO XRD spectra of calcined Cao without sodium doping contain peaks corresponding to CaO only. No peaks relevant to sodium were found. Meanwhile, the XRD spectra of calcined CaO doped with sodium clearly showed additional peaks, indicating the successful doping of sodium responsible for enhancing the catalytic activity of calcined CaO.

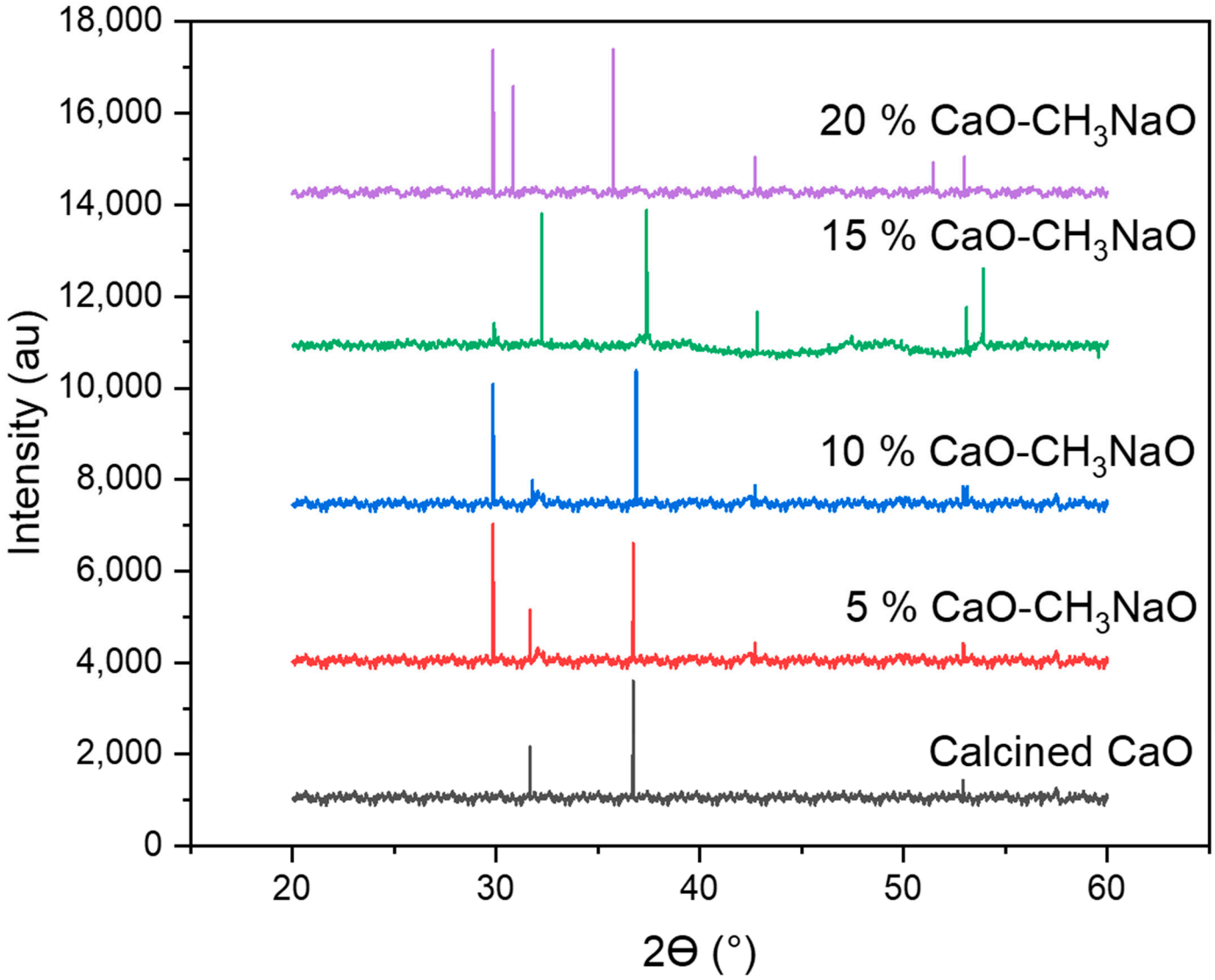

Figure 2. XRD studies of calcined CaO and CH_3NaO-doped CaO catalyst with different doping ratios.

2.3. GC-MS Analysis

The GC-MS analysis was performed to determine the composition of biodiesel obtained from chicken fat oil. Figure 3 shows the chromatogram of biodiesel obtained using 5% catalyst loading (sample B1), while Figures 4 and 5 show the chromatograms of biodiesel generated using 10% (sample B2) and 15% (sample B3) catalyst loading, respectively. Moreover, the detailed summary of the GC-MS analysis of biodiesel obtained by using CaO catalysts with 5, 10, and 15% loadings of sodium methoxide is presented in Table 1. The biodiesel produced using 5% CaO-CH_3NaO was composed of methyl esters at retention peaks of 18.46, 19.76, 33.49, and 35.57, with octenyl ester at 44.52. Similarly, the biodiesel produced using 10% CaO-CH_3NaO contained butyl esters at peaks of 8.24 and 11.41 and methyl esters at peaks of 14.71, 17.01, 20.12, 26.62, and 36.85. Meanwhile, the biodiesel produced using 15% CaO-CH_3NaO comprised methyl esters at peaks of 8.22, 29.86, 33.64, 37.04, 40.35, and 44.5.

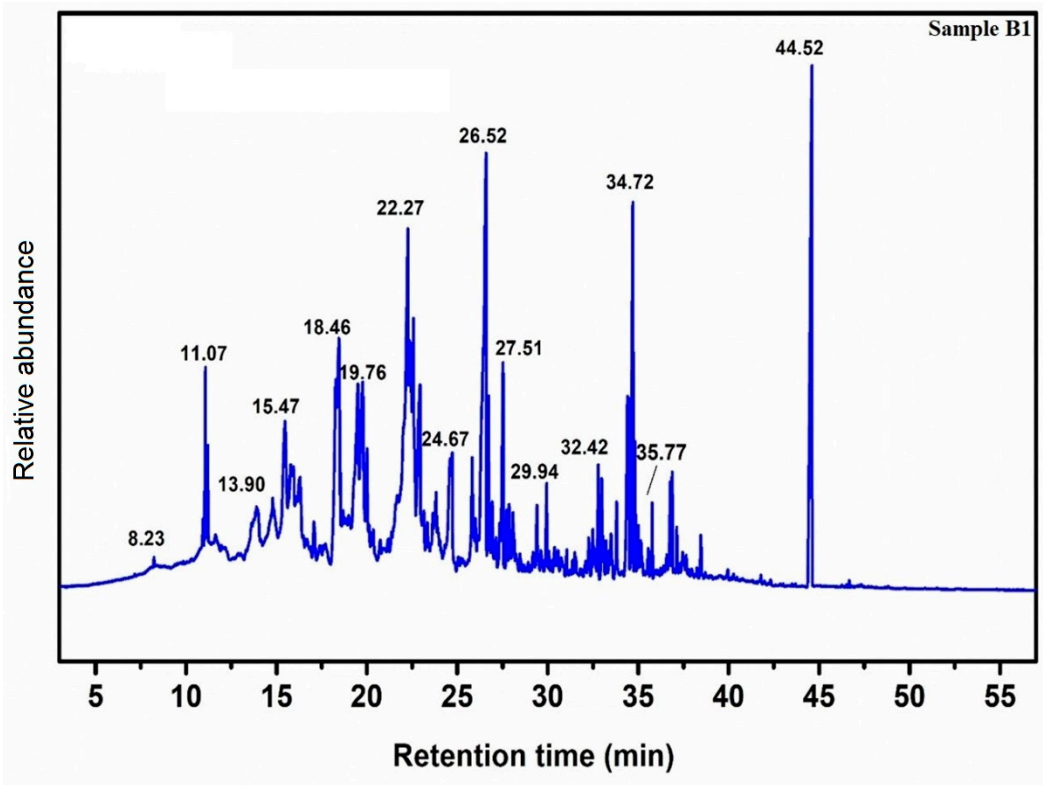

Figure 3. GC-MS analysis of sample B1.

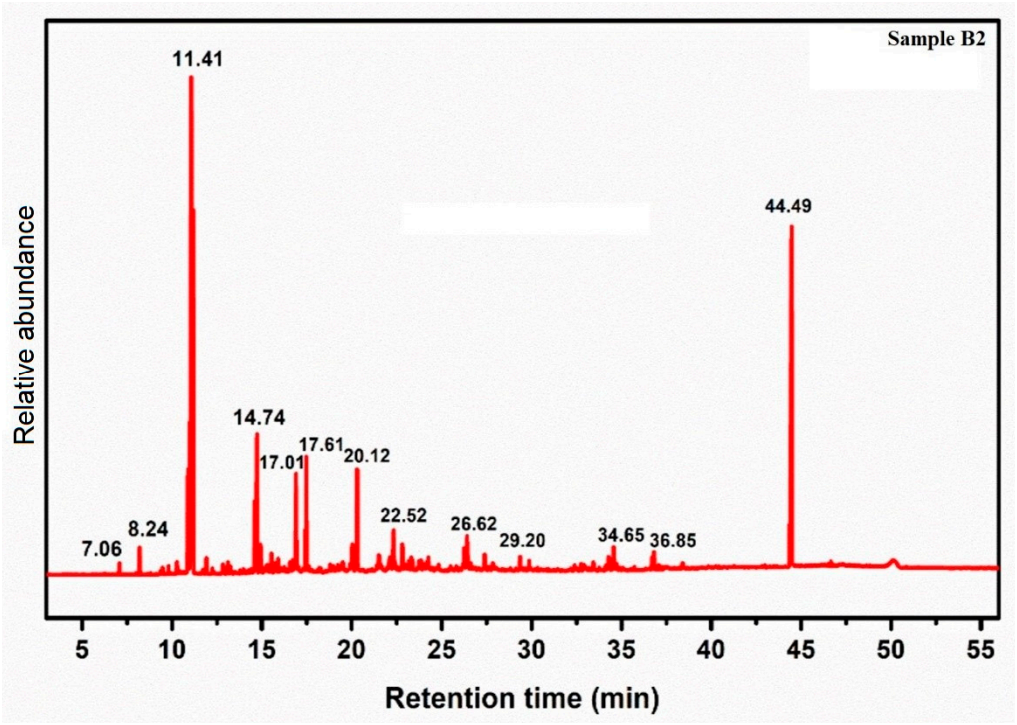

Figure 4. GC-MS analysis of sample B2.

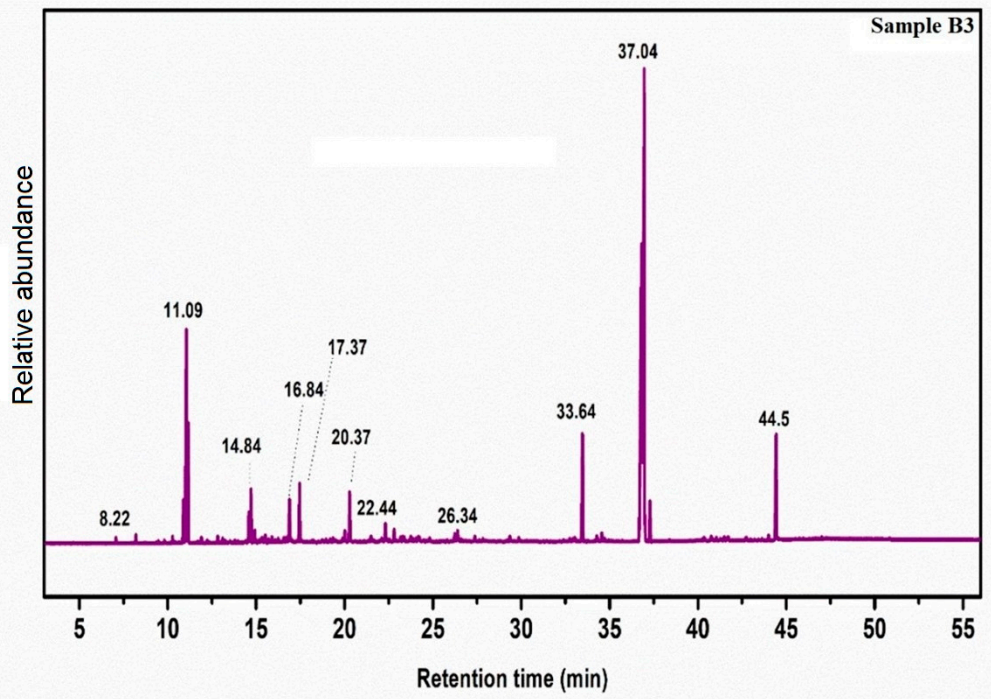

Figure 5. GC-MS analysis of sample B3.

Table 1. Summary of GC-MS analysis of biodiesel produced using CaO-CH_3NaO catalysts with different doping ratios.

5% CaO-CH_3NaO			10% CaO-CH_3NaO			15% CaO-CH_3NaO		
Ret. Time	**Composition**	**M_w**	**Ret. Time**	**Composition**	**M_w**	**Ret. Time**	**Composition**	**M_w**
8.23	Cyclohexene,1-methyl-5	270	8.23	Cyclohexene,1-methyl-5	128	8.22	Methyl ethyl ester	186
13.90	5-dimethyl-benzene methanol	398	8.24	Isobutyl ester	128	11.09	Encalyptol	284
18.46	6-heptanoic acid, methyl ester	438	11.41	3-methyl butyl ester	284	14.84	Cyclo hexene	296
19.76	2,4-hexadenoic acid, methyl ester	264	14.71	2-propenoic acid, methyl ester	296	16.84	Citronellol	208
22.27	3-hexadiene-1-ol	100	17.01	7-methylene-2,4,4-timethyl, methyl ester	320	22.24	2-cyclo hexe-1one	296
32.42	6- Octenoic acid	214	17.61	Mono-(2,2-dimethyl cyclo hexyl acid) ester	250	26.34	Napthalene	156
33.49	Hexadecanoic acid, methyl ester	438	20.12	Hexa decanoic acid, methyl ester	138	29.86	Docosaptenoic acid, methyl ester	214
35.577	Pentadecanoic acid, methyl ester	466	26.62	6-octenoic acid, methyl ester	284	33.64	Hexa decenoic acid, methyl ester	310
44.52	7-dimethyl-6-octenyl ester	389	34.65	Tetra methyl thioctic acid	160	37.04	Hepta deconic acid, methyl ester	348
			36.85	9-octenoic acid, methyl ester	203	40.35	11-eicosenoic acid, methyl ester	408
			44.49	Mono ethyl hexyl ester	307	44.5	Docasenoic acid, methyl ester	450

2.4. Effect of Reaction Parameters

2.4.1. Effect of Oil to Methanol Ratio

Methanol to oil molar ratio is one of the most important elements affecting biodiesel formation. Even though the transesterification reaction requires a 3:1 M ratio to produce

three moles of ester and one mole of glycerol, most experiments revealed that more alcohol was needed to complete the reaction [45]. The methanol to oil ratio ranged from 6:1 to 14:1 at 55–70 °C in the investigation. The biodiesel yield was increased when the methanol to oil ratio was increased, as illustrated in Figure 6. When the molar ratio is greater than 13:1, the biodiesel output decreases. The yield of biodiesel decreases if the molar ratio is increased over 13:1 because too much methanol and glycerol dissolve in methanol, which stops the reaction. Additionally, the reaction inhibition would cause a reaction direction to reverse and reduce the yield. On the other hand, the reactions would not continue, and no fatty acid methyl ester (FAME) would be produced if the molar ratio were too low.

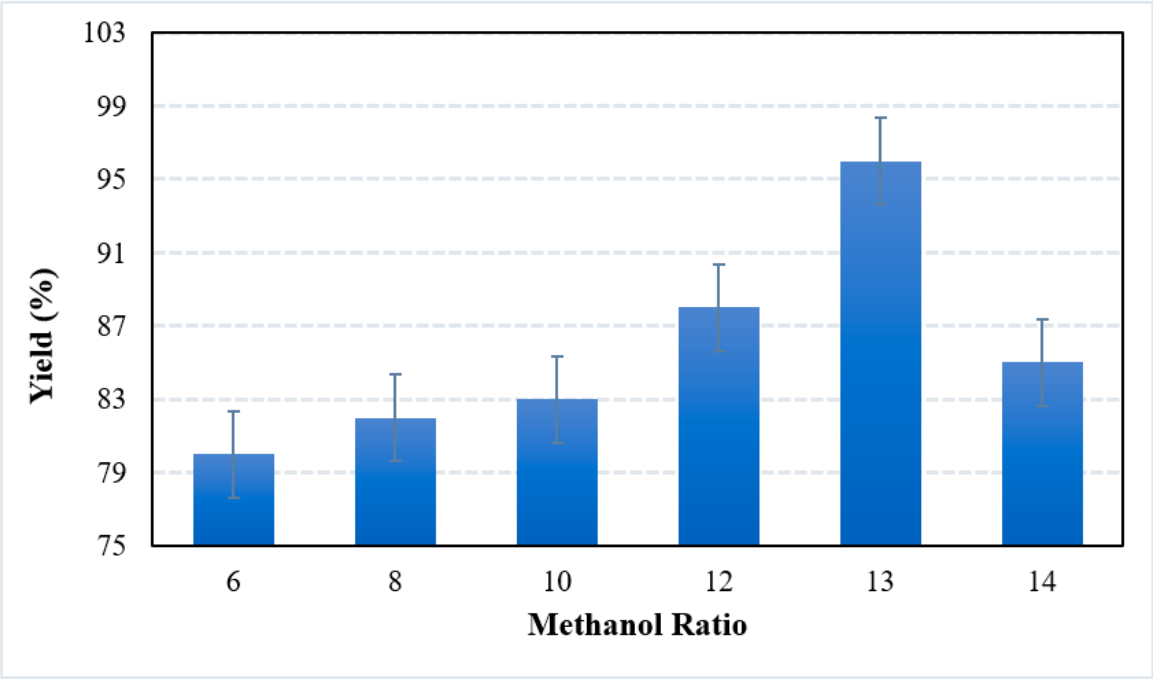

Figure 6. Effect of methanol to oil ratio on biodiesel production.

2.4.2. Effect of Catalyst Loading

The choice of the catalyst and its concentration are crucial in the transesterification reaction since they both influence how well methanol and oil combine. The catalyst's loadings wt.% of oil varied from 1 to 5 wt.% to examine the biodiesel yield (Figure 7). The yield increases with time with an oil catalyst loading of 2wt.% and subsequently falls after reaching the maximum point that kept the others factor constant, as given in Figure 8. The reason was that as more catalyst was added, the viscosity of the reaction mixture was changed as a result of soap formation and the difficulties in separating biodiesel from glycerol and catalyst. Therefore, a catalyst concentration that is either too low or too high would reduce the output of biodiesel.

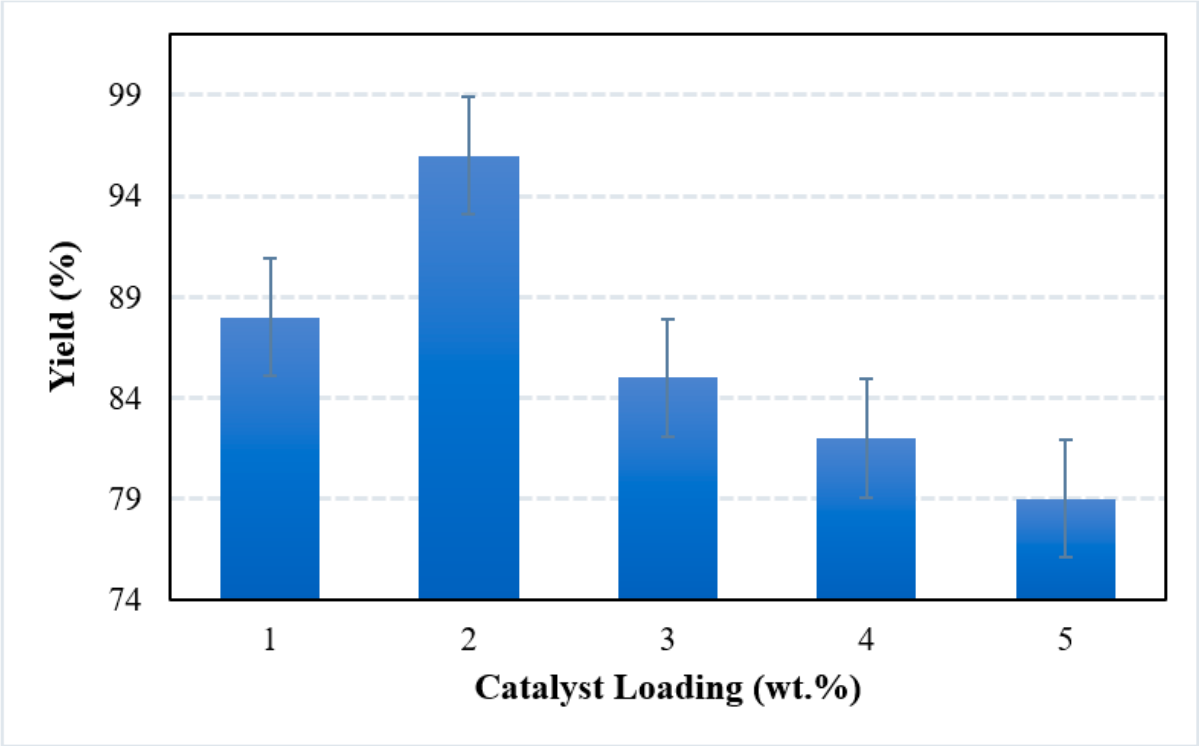

Figure 7. Effect of catalyst loadings on biodiesel production.

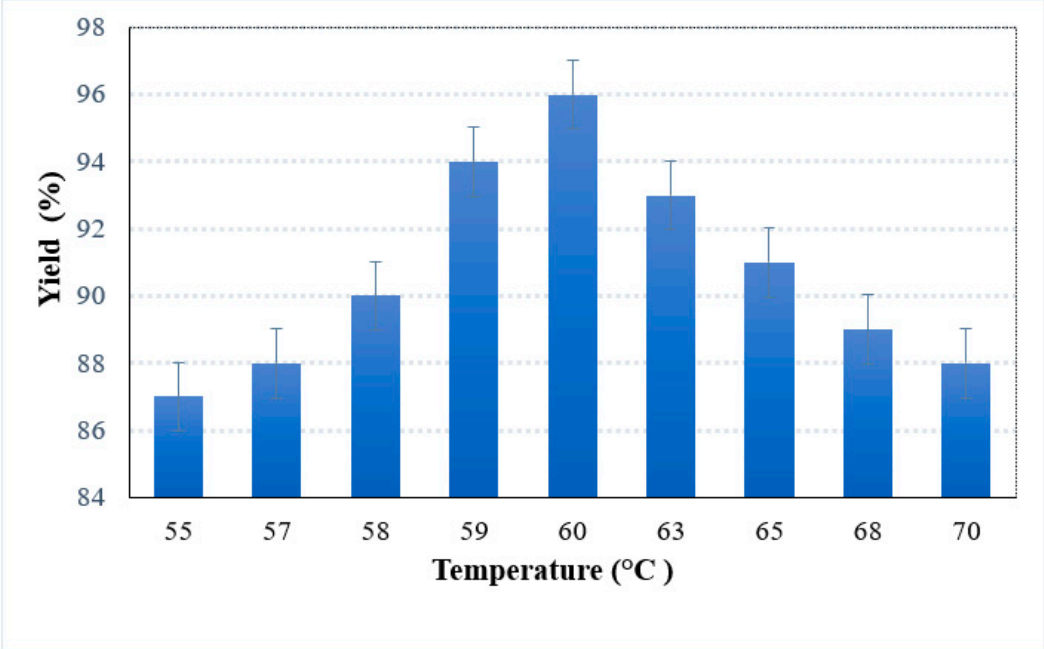

Figure 8. Effect of reaction temperature on biodiesel production.

2.4.3. Effect of Temperature

Figure 8 shows the effect of the reaction temperature on biodiesel production from catalyzed transesterification. The biodiesel yield was improved when the temperature was increased. When the temperature is increased from 45 to 60 °C, the biodiesel yield increased. This was due to the fact that as the temperature rises, so does the miscibility of alcohol in the waste chicken fat oil, as does the average speed (kinetic energy) of the molecules, resulting in more successful collisions and higher reaction rates. The viscosity

of the reaction mixture was reduced as the reaction temperature was increased, lowering the diffusion barrier between the distinct phases (oil, methanol, and catalyst). As the temperature rises to 65 °C, methanol evaporation causes the cavitation bubble to become supersaturated with methanol vapor, cushioning the collapse. Bubbles collapse with less force as a result, reducing mass transfer and yield. The effect of temperature on biodiesel yield was investigated in this study at temperatures ranging from 55 to 70 °C. By keeping the remaining parameters constant, the reaction at 65 °C yielded the highest yield. At 55 °C, the reaction was partial, resulting in reduced conversion. Further increasing the temperature to 65 °C yielded the best results; however, as the temperature was increased, the yield dropped due to the evaporation of alcohol, resulting in a loss in mass transfer.

2.4.4. Effect of Reaction Time

At reaction temperature of 60 °C and 1 h reaction time, the highest biodiesel yield of 96% was produced, as is shown in Figure 9. The yield was found to be lower during the shortest reaction time due to incorrect diffusion between the three phases of the reaction mixture. Increasing the reaction time beyond 1 h, on the other hand, resulted in a reduced yield. The longer reaction time leads to a reduction in biodiesel yield due to the reversible reaction of transesterification resulting in the loss of esters, as well as soap formation.

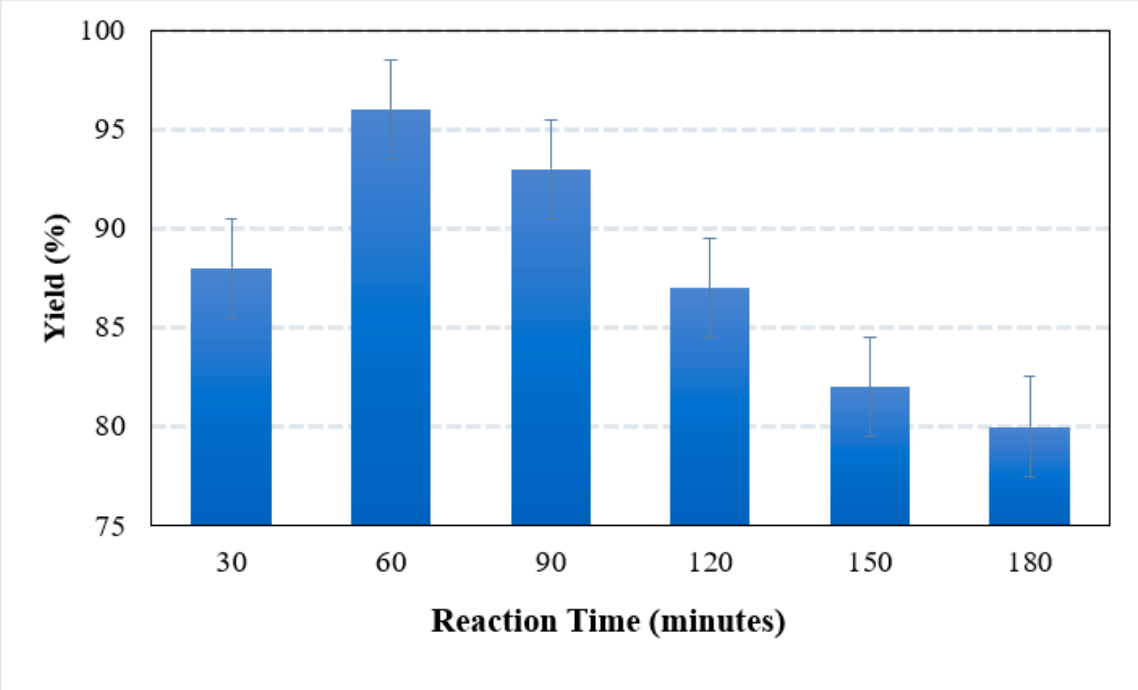

Figure 9. Effect of reaction time on biodiesel production.

2.4.5. Comparative Study of Biodiesel Yield from Waste Chicken Fat

Table 2 shows the comparative study of biodiesel yield from waste chicken fat as feedstock using CaO and different catalysts. The catalysts used for biodiesel production from waste chicken fat other than CaO showed lower yields of biodiesel, as shown in Table 2. However, using the CaO catalyst, the biodiesel yield was obtained to 90.2%. Similarly, a biodiesel yield up to 94.5% was observed using $CaO/CuFe_2O_4$ but with catalyst loading higher than 2 wt%. In this study, the developed catalyst produced biodiesel up to a maximum of 96% with 2 wt% catalyst loading due to enhanced activity.

Table 2. Comparative study of biodiesel from waste chicken fat using different catalysts.

Sr. No	Catalysts	Catalyst Loading, wt%	Biodiesel Yield, %	Reference
1.	KOH	0.5	67	[46]
2.	NaOH	1	71.3	[47]
3.	KOMe	0.5	88.5	[47]
4.	KOH	0.8	76.8	[46]
5.	CaO	2	90.2	[48]
6.	$CaO/CuFe_2O_4$	3	94.5	[49]
7.	$CaO\text{-}CH_3NaO$	2	96	This study

3. Materials and Methods

3.1. Materials

Chicken fat and waste eggshells were collected from the nearby slaughterhouse and bakery shop, respectively, and washed with distilled water several times to eliminate impurities such as dust particles and other odorous wastes.

3.2. Methods

3.2.1. Oil-Extraction Method

This step involved oil extraction from chicken fat, which was achieved by placing chicken fat in microwave oven until the oil was produced. To remove the water content, the collected oil was heated over 100 °C before being purified. The waste chicken fat oil was filtered for further purification and stored.

3.2.2. Determination of Acid Value

High free fatty acids (FFA) reduce biodiesel yield by generating soap during the transesterification cycle. The acid value was determined using the following equation:

$$\text{Acid value (AV)} = V \times C \times 56.11/m$$

where 'V' represents the volume of the KOH solution (mL), 'C' represents the KOH concentration (mol L^{-1}), and 'm' represents the mass of oil extracted (gram).

The acid value (AV) was 0.86 mg KOH/g of oil, which equates to 0.43% free fatty acids (FFA).

3.2.3. Catalyst Synthesis and Characterization

The sodium-methoxide-doped CaO was prepared by the simple impregnation method [34]. The complete synthesis procedure is as follows. The washed waste eggshells were crushed into tiny pieces and heated to 105 °C for 24 h in a hot air oven to eliminate the moisture. The dried shells were then ground with a pestle and mortar followed by calcination at 700 °C for 5 h in a muffle furnace. The obtained powder was labeled as an active CaO catalyst and was stored in tightly closed vial for further use. Further, the aqueous solution of sodium methoxide with a suitable concentration was prepared and then drop-wise added to CaO powder carefully. The resulting mixture was placed in an oven for drying for 10 h at 110 °C. After drying, the resulting solid was named the $CaO\text{-}CH_3NaO$ catalyst and was used for the transesterification process and characterized. The X-ray diffraction (XRD) patterns were acquired by using the PRO analytical X-ray diffractometer. Fourier transform infrared spectroscopy (FTIR) spectra were recorded by infrared spectroscopy with KBr pellets in the range 400–4000 cm^{-1}. The signal resolution of 4 cm^{-1} with 40 scans was applied. The same procedure was followed to develop different catalysts with varying loadings of dopant. Figure 10 shows the complete synthetic procedure of the $CaO\text{-}CH_3NaO$ catalyst.

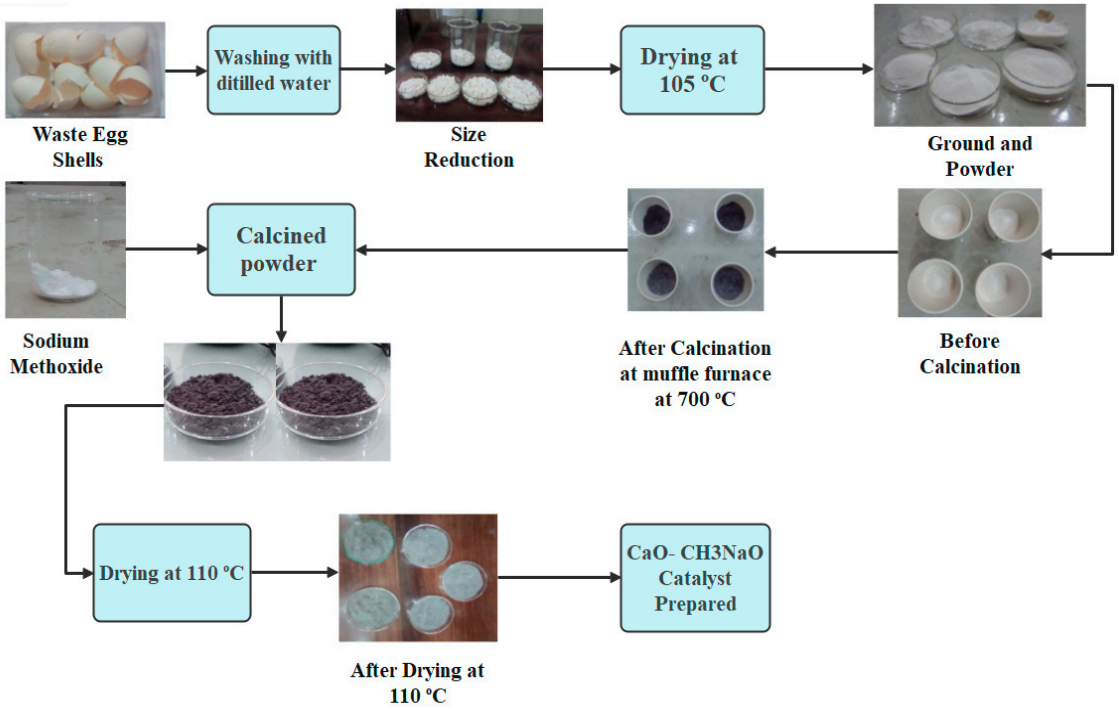

Figure 10. Steps involved in complete synthesis of CH_3NaO-doped CaO catalyst.

3.2.4. Transesterification of Chicken Fat Oil

The transesterification reaction was carried in a two-neck round-bottom flask (250 mL) connected with a refluxing condenser on a magnetic stirrer. An appropriate volume of oil and methanol was poured into a flask followed by the addition of the synthesized catalyst. The reaction was conducted under continuous stirring with different catalyst loadings and a methanol to oil ratio at suitable temperatures. The catalyst was removed by centrifugation after the reaction was completed. The resulting mixture after centrifugation was transferred into a separating funnel. The biodiesel and glycerol layers were separated in a separating funnel after 34 h. The biodiesel layer was carefully collected and heated up to 100 °C to remove any unreacted methanol. The biodiesel sample was sent for GC-MS analysis. The FAME of biodiesel was characterized by a Perkin Elmer (Waltham, MA, USA) Clarus 600 gas chromatograph mass spectrometry (GC-MS) using a DB-Wax column. Helium was used as a carrier gas with constant flow of 1.0 mL/min, with a 1 µL sample injected with a mass spectrometer set to scan a frequency range of 40–550 amu. The initial oven temperature was set to 80 °C and held for 5 min before being increased to 240 °C at a heating rate of 4 °C/min. Finally, the biodiesel yield was calculated as given below. In addition, multiple reactions were performed to study the effect of different parameters such as the catalyst loading (1–5 wt%), the methanol to oil ratio (6–14), the temperature (55–70 °C), and the reaction time on biodiesel yield (30–180 min).

$$Yield = \frac{Mass\ of\ biodiesel\ in\ grams}{Mass\ of\ oil\ taken\ in\ grams} \times 100$$

4. Conclusions

Waste chicken fat and eggshell are examples of poultry wastes that could serve as inexpensive sources of raw materials for the production of biodiesel. In this work, used chicken eggshells were calcined at 700 °C and effectively turned into CaO and doped with sodium methoxide for an effective catalyst for biodiesel production. The waste chicken fat that was recovered using a straightforward non-solvent approach was trans-esterified (valorized) using a heterogenous catalyst made from chicken eggshell. The maximum yield of 96% biodiesel was obtained with catalyst loading of 2 wt% of oil, and a methanol to

oil ratio of 13:1 at 60 °C in 1 h. The analysis of the resulting biodiesel provides additional evidence for the viability of the raw materials for the synthesis of biodiesel. This research has established the transesterification of oil from chicken slaughter waste using a low-cost, non-solvent extraction method and a low-cost catalyst source. A future study for a suitable and feasible commercialization of the process is proposed, including optimization studies, eggshell catalyst treatment with metal oxide reagents, and pilot-scale investigations of the procedure.

Author Contributions: Conceptualization, F.J. and M.H.; methodology, M.S., O.A.Q., P.A.; software, O.A.Q.; validation, P.A., M.S.K. and A.H.A.-M.; formal analysis, A.I. and N.S.S.; investigation, M.S.K; resources, F.J. and M.H.; data curation, O.A.Q.; writing—original draft preparation, M.S. and O.A.Q.; writing—review and editing, F.J., P.A., M.H., M.S.K., A.H.A.-M., A.I. and N.S.S.; visualization, F.J., M.H. and M.S.K.; supervision, F.J., M.H. and M.S.K.; project administration, F.J., M.H. and M.S.K.; funding acquisition, M.H. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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