

Article

Biodiesel Production through the Transesterification of Waste Cooking Oil over Typical Heterogeneous Base or Acid Catalysts

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Abstract: For the production of biodiesel from waste cooking oil with an acid value of 1.86 mg KOH/g, five heterogeneous catalysts—Ba(OH)₂, CaO, MgO, ZnO, and AlCl₃—were employed. To optimize the reaction parameters of each catalyst, the influence of crucial process variables, such as catalyst loading, methanol-to-oil ratio, and reaction duration, was investigated. In addition, the effect of acetone as a cosolvent toward the progress of biodiesel production and the reusability of the heterogeneous catalysts were also examined, and the data were statistically evaluated with a 95% confidence level. Ba(OH)₂ performed exceptionally well, with a 92 wt.% biodiesel yield, followed by CaO with an 84 wt.% yield. However, none of the results for MgO, ZnO, or AlCl₃ were adequate. In addition, regardless of the type of catalyst utilized, adding 20 vol.% acetone to the biodiesel manufacturing process led to an increase in output. Furthermore, every heterogeneous catalyst was reusable, but only Ba(OH)₂ and CaO produced a significant yield until the third cycle. The other catalysts did not produce yields of any significance.

Keywords: biodiesel; biofuel; bioenergy; catalyst; heterogenous; renewable energy; transesterification; optimization; waste cooking oil



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1. Introduction

Due to the probable depletion of fossil fuels and environmental concerns over greenhouse gas emission, the quest for alternatives to fossil fuels is attracting growing attention [1]. In recent years, there has been a great deal of interest in vegetable oil's potential as a renewable energy source that is also advantageous for decreasing greenhouse gas emissions. For the conversion of vegetable oil to fuel oil, pyrolysis, emulsification, and dilution with liquid hydrocarbon are all possible processes [2]. However, vegetable oils typically have negative characteristics, such as high viscosity, a high ignition point, poor volatility, a high cloud point, and turbidity, and they contain phosphorus, which decreases abrasion resistance. Diesel engines are susceptible to piston ring exhaust, oil pipeline or filter freezing, difficult cold starting, insufficient atomization, incomplete combustion, and high fuel consumption. The long-term use of vegetable oils can result in severe carbon dioxide emissions and other complications [3]. Therefore, the methanol-based transesterification process is by far the most feasible method [2]. The transesterification of vegetable oil results in the creation of biodiesel, which is regarded as clean, biodegradable, and acceptable for the environment [4,5].

This technique has gained extensive use in recent years as a means of reducing the viscosity of triglycerides [6]. The transesterification reaction is represented by the general overall reaction shown in Figure 1. The transesterification procedure is comprised of three distinct reversible stages that occur sequentially. The first stage involves the conversion

of triglycerides to diglycerides; the second stage involves the conversion of diglycerides to monoglycerides; the final stage involves the conversion of monoglycerides to glycerol, as illustrated in Figure 1. For each glyceride, a single ester molecule is produced. Even though the equilibrium favors the synthesis of fatty acid esters and glycerol, the processes are reversible [7].

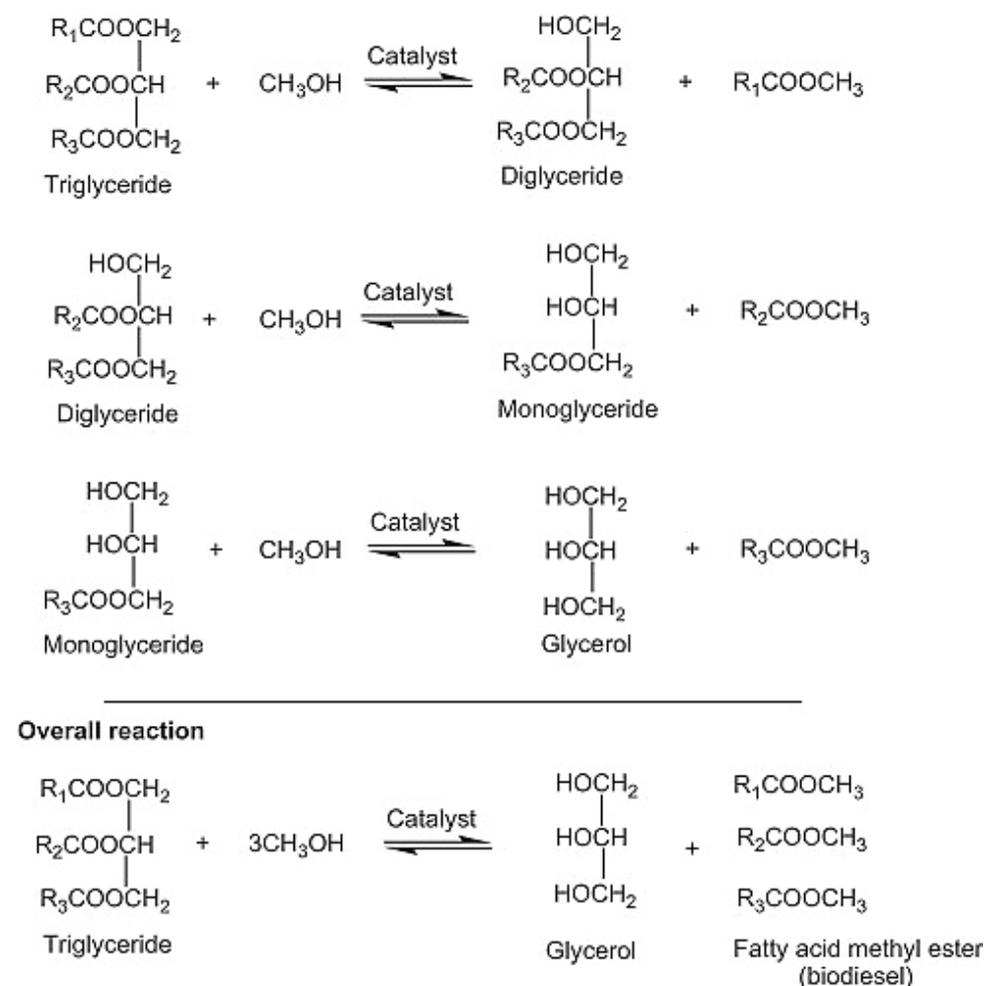


Figure 1. The overall transesterification reaction of triglyceride [8].

A catalyst is regularly utilized to accelerate a process and boost its yield. Since the transesterification reaction is reversible, more alcohol is required to shift the equilibrium toward the product [7,9,10]. However, the increased density of carbinol can result in a polycondensation process, which reduces the effective concentration of carbinol and complicates biodiesel separation. In addition, more carbinol relates to increased expenditures [11]. The mechanism of biodiesel generation is usually assumed to consist of an initial mass-transfer-controlled area followed by a kinetically controlled region. The mass-transfer-controlled phase can be skipped by promoting mixing [12]. However, the activation energy required to overcome kinetically controlled steps should be less. Therefore, catalysts are essential for transesterification [13]. Therefore, the catalyst, which acts as an activator of the reaction, receives increased attention.

In the transesterification reaction, the three most common types of catalysts are enzyme catalysts, acid catalysts, and alkali catalysts. Throughout the entire reaction process, each catalyst has its advantages and disadvantages. As the catalyst, an enzyme is constrained to stringent reaction conditions and activity loss of lipase, etc.; it has not yet been applied to large-scale commercial manufacturing [11]. Consequently, alkaline and acid catalysts are commonly utilized in biodiesel generation. Figure 2 depicts the mechanism of acid-

catalyzed transesterification of vegetable oils for a monoglyceride. It can also be applied to di- and triglycerides. The protonation of the carbonyl group of the ester produces the carbocation (II), which, upon nucleophilic attack by the alcohol, generates the tetrahedral intermediate (III), which removes glycerol to form the new ester (IV) and regenerates the catalyst H^+ [14].

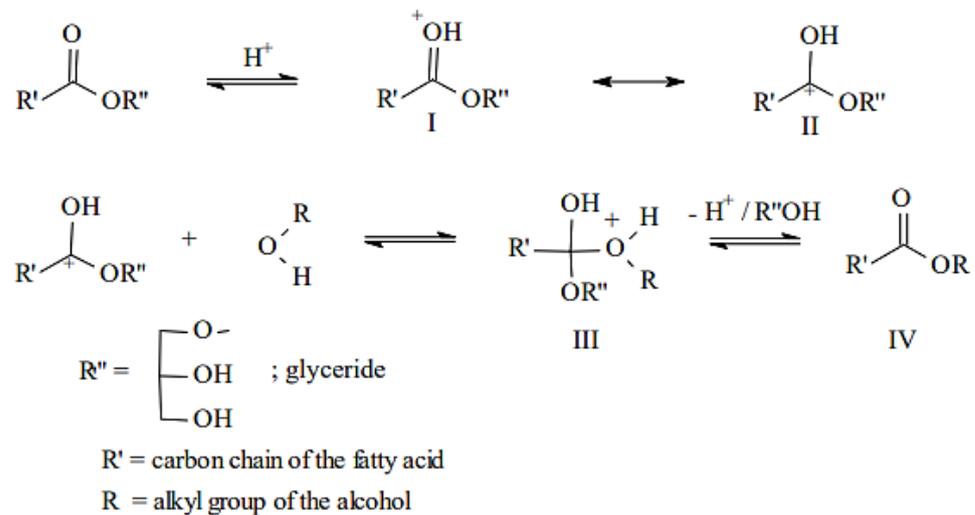


Figure 2. Mechanism of the transesterification of vegetable oils by acid catalyst [14].

Figure 3 depicts the mechanism of the base-catalyzed transesterification of vegetable oils. The first step is the reaction of the base with the alcohol, which results in the formation of an alkoxide and a protonated catalyst. The alkoxide's nucleophilic attack on the carbonyl group of the triglyceride forms a tetrahedral intermediate, from which the alkyl ester and corresponding anion of the diglyceride are generated. The latter deprotonates the catalyst, thereby regenerating the active species, which can now combine with a second molecule of the alcohol to initiate a new catalytic cycle. The same mechanism converts diglycerides and monoglycerides to a combination of alkyl esters and glycerol [14].

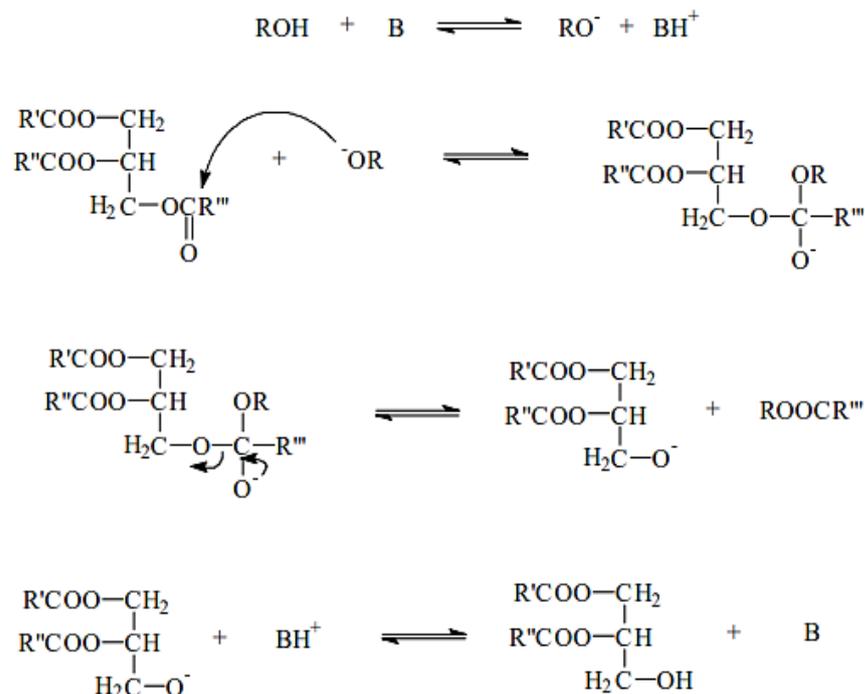


Figure 3. Mechanism of the transesterification of vegetable oils by alkali catalyst [2].

Using very effective homogeneous alkali catalysts, such as sodium or potassium hydroxides, carbonates, or alkoxides, the great majority of commercial biodiesel is produced from vegetable oils. In general, this method constitutes the vast majority of biodiesel manufacturing [15,16]. The speed of the alkali-catalyzing process is considerably faster than the acid-catalyzing process. In addition to this factor, the exceptional corrosion resistance of alkali catalysts contributes to their extensive use in industrial settings. Nonetheless, the alkali catalytic process is highly sensitive to the presence of water and free fatty acids. In addition, the procedure requires a substantial amount of methanol and is accompanied by a saponification reaction, both of which impede the separation of biodiesel and glycerin. Because alkali catalysts contribute to a rise in the medium's pH value, the medium's pH must be neutralized by eliminating hydroxide ions. Since homogeneous alkali catalysts can be dissolved in water more quickly than in ester medium, neutralization has been carried out with water. However, neutralization with water produces wastewater, which is a significant issue. Furthermore, homogeneous catalysts cannot be reused, as they cannot be recovered, and therefore the produced glycerol is very impure due to the dissolution of undesirable materials in aqueous solution [17,18].

Transesterification with heterogeneous catalysts is a potential answer to these problems. In contrast, because heterogeneous catalysts are often solid, homogeneous base catalysts yield reaction rates that are substantially faster than those of heterogeneous catalysts. However, it is significantly more expensive to remove homogeneous catalysts from the reaction mixture. In the heterogeneously catalyzed reaction medium, the reaction mixture and the catalyst exist in different phases as a direct result of this. Consequently, the principal reaction site in a heterogeneously catalyzed reaction medium is the catalyst's surface [19,20].

It is feasible to lessen the consequences of these problems by adopting heterogeneous transesterification catalysts. There is a rising interest in the prospect of substituting homogeneous alkaline hydroxides, carbonates, or metal alkoxides with heterogeneous solid catalysts. This could make it easier and less expensive to refine the biodiesel and glycerol produced. These catalysts can be reused, thereby reducing the quantity of hazardous waste generated. Additionally, heterogeneous catalysts have the advantages of simple separation from the product, reusability, and environmental friendliness [11,21].

The effectiveness of various heterogeneous catalysts for the generation of biodiesel has been described in earlier investigations [4]. To our knowledge, no prior research has been carried out on the performance of moderately basic (MgO) and lowly basic (ZnO and AlCl_3) heterogeneous catalysts combined with high basic heterogeneous catalysts such as $\text{Ba}(\text{OH})_2$ and CaO. This study evaluates the catalytic efficacy of these heterogeneous catalysts in an effort to fill this gap in the literature. To determine the viability of using heterogeneous catalysts for biodiesel synthesis, it is crucial to evaluate the optimization of these catalysts. Therefore, this study investigates the particular process behaviors of alkaline earth oxides such as CaO, and MgO, an oxide of D block such as ZnO, alkali hydroxides such as $\text{Ba}(\text{OH})_2$, and a heterogeneous acid catalyst such as AlCl_3 catalyzed transesterification of waste cooking oil with methanol. Before this study, a great number of research studies were undertaken to assess the effect of altering the reaction parameters in the presence of the above-mentioned heterogeneous catalysts on biodiesel yield. Table 1 outlines the contributions of various heterogeneous catalysts to the production of biodiesel.

Since the transesterification reaction is influenced by a number of parameters, it is necessary to determine their effects on these five heterogeneous catalysts, $\text{Ba}(\text{OH})_2$, CaO, MgO, ZnO, and AlCl_3 , and it is essential to determine the impacts of major process variables such as catalyst concentration, reaction duration, and methanol-to-oil molar ratio on biodiesel yield. On the other hand, there are relatively few publications that compare the heterogeneous catalysts mentioned above in a single study. This study also investigates the influence of introducing acetone as a cosolvent to a heterogeneous catalytic reaction medium containing the abovementioned heterogeneous catalysts. Moreover, this study

provides a cost-benefit analysis of utilizing each heterogeneous catalyst, Ba(OH)₂, CaO, MgO, ZnO, and AlCl₃.

Table 1. Various heterogeneous and homogeneous-catalyzed biodiesel synthesis under diverse reaction conditions.

Catalyst	Feedstock	Condition ^a	Yield (%)	References
CaO	Soybean oil	12: 1, 8, 65, 180	95	[22]
CaO	Sunflower oil	13: 1, 3, 60, 120	94	[23]
Ba(OH) ₂	Rubber seed oil	8.01: 1, 5.38, 30, 13.20	97	[24]
Ba(OH) ₂	Jatropha oil	6: 1, 8, 60, 360	73.03	[25]
Ba(OH) ₂	Rapeseed oil	9: 1, 0.7, 30, 120	98.3	[26]
MgO	Waste cooking oil	10: 1, 2, 60, 120	80	[27]
ZnO	Coconut oil	6: 1, 3, 300, 60	77.5	[28]
ZnO	Palm kernel oil	30: 1, 10, 60, 180	0.4	[29]
SrO	Soybean oil	6: 1, 3, 70, 30	95	[30]
BaO	Palm oil	9: 1, 3, 65, 60	95.2	[31]
SO ₄ ²⁻ /ZrO ₂	Crude palm kernel oil	6: 1, 3, 200, 60	90.30	[28]
Na ₂ MoO ₄	Soybean oil	54: 1, 3, 120, 180	95.6	[32]
Zeolite X	Sunflower oil	6: 1, 10, 60, 420	95.1	[33]
KOH/zeolite	Waste sunflower oil	11.5: 1, 6, 50, 120	96.7	[34]
CaO@Al ₂ O ₃	<i>Nannochloropsis oculata</i>	30: 1, 2, 50, 240	97.5	[35]
Mg–Al HT	Waste cooking oil	6: 1, 1.5, 80, 150	95.2	[36]
KOH	Crude rubber/palm oil	8: 1, 2, 55, 300	98	[37]
KOH	Roselle oil	8: 1, 1.5, 60, 60	99.4	[38]
NaOH	Canola oil	6: 1, 1, 45, 15	98	[39]
NaOH	Refined palm oil	6: 1, 1, 60, 30	95	[40]

^a Methanol-to-oil molar ratio, catalyst loading (wt.%), temperature (°C), reaction time (min).

2. Results and Discussion

The acid value of the collected waste cooking oil was determined to be 1.86 mg KOH/g, while the FFA content of the oil was determined to be 0.93%. The WCO was employed for direct transesterification in order to examine the effect of varying the catalyst concentration, the methanol-to-oil molar ratio, and the reaction time, while keeping all other parameters constant. The results are detailed in the sections below.

2.1. Effect of Catalyst Concentration

The effect of catalyst concentration on the optimization reaction was studied under reaction conditions determined by a previous study [4]: a 12:1 methanol-to-oil molar ratio, a 60 °C reaction temperature, a 600 rpm stirring speed, and 120 min of reaction time. The result is depicted in Figure 4. It was anticipated that a catalyst with several potent basic sites and a broad surface area would exhibit significant activity [41]. Within the scope of this study, the catalyst concentration was altered to 1, 2, 3, 4, and 5% by oil weight. According to the results, Ba(OH)₂ is the most efficient in producing biodiesel, whereas AlCl₃ is the least efficient. The amount of biodiesel production increased when more Ba(OH)₂ was added, and the largest amount of biodiesel was produced when 5 wt.% Ba(OH)₂ was added, reaching 92% after 120 min. According to the previous study [42], Ba(OH)₂ acted both homogeneously and heterogeneously as a catalyst, further contributing to its high activity. Therefore, the methanolysis process occurs simultaneously at the methanol/oil interface (homogeneously) and on the active sites of the solid catalyst particles (heterogeneously) in the presence of Ba(OH)₂. With an increase in the initial quantity of catalyst, the number of solid particles and active sites increased, causing the methanolysis reaction rate to rise. Despite this, CaO exhibited a substantial yield that was different from that of Ba(OH)₂. An 85% yield was produced when the mass ratio was 3 wt.%. After 120 min, the addition of CaO solid-base catalyst increased the reaction area, resulting in a faster reaction rate and a higher biodiesel yield. Nevertheless, the production of biodiesel was consistently higher for CaO than for MgO, ZnO, and AlCl₃. The basicity of alkaline earth metal oxide complexes

increases in the sequence $\text{MgO} < \text{CaO}$, which corresponds to the rising radii of metal cations and decreasing electro-negativity. ZnO was less successful than $\text{Ba}(\text{OH})_2$, CaO , and MgO , resulting in 44% of the greatest biodiesel yield at 5 wt.%. One probable explanation is that ZnO has a lower degree of basicity compared to that of other heterogeneous catalysts, except for AlCl_3 . However, AlCl_3 did not respond to transesterification at lower doses of the catalyst. On the other hand, a trace yield of 5 wt.% AlCl_3 was very low (<10%). Overall, it displayed a high density of basicity, resulting in a strong basic strength that was favorable for the transesterification procedure. This phenomenon was consistent with previous studies [43,44].

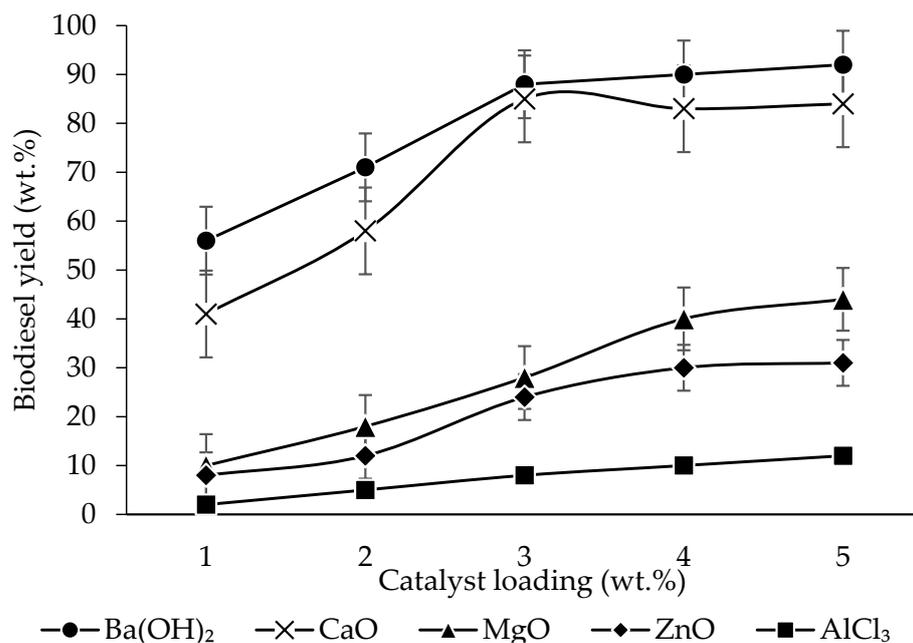


Figure 4. Effect of catalyst type and catalyst dose on biodiesel yield (methanol-to-oil molar ratio of 12:1; temperature 60 °C; time 120 min, speed 600 rpm).

The mechanism of the heterogeneous catalysts can be stated as follows. In the initial stage of transesterification with methanol using a solid-base catalyst, a proton is removed from the methanol by the basic sites, resulting in the synthesis of methoxide anion. The attack of the methoxide anion on the carbonyl carbon of a triglyceride molecule leads to the formation of an alkoxycarbonyl intermediate. The alkoxycarbonyl intermediate will then divide into two molecules, one of which will be fatty acid methyl ester and the other an anion of diglyceride. Therefore, having a high basic strength likely to be extremely active in the aforementioned mechanism may be the reason that both $\text{Ba}(\text{OH})_2$ and CaO exhibit a high yield at a low concentration. Figure 5 depicts, according to Kouzu et al. [2], the reaction mechanism diagram with CaO as the solid base.

2.2. Effect of Methanol-to-Oil Molar Ratio

According to several studies conducted on the subject, the molar ratio of alcohol to triglyceride is one of the most influential factors in determining the amount of biodiesel that may be produced [45,46]. Theoretically, one mole of triglyceride must be coupled with three moles of alcohol for the transesterification process to provide three moles of fatty acid ester and one mole of glycerol. However, because the reaction is reversible, a large quantity of alcohol is employed to propel the reaction forward direction, resulting in a bigger quantity of ester conversion in much less time. Once the triglyceride ratio hits a value of three, it continues to climb until it reaches its maximum. However, exceeding the maximum ratio will not enhance the end product's yield, but instead raise its price. When present in quantities of more than 1.75 equivalents, methanol could reduce the specific

gravity [47]. The molar ratio is an additional point of interest, which is defined as associated with the specific type of catalyst used in the experiment. As a direct result of this, the influence of the methanol-to-oil molar ratio must be investigated for every catalyst under consideration in this work.

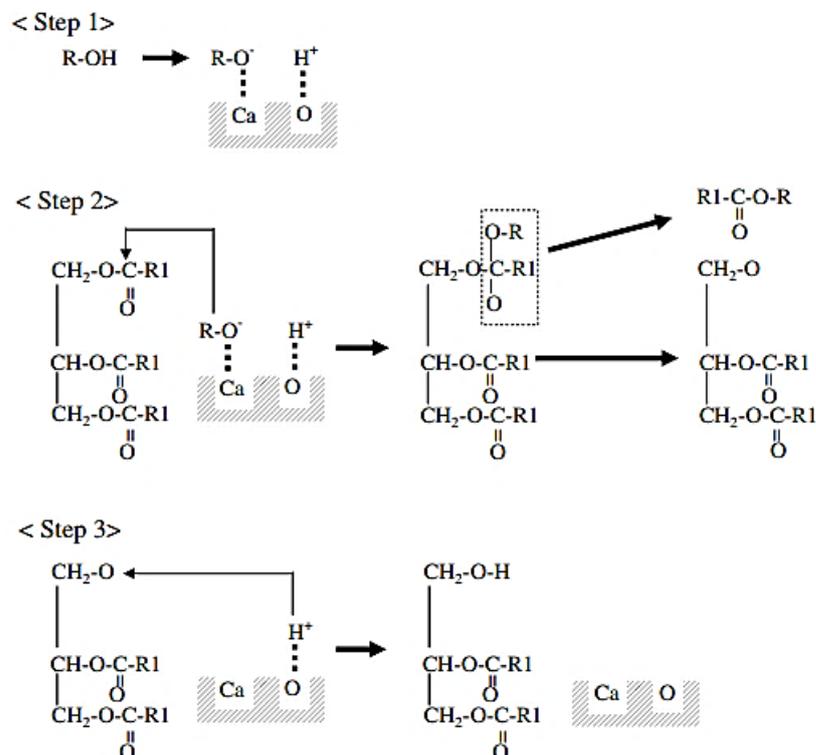


Figure 5. Reaction route of transesterification of triglyceride with methanol using CaO [2].

In this experiment, a molar ratio of 3:1 was used as a starting point, and this ratio was altered to 15:1, while the reaction time and temperature remained constant at 120 min and 60 °C, respectively. The baseline condition of the reaction was derived from a prior study [4]. The catalyst concentration was maintained at 5% by weight throughout the reaction, which was agitated at 600 rpm.

Figure 6 emphasizes the causes of the variation in biodiesel production as a result of adjusting the molar ratio of each heterogeneous catalyst. As seen in Figure 6, Ba(OH)₂, followed by CaO, had the greatest yield compared to all others investigated. In all instances, changing the ratio from 3:1 to 12:1 resulted in a significant increase in biodiesel production. Ba(OH)₂ and CaO exhibited the highest yield at 9:1 and 12:1 methanol-to-oil molar ratios, respectively. However, raising the ratio further did not result in the same increase in biodiesel production. In addition, it was observed that an excessive amount of methanol increases the amount of soluble glycerol in biodiesel, and an excessive amount of the byproduct's solute may make biodiesel separation more difficult. This finding may be related to the fact that the solution included an excessive amount of alcohol that exceeded the allowed limits. AlCl₃ exhibited a far more sluggish improvement in biodiesel yield, and a larger ratio was needed to expose its maximum output. Consequently, it was observed that the molar ratio of alcohol to triglycerides in alkaline catalysis was less than the quantity required for acid-catalyzed transesterification.

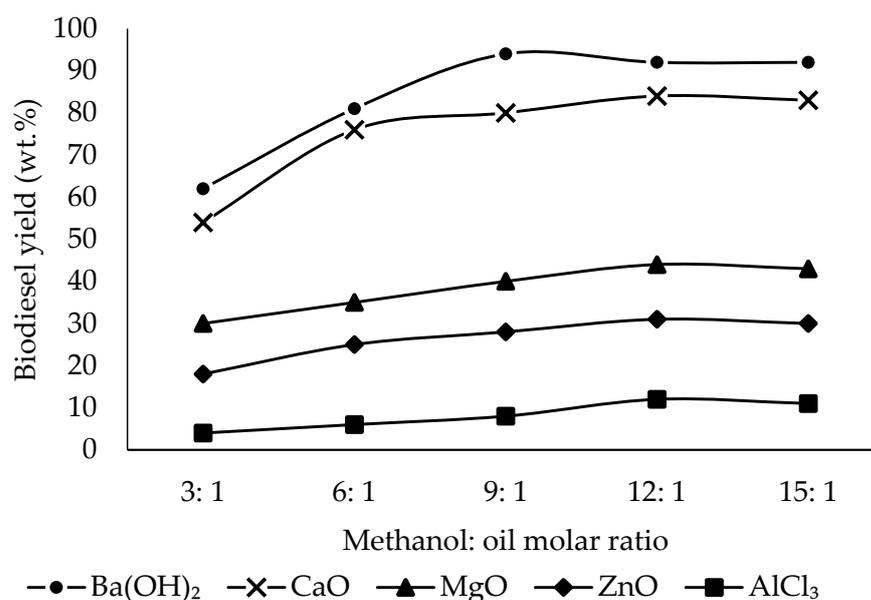


Figure 6. Effect of methanol-to-oil molar ratio on biodiesel yield. (Catalyst loading 5 wt.%; temperature 60 °C; time 120 min, speed 600 rpm.)

2.3. Effect of Reaction Time

In the great majority of instances, an increase in the overall reaction time results in a rise in the total quantity of biodiesel produced. Once a specified threshold for the minimal response time has been reached, any more development is futile. This research studied the influence of reaction time on biodiesel production, depending on catalyst type, by altering the reaction period from 60 min to 180 min. The baseline condition of the reaction was derived from a prior study [4]. Under the reaction conditions of a 12:1 methanol-to-oil molar ratio, a 60 °C reaction temperature, 600 rpm, and 5 wt.% of catalyst, the effect of reaction time on the yield was determined. Figure 7 depicts the test findings, which provide a crystal-clear illustration of the pattern that can be seen in the data. When the length of time for the reaction is increased from 60 min to 120 min, the amount of product produced increases by 5% for CaO and Ba(OH)₂. The catalytic activity of the catalysts was mostly a function of their basic strength [46].

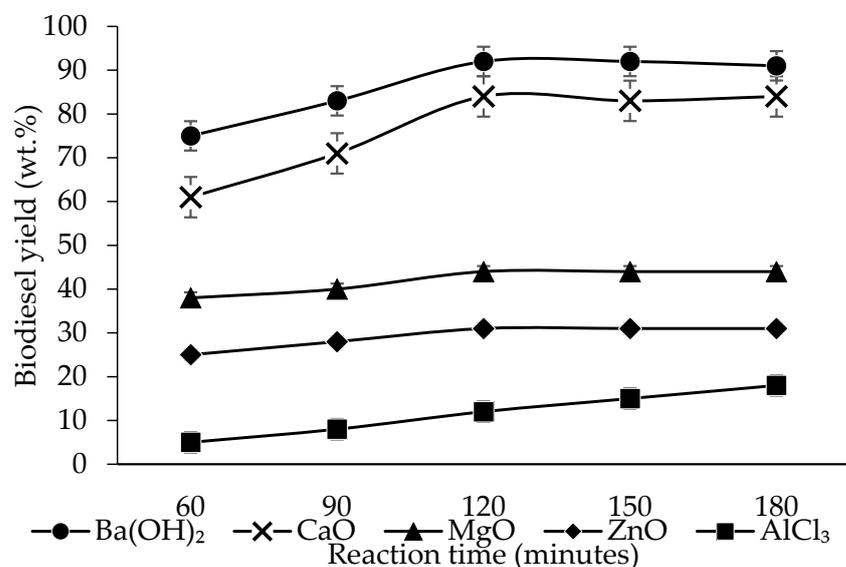


Figure 7. Effect of reaction time on biodiesel yield (catalyst loading 5 wt.%; methanol-to-oil molar ratio of 12:1, speed 600 rpm).

Among the alkaline heterogeneous catalyst, $\text{Ba}(\text{OH})_2$ has the greatest basic strength, while CaO has a moderate basic strength. Therefore, these two catalysts demonstrated more activity than others, even in a shorter time frame. In contrast to the other heterogeneous catalyst, $\text{Ba}(\text{OH})_2$ exhibited very high activity levels. This may be because $\text{Ba}(\text{OH})_2$ operates both homogeneously and heterogeneously [48], causing the rate of the reaction to dramatically rise and the reaction time to decrease as a result of the decreased mass-transfer barrier. As with all other cases, AlCl_3 exhibited the lowest yield and did not reach the optimal level after 180 min. Despite this, there was no indication of a yield for other catalyst rises after 120 min. At 120 min, all catalysts except AlCl_3 had attained their optimal performance and the amount of biodiesel produced did not rise appreciably, despite the reaction time being raised from 120 to 180 min. This may have been because during the first phase of a reaction, when it is at its most active, the conversion process progresses at a dizzyingly rapid pace. Consequently, it could be observed in almost all instances that the conversion operation may be completed within 2 h.

2.4. Effect of Cosolvent

During the biodiesel synthesis procedure that employs heterogeneous catalysts, a three-phase system consisting of oil, alcohol, and catalyst is formed in the reaction mixture. In general, the reaction rate that occurs in the presence of a heterogeneous catalyst is slower than the rate that occurs in the presence of a homogeneous catalyst. This is due to the mass-transfer constraint that arises when using a heterogeneous catalyst, as mass transfer between the phases becomes a crucial factor in determining the reaction rate [49]. Consequently, the response may take longer than usual to complete. As a consequence, the impact of the cosolvent in a heterogeneous catalyst reaction system is a crucial area of study. On other hand, as the alcohol used to generate biodiesel has a high polarity level and triglyceride has a low polarity level, it is preferable to utilize a solvent with a medium polarity [50]. Hence, acetone, a solvent with moderate polarity, was chosen in the present study.

In this work, to examine the behavior of heterogeneous catalysts in terms of biodiesel production over a given period, acetone was used as a cosolvent. To achieve single-phase formation, 20 vol.% acetone and WCO were pre-mixed on a magnetic stirrer for three minutes at 200 rpm. All other variables were held constant during the duration of the research. As the boiling point of acetone was lower than the initial reaction temperature of $60\text{ }^\circ\text{C}$, the reaction temperature was reduced to $50\text{ }^\circ\text{C}$. The reaction parameters were maintained at 12:1 of methanol-to-oil molar ratio, $50\text{ }^\circ\text{C}$ reaction temperature, 600 rpm, 120 min of reaction time, and 5 wt.% of catalyst loading.

Figure 8 depicts the increase in biodiesel production for heterogeneous catalysts in the presence of acetone, compared to non-cosolvent systems, even as the reaction temperature was reduced. As can be seen, the use of cosolvent permits greater yield. Regardless of the kind of catalyst, adding a cosolvent in a heterogeneous reaction system has a definite favorable effect on the yield. In each instance, the addition of acetone improved biodiesel production by around 5% by weight for $\text{Ba}(\text{OH})_2$ and CaO , and by nearly 12% by weight for MgO , ZnO , and AlCl_3 . In addition, statistical analysis (paired T-test) confirmed that the integration of acetone into the heterogeneous catalytic reaction medium results in a greater yield, as the *p*-values for each statistical test were greater than 0.05, supporting the alternative hypothesis (the mean biodiesel yield with acetone greater than the mean biodiesel yield without acetone).

2.5. Reusability of the Heterogeneous Catalysts

Stability and reusability are the two features of a catalyst that are most important when considering its suitability for industrial application. There is a negative correlation between biodiesel output and the number of times the catalysts are reused. On the other hand, it was concluded that the negative relationship could be attributable to two distinct causes: (1) the dissolution of metals from metal earth oxide catalysts into the alcoholic

phase, and (2) the deactivation of active sites due to their poisoning by metal diglycerides with some absorbed intermediates, such as diglyceride, monoglyceride, glycerin, and the contamination by O_2 , H_2O , and CO_2 in the air [51]. Therefore, it is vital to undertake an examination of the reusability of each heterogeneous catalyst to establish that each catalyst may be applied on an industrial scale.

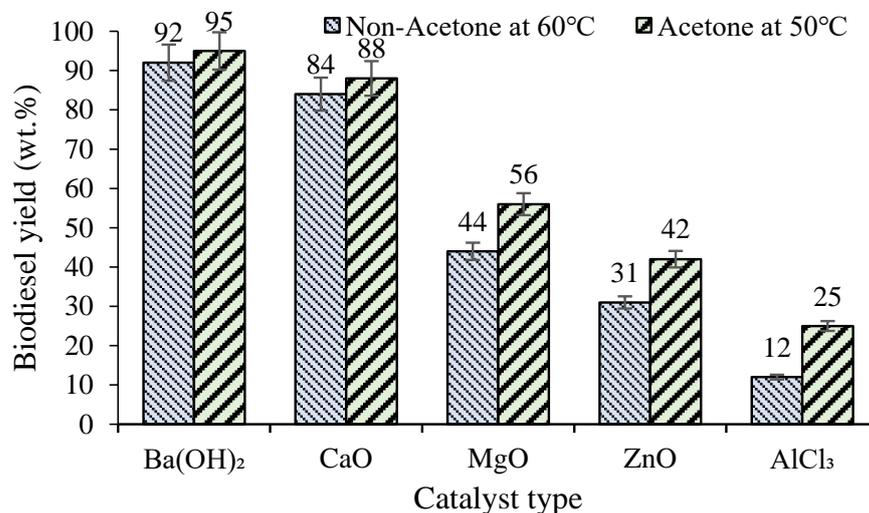


Figure 8. Effect of cosolvent on biodiesel yield (catalyst amount 5 wt.%; methanol-to-oil molar ratio of 12:1; acetone content of 20 vol%; time 120 min, speed 600 rpm).

A series of 120 min transesterification cycles was considered to evaluate the reusability of the heterogeneous catalyst using the common level of parameters for each catalyst. The examination was done at 12:1 of methanol-to-oil molar ratio, 60 °C reaction temperature, 600 rpm, 120 min of reaction time, and 5 wt% of catalyst loading. After each cycle, the catalyst was washed with methanol to remove surface contaminants such as FFAs, trace biodiesel, glycerol, and oil molecules, and then dried at 90 °C to remove any remaining moisture.

The purpose of this investigation was to reassess the degree of correlation that exists between those two variables of biodiesel yield and reusing attempts. The findings are presented in Figure 9. According to Figure 9, the current reusability investigation revealed identical results; after three repeated cycles, it was noted that the Ba(OH)₂ and CaO yields decreased moderately. Ba(OH)₂ produces a higher yield in the first cycle compared to the other catalysts under their optimal conditions. However, a progressive decline in conversion yield was found, with a 10 wt% drop occurring by the fourth cycle for Ba(OH)₂. However, at the end of the fifth cycle, Ba(OH)₂ was determined to be an effective catalyst that provided the highest yield compared to others for all five cycles of reusing.

CaO exhibited comparable catalytic activity as a heterogeneous catalyst; however, according to certain investigations, the Ca^{2+} active metal of the CaO catalyst readily leached into the methanolic solution, resulting in a drop-in catalytic activity [52]. Moreover, the high surface basicity of CaO expedites the neutralization reaction with FFA, resulting in the creation of large-molecule calcium soap [2]. Consequently, this inhibits the response from cycling continually. This may explain the decrease in CaO biodiesel yield while the reusability cycle increases. The increased solubility of magnesium in the methanol FFA medium [53,54] resulted in the poor reusability performance of the magnesium-based catalyst (MgO), which precipitated a dramatic decline in yield after the fourth cycle. In terms of the catalyst's ability to be reused, this resulted in poor performance.

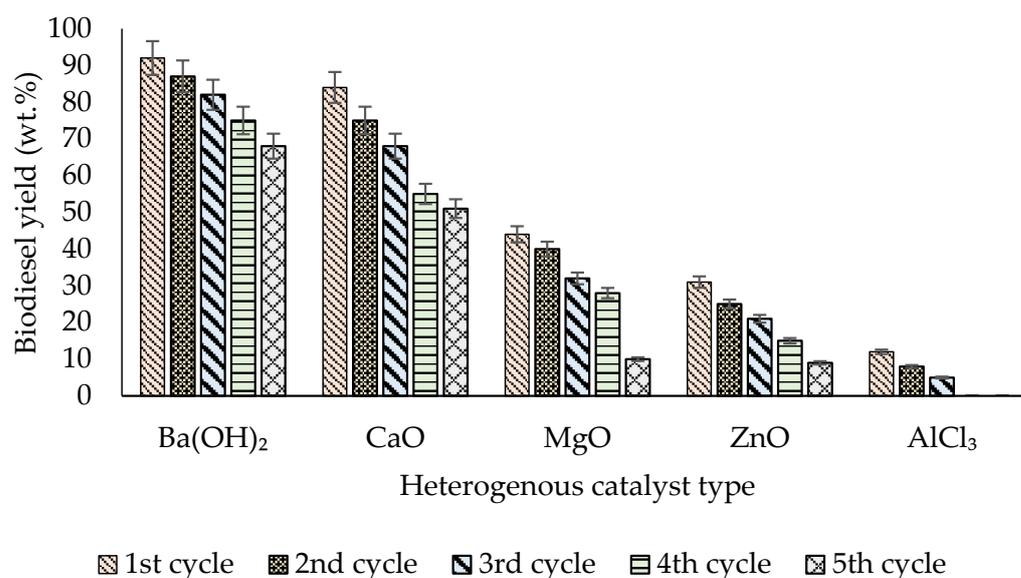


Figure 9. Effect of reuse of heterogeneous catalyst on biodiesel yield. (Catalyst loading 5 wt%; methanol-to-oil molar ratio of 12:1, time 120 min temperature 60 °C; reaction speed 600 rpm.)

On the other hand, ZnO and AlCl₃ performed worst in the reusability test. Their impact on biodiesel production during the first cycle was also weaker than that of others. Consequently, poor performance was probable. In addition, AlCl₃ exhibited total deactivation as a catalyst after the third cycle, in which no transesterification occurred. The one-way ANOVA test revealed that the *p* value (0.000) for each catalyst was less than 0.05, indicating that there are significant differences between each cycle for each catalyst, by rejecting the null hypothesis. Therefore, this investigation revealed that the reusability of each catalyst demonstrates a considerable biodiesel production drop from cycle to cycle.

2.6. Catalyst Characterization

The size and shape of the particles of heterogeneous catalysis were investigated using SEM analysis. Figure 10 depicts the results of an SEM analysis of the morphology of each heterogeneous catalyst. In the case of Ba(OH)₂, the micrograph displays particle aggregation. The ribbon-shaped particles have a length larger than 500 nm and an apparent width of approximately 200 nm. Additionally, a hexagonal crystal structure can be recognized. CaO particles have a cubic shape with three crystallographic surfaces and sizes between 200 and 250 nm. The spongy, round, and hedgehog-like shapes of the MgO nanoparticles are evident in the SEM analysis. For additional confirmation of the morphology, MgO nanoparticles are composed of hair-like flexes. The particles' surfaces are extremely abrasive and flawed. According to Figure 10, ZnO is spherical and composed of nanocrystallite aggregates. The approximate average diameter of the ZnO particle is between 200 and 250 nm. However, AlCl₃ is the only catalyst that exhibits the round shape morphology with a diameter ranging from 1 to 3 μm.

X-ray powder diffraction (XRD) studies were carried out to confirm the crystallinity using an X-ray diffractometer in the range of 0–90° to determine their crystal structure and phase. A typical XRD spectrum of Ba(OH)₂ is shown in Figure 11. This spectrum has four peaks that can be detected at angles of 15.280°, 30.667°, 46.635°, and 63.635°. The diffraction peaks of Ba(OH)₂ can be matched with standard Joint Committee on Powder Diffraction Standards (JCPDS) data [JCPDS file: 00-026-0154]. Figure 12 depicts a typical XRD spectrum of CaO; there are five peaks in this spectrum, and they can be found at angles of 32.248°, 37.400°, 53.906°, 64.196°, and 67.423°, respectively. The diffraction peaks of CaO can be matched with CPDS data [JCPDS file: 00-0 70-4068]. Figure 13 illustrates a typical XRD spectrum of MgO. Six diffraction peaks were seen at angles of 18.089°, 36.897°, 42.837°, 62.146°, 74.461°, and 78.454°. The diffraction peaks of MgO can be matched with JCPDS

data [JCPDS file: 45-0946]. The XRD spectra indicate that the ZnO crystal is as shown in Figure 14. The major diffraction peaks were seen at angles of 31.796° , 34.452° , 36.282° , 47.568° , 56.624° , 62.886° , 66.402° , 67.975° , 69.113° , 72.592° , and 76.983° . The diffraction peaks of ZnO can be matched with CPDS data [JCPDS file: 00-036-1451. Figure 15 illustrates the XRD pattern of the compound AlCl_3 . At several different 2θ values, the principal peaks can be recognized. The diffraction peaks of AlCl_3 can be matched with CPDS data [JCPDS file: 00-08-04531].

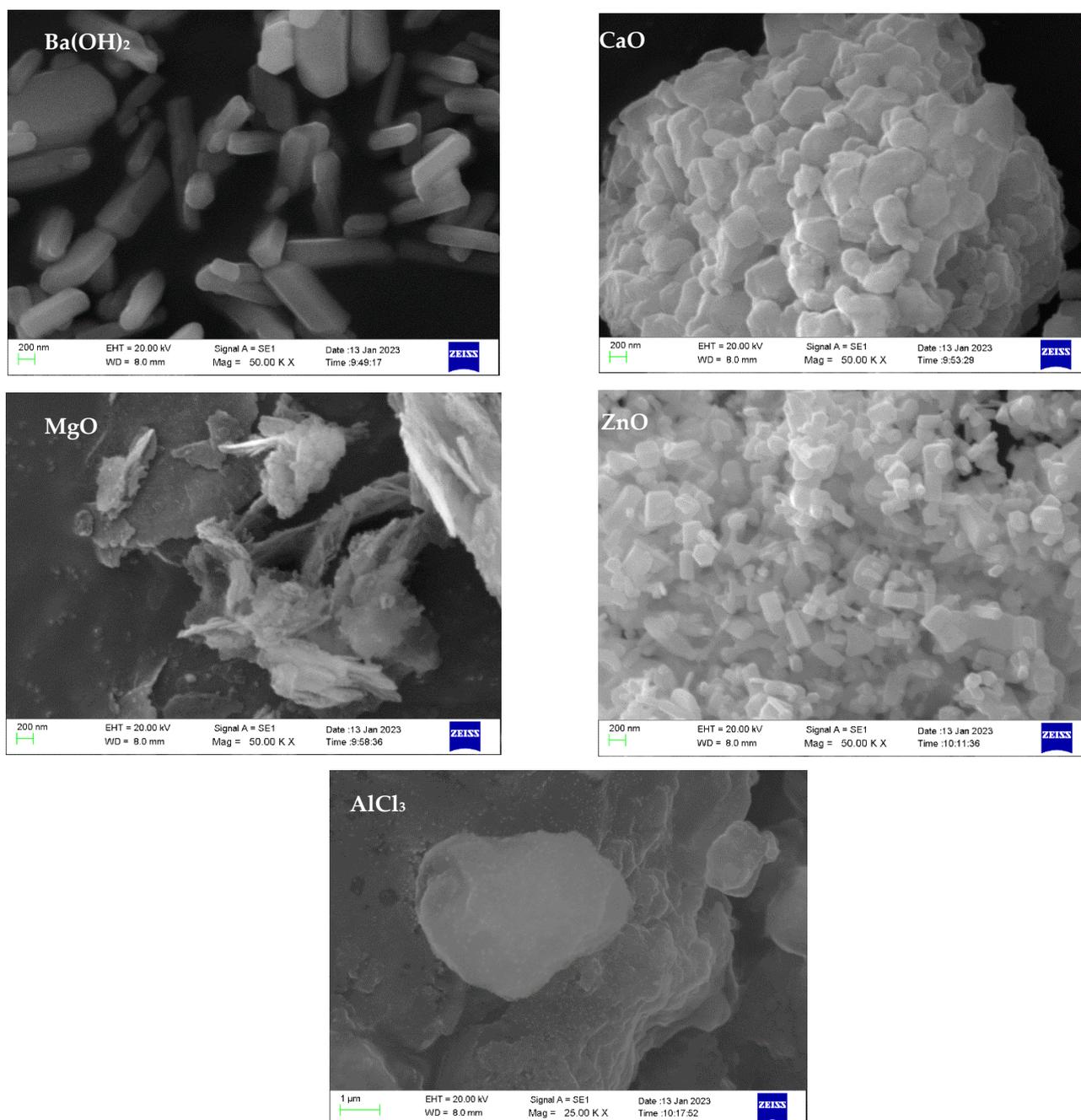


Figure 10. SEM micrographs of Ba(OH)_2 , CaO , MgO , ZnO (50.00 K X), and AlCl_3 (25.00 K X).

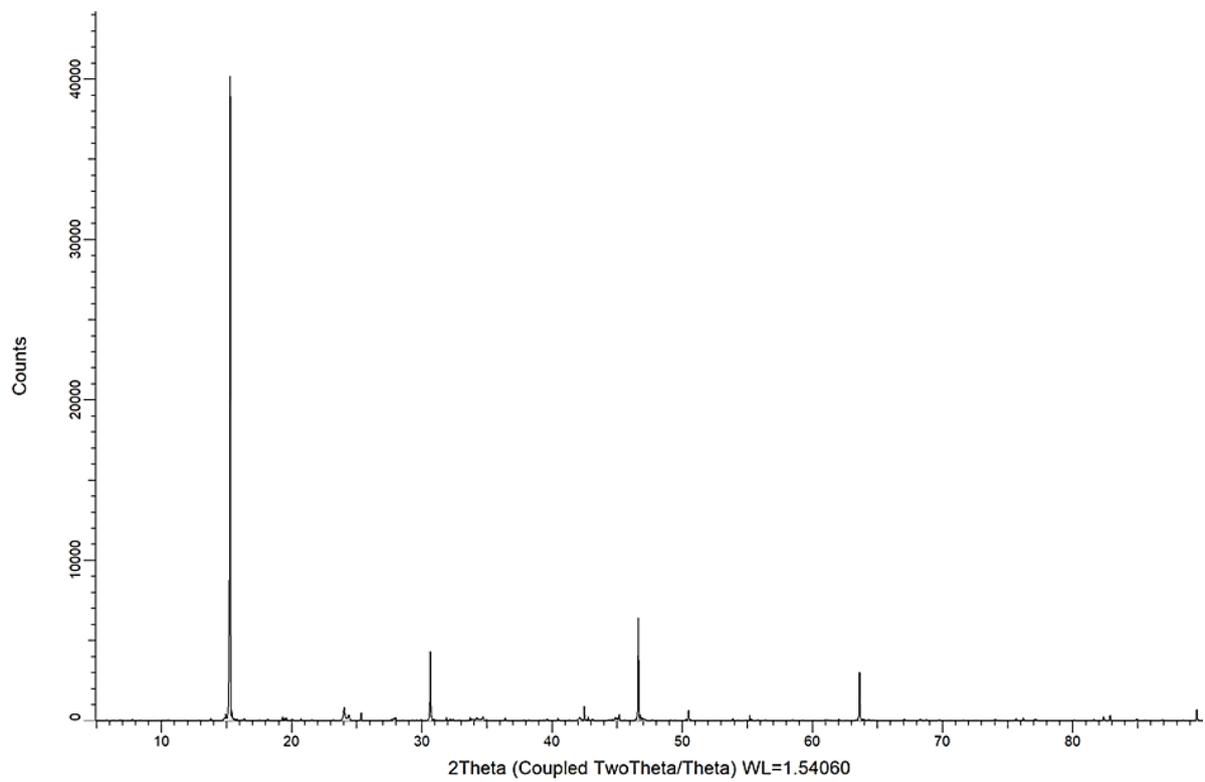


Figure 11. The XRD pattern of Ba(OH)₂ powder.

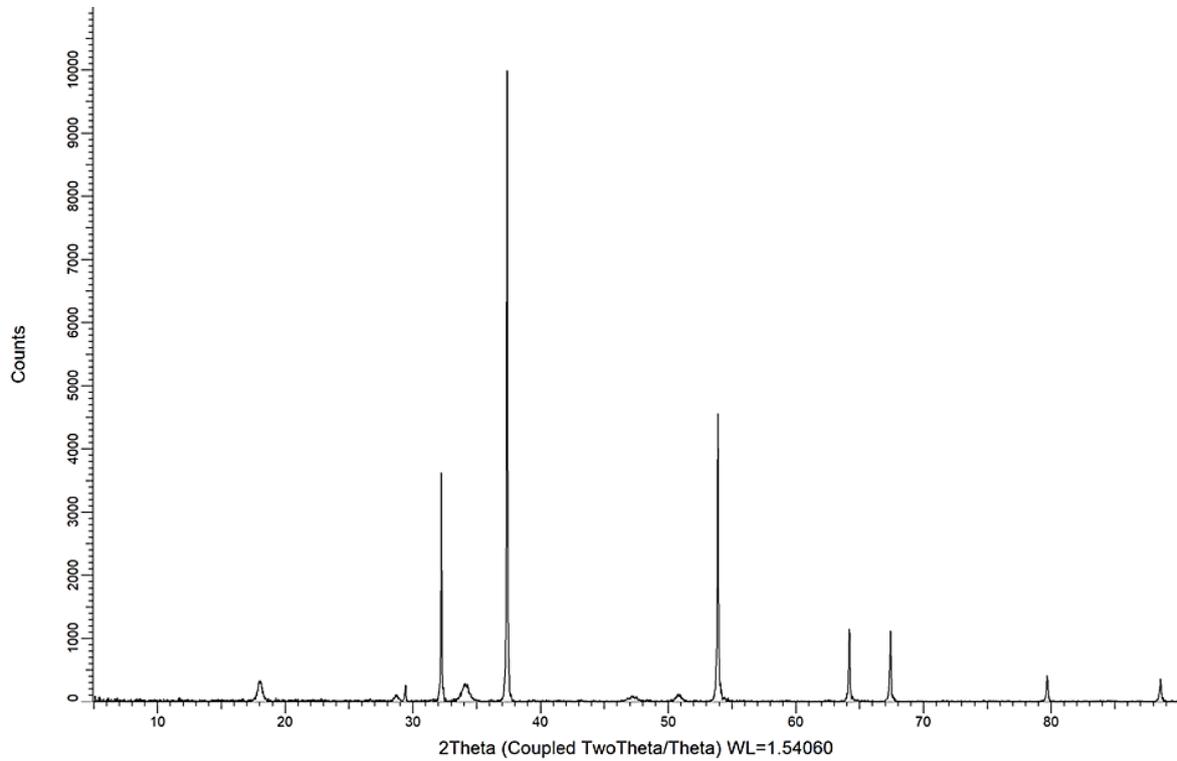


Figure 12. The XRD pattern of CaO powder.

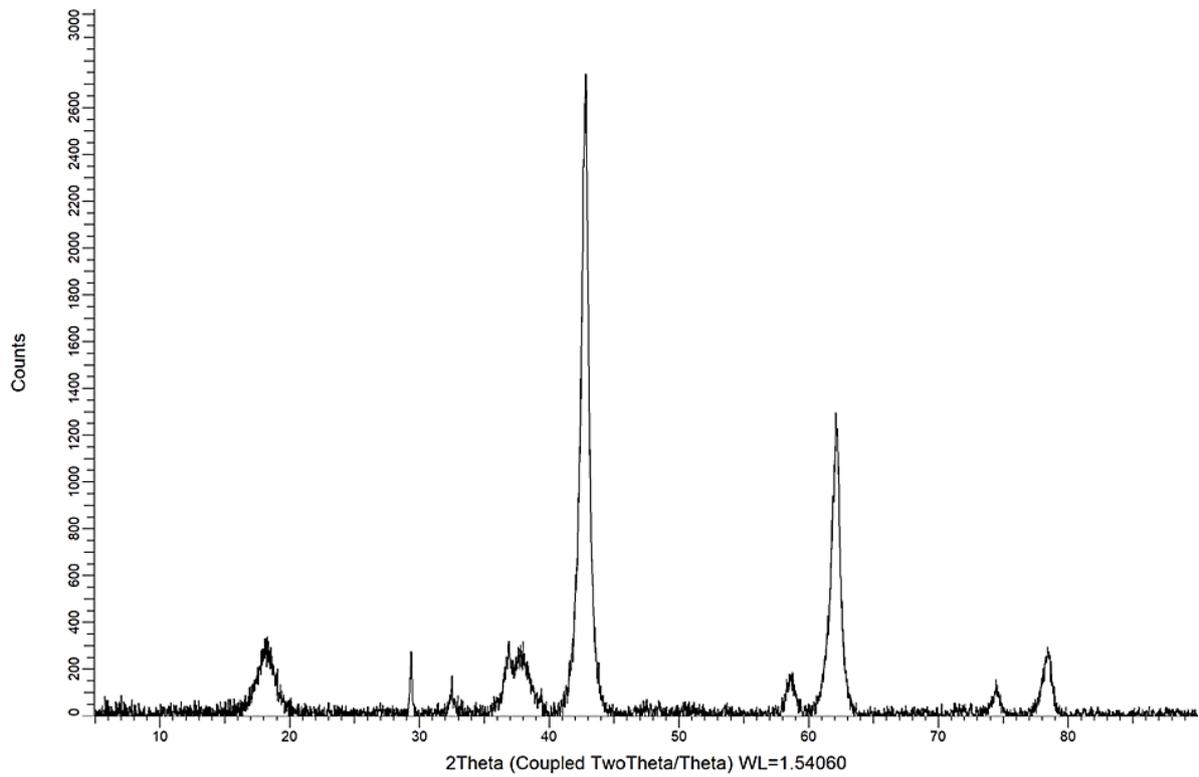


Figure 13. The XRD pattern of MgO powder.

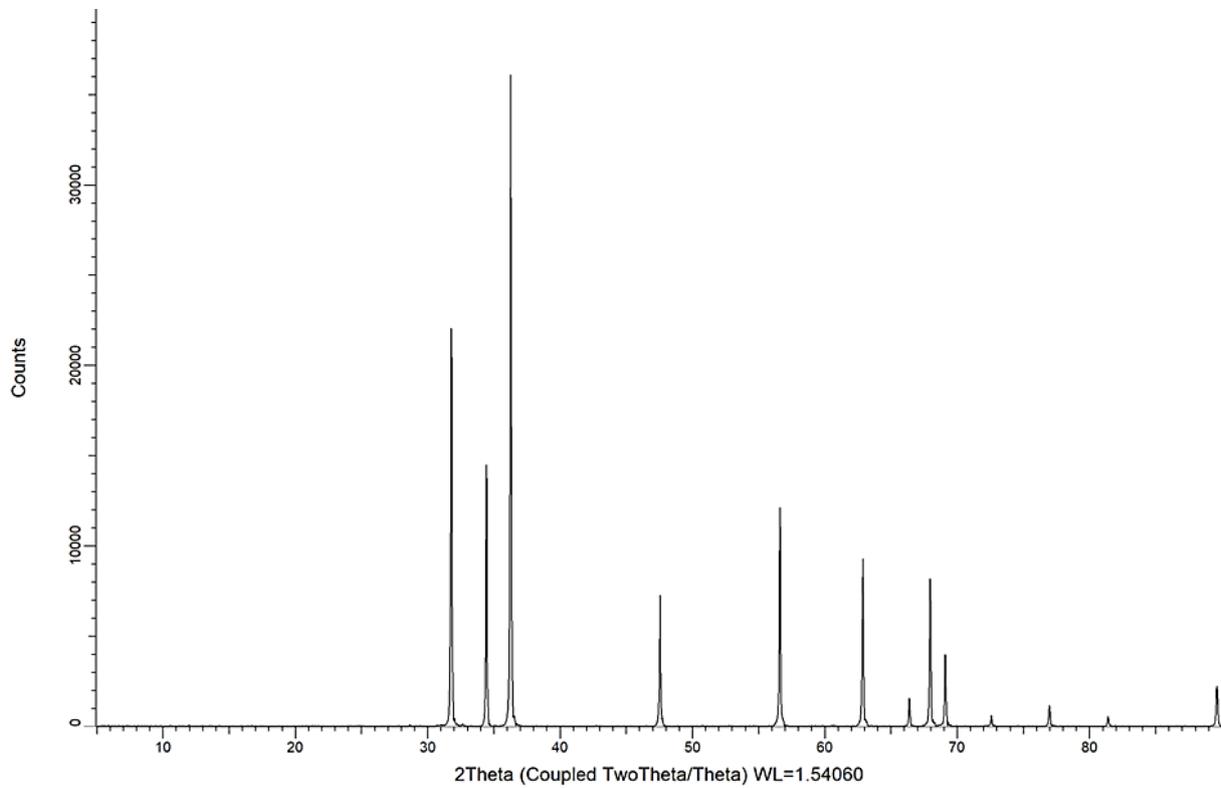


Figure 14. The XRD pattern of ZnO powder.

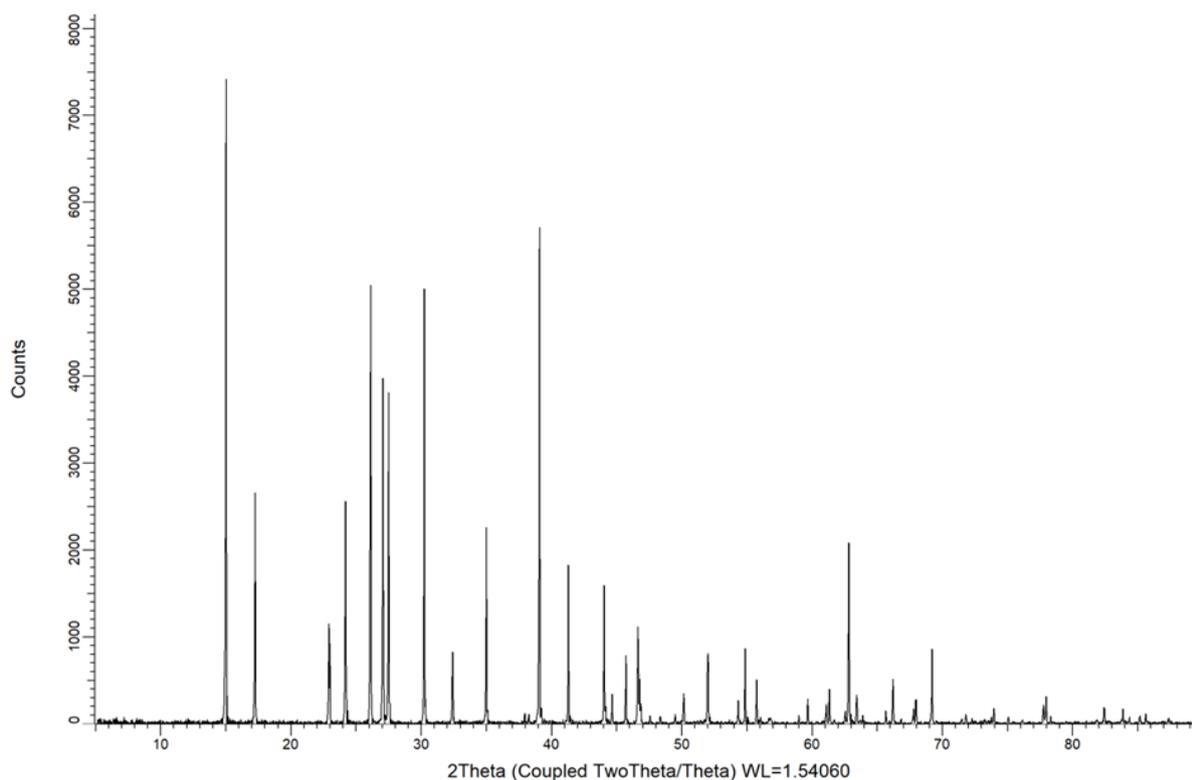


Figure 15. The XRD pattern of AlCl_3 powder.

2.7. Physicochemical Properties of Biodiesel

A study of the physicochemical properties of WCO-based biodiesel products was conducted to identify the effect of catalyst type on biodiesel quality. The investigation was conducted with a 12:1 methanol-to-oil molar ratio, a 60 °C reaction temperature, 600 rpm, 120 min of reaction duration, and a catalyst loading of 5% by weight. Table 2 presents a succinct overview of the physicochemical properties of biodiesel products produced by a range of heterogeneous catalysts. According to the findings, each heterogeneous catalyst evaluated in this study is suitable as a biodiesel synthesis catalyst. However, each biodiesel produced from each catalyst had slightly varied values for each of its properties, and these values fell within the range defined by the ASTM D6751 standard for biodiesel.

Table 2. Physicochemical properties of biodiesel.

Physicochemical Property	Specification for B100 as per ASTM D6751	Biodiesel Derived from a Variety of Heterogeneous Catalysts				
		$\text{Ba}(\text{OH})_2$	CaO	MgO	ZnO	AlCl_3
Acid value (mg KOH/g)	<0.5	0.2	0.3	0.2	0.2	0.4
Flashpoint (°C)	>130	142	154	149	151	147
Density at 15 °C (g/cm^3)	0.860–0.900	0.895	0.881	0.875	0.886	0.869
Kinematic viscosity (cSt at 40 °C)	1.9–6.0	3.9	2.5	3.1	3.2	3.1

2.8. Economic Analysis of Heterogeneous Catalyst-Based Biodiesel Synthesis under Optimal Conditions

An essential component of economic analysis is the study of both the costs and benefits connected with biodiesel manufacturing. The findings of an examination of the cost of a heterogeneous catalyst functioning under ideal conditions are shown in Table 3. According to the displayed data, $\text{Ba}(\text{OH})_2$ has the highest unit price, whereas CaO has the lowest. The remaining heterogeneous catalysts have values in the same ballpark, ranging from USD 30 to USD 35 per 1 kg. This analysis indicated that CaO had the lowest demand for an

optimum catalyst at 3 wt.%, whereas the other catalysts required 5 wt.%. Consequently, Ba(OH)₂ was responsible for a major amount of the cost of the final product (USD 2.52 for 1 kg WCO), which was significantly more than CaO, which was responsible for the least significant portion (USD 0.31 for 1 kg WCO). Therefore, substituting CaO for Ba(OH)₂ can reduce the cost of the catalyst by up to 80 percent. CaO has been determined to be the most economical catalyst imaginable. Despite this, Ba(OH)₂ was found to be the most efficient catalyst, in terms of yield, in this study.

Table 3. Analysis of the prices of the heterogeneous catalysts under optimal conditions.

Catalyst	Unit Price ^a /\$/kg ⁻¹	Catalyst Content Required in Optimal Condition/wt%	Catalyst Price at the Required Level for 1 kg WCO/\$
Ba(OH) ₂	50.37	5	2.52
CaO	10.40	3	0.31
MgO	36.55	5	1.83
ZnO	31.76	5	1.59
AlCl ₃	34.96	5	1.75

^a All pricing were obtained from a local chemical supplier.

3. Materials and Methods

3.1. Pre-Treatment

A representative sample of waste cooking oil (WCO) was purchased at a market in Colombo, Sri Lanka, where the oil was being prepared for disposal alongside the rest of the city's garbage. Filtration with a monofilament filter cloth with a pore size of 20 µm and preheating at 110 °C for 20 min were employed to remove suspended matter and moisture from WCO, respectively.

3.2. Determination of Acid Value and FFA Content

Following the ASTM D974 procedure, the acid value of pretreated WCO was determined. Accurately measured 1 g of pretreated WCO was added to a titration flask that previously contained 125 mL of solvent mixture of toluene (Loba Chemie, Mumbai, India):isopropyl alcohol (Loba Chemie, Mumbai, India):water at 500:499:1 and 5–6 drops of phenolphthalein (ISOLAB Laborgeräte GmbH, Eschau, Germany) as an indicator. Using titration, the volume of 0.1 M KOH (Loba Chemie, Mumbai, India) required (V1) to change a colorless solution to a light pink hue was determined. The same procedure was performed with a sample that did not contain oil (blank sample), and the volume of KOH utilized was recorded (V2). To limit the probability of errors being made by an individual researcher, the analysis was triplicated for each sample. After that, Equations (1) and (2) were used to calculate the acid value and FFA content of each sample.

$$\text{Acid value (mg KOH/g)} = \frac{56.1 \times 0.1 \times (V1 - V2)}{1} \quad (1)$$

$$\text{FFA\%} = \frac{\text{Acid value (mg KOH/g)}}{2} \quad (2)$$

where V1 is the 0.1 M KOH volume required for the sample and V2 is the 0.1 M KOH volume required for the blank sample

3.3. Transesterification

Transesterification was carried out in a 250 mL two-necked flask, which was equipped with a thermometer. A mass of 100 g of waste cooking oil, with a molecular mass of 679.3 g mol⁻¹, was mixed with methanol (Loba Chemie, Mumbai, India) at a methanol-to-oil molar ratio of 12:1. A corresponding heterogeneous catalyst was added at 5 wt.% and the mixture was agitated at 600 rpm for a specific duration of 120 min at a temperature of 60 °C. After the reaction, the catalyst was separated by centrifugation at 6000 rpm for

5 min, followed by the separation of glycerol and biodiesel in a separating funnel. In order to increase the biodiesel's purity, it was heated at a temperature of 110 °C for 20 min at a rotational speed of 600 rpm. The yield of biodiesel was calculated, using the formula presented in Equation (3).

$$\text{Biodiesel yield (\%)} = \frac{\text{Dry weight of biodiesel}}{\text{Dry weight of WCO}} \times 100 \quad (3)$$

3.4. Process Optimization

The transesterification reaction was performed to demonstrate the viability of producing biodiesel from various heterogeneous catalysts, including CaO 90% (Loba Chemie, Mumbai, India), MgO 96% (Loba Chemie, Mumbai, India), ZnO 99% (Loba Chemie, Mumbai, India), Ba(OH)₂ 98% (Loba Chemie, Mumbai, India), and AlCl₃ 99% (Loba Chemie, Mumbai, India). To determine the optimal transesterification reaction conditions for each heterogeneous catalyst, various catalyst concentrations (1, 2, 3, 4, and 5 wt%), various methanol-to-oil molar ratios (6:1, 9:1, 12:1, 15:1, and 18:1), and various reaction times (30, 60, 90, 120, and 150 min) were applied to transesterification reactions. The influence of each parameter was examined by varying the value-defined range while holding the level of the other parameter constant. Moreover, all testing was performed twice to reduce the possibility of error.

3.5. Catalyst Reused

The reaction mixture was centrifuged at 6000 rpm for 5 min to recover the exhausted catalyst. Before a spent catalyst could be reused, methanol was utilized to purify it to eliminate any contamination that occurred during transesterification. A combination of methanol and catalyst was heated to 90 °C using a low-speed mixer (100 rpm) until all of the methanol had evaporated.

3.6. Catalyst Characterization

The heterogeneous catalysts were characterized by scanning electron microscopy (SEM) (ZEISS EVO LS 15, Oberkochen, Germany) and powder X-ray diffraction (XRD) (Bruker D8 Advance Eco Powder X-ray diffraction system, Leipzig, Germany).

3.7. Acetone Effect on Biodiesel Yield

As established by Miyuranga et al. [5], acetone (Loba Chemie, Mumbai, India) was utilized in heterogeneous reaction systems as a cosolvent. To accomplish single-phase formation, 20 vol.% acetone and WCO were pre-mixed for 3 min at 200 rpm on a magnetic stirrer. When two components were appropriately combined, transesterification was carried out to determine the impact on yield. The reaction temperature was maintained at 50 °C.

3.8. Physicochemical Properties of Biodiesel

Physicochemical parameters, such as flash point (GD-261A Automatic PMCC Flash point tester) (ASTM D93), density (pycometer) (ASTM D1298), kinematic viscosity (GD-265C petroleum products kinematic viscosity meter) (ASTM D445), and acid value (ASTM D974) of produced biodiesel, were determined according to internationally recognized ASTM procedures.

3.9. Statistical Analysis

Using Minitab 2016 software and one-way ANOVA, the mean value of biodiesel generation from heterogeneous catalysts in reusability experiments (see Section 2.5) was analyzed statistically. The confidence level utilized was 95%. As the null hypothesis, it was stated that there are significant differences in the mean values of each data set, whereas the alternative hypothesis was that there are no such differences.

Minitab 2016 software and a paired T-test were employed to assess the effect of cosolvent on biodiesel yield for each heterogeneous catalyst. The level of confidence utilized was 95%. As the null hypothesis, it was stated that the mean biodiesel yield with cosolvent is greater than the mean biodiesel yield without acetone, whereas the alternative hypothesis stated the opposite.

4. Conclusions

The primary purpose of this work was to optimize some of the important reaction parameters for five heterogeneous catalysts, Ba(OH)₂, CaO, MgO, ZnO, and AlCl₃, which have been extensively used in recent years in biodiesel industry research and studies. Utilizing waste cooking oil as the feedstock and methanol as the source of alcohol, biodiesel was produced through the direct transesterification process because the acid value of the feedstock was less than 2 mg KOH/g. In terms of process optimization performance, it was discovered that Ba(OH)₂ had a greatest effect on the production of biodiesel, followed by CaO. In terms of biodiesel yield, other catalysts such as MgO and ZnO performed poorly and AlCl₃ demonstrated extremely poor activity. Only CaO was able to achieve the ideal quantity of catalyst loading, which was discovered to be 3 wt%, while the other catalysts only demonstrated growth yield at the maximum concentration, 5 wt%. In contrast, Ba(OH)₂ had the highest biodiesel yield with the lowest methanol requirement. It produced the highest yield at a 9:1 molar ratio of methanol to oil, but the other catalysts required much higher molar ratios, such as 12:1. AlCl₃ consistently produced the lowest yield, which was noted as preventing the ideal reaction time from being reached until 180 min had passed. Catalysts other than AlCl₃ were capable of producing biodiesel at a maximum level for 120 min. It was established that a cosolvent, such as acetone, is crucial for overcoming mass-transfer resistance and allowing each catalyst to function well. Regardless of the type of catalyst employed, the addition of acetone as a cosolvent increased the amount of biodiesel produced. The results of a reusability test on a heterogenous catalyst indicated that all heterogeneous catalysts can be reused for up to five cycles. Of the catalysts studied, Ba(OH)₂ and CaO had a significant impact on yield. This continued to occur after the third cycle. Despite this, all catalysts fell within the allowed range for biodiesel properties when evaluated against the ASTM standard. Although Ba(OH)₂ had the best yield under ideal conditions, it had a significant impact on the total production cost of biodiesel. CaO, on the other hand, appeared to have the lowest cost for biodiesel production under optimal conditions.

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