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Innovative Catalysts For Biodiesel Synthesis: Transforming Waste Cooking Oil With Mango And Banana Peel Extracts And Koh

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Abstract **-** The global need for energy is increasing steadily. Fossil fuels, namely coal, gas, and crude oil, are the primary energy sources worldwide. Nevertheless, fossil fuels will eventually exhaust, and renewable energy emerges as the most rational substitute, given that fossil fuels contribute to acid rain, the greenhouse effect, and other ecological issues. Renewable biofuels provide the capacity to satisfy the worldwide energy requirement and offer substantial potential. Biodiesel is a significant alternative from biological sources that can replace petroleum. Waste cooking oil was employed as a primary resource for biodiesel production. This study examines the disparities in utilizing three distinct catalysts: a homogeneous catalyst such as KOH and heterogeneous catalysts such as mango and banana peels. Before biodiesel extraction, Mango powder and banana powder were subjected to analysis using FT-IR, SEM, EDS, and XRD techniques. The mango catalyst yielded the most significant amount of synthesized biodiesel (74.97%), followed by the banana catalyst (63.44%) and the KOH catalyst (45.06%). The GC-MS analysis revealed that the biodiesel produced using potassium hydroxide (KOH) exhibited the most significant amounts of all components. This observation supports that potassium hydroxide is a highly efficient and active catalyst, surpassing banana and mngo in catalytic activity.

Keywords**:** fossil fuels, renewable energy, greenhouse, biodiesel, waste cooking oil, catalyst.

1. Introduction

The depletion of fossil fuel reserves and the increasing environmental pollution caused by their extraction and combustion have created an urgent need for sustainable energy alternatives [1]. Fossil fuels, such as coal, oil, and natural gas, are currently the dominant energy sources; however, their availability is declining, and their continued use contributes significantly to greenhouse gas emissions and environmental degradation [2]. As a result, the focus has shifted toward renewable energy sources, with biodiesel emerging as a viable and eco-friendly alternative [3]. Biodiesel is produced from vegetable or animal fats through the chemical process of transesterification or esterification, making it a promising substitute for conventional diesel fuel. One of the most widely used feedstocks for biodiesel production is waste cooking oil (WCO), which not only provides a cost-effective raw material but also helps mitigate the environmental damage caused by improper oil disposal. WCO is a major source of water pollution, as even small amounts can contaminate vast quantities of water, disrupt aquatic ecosystems, and contribute to sewage blockages. Biodiesel production from WCO relies on catalysts to enhance the transesterification reaction, with three main categories: homogeneous, heterogeneous, and biocatalysts.

Homogeneous catalysts, such as potassium hydroxide (KOH) and sulfuric acid, are widely used due to their efficiency in accelerating the reaction. However, they present several challenges, including difficulties in separation, soap formation, and the generation of polluted wastewater that requires extensive treatment. Heterogeneous catalysts, on the other hand, offer significant advantages, such as easy separation from the reaction mixture, reusability, and reduced soap formation, making them a more sustainable option [4]. Given the high cost associated with biodiesel production, particularly in terms of catalysts and feedstock, there is a growing interest in developing cost-effective and environmentally friendly alternatives. Biomass waste materials, such as banana and mango peels, have shown potential as inexpensive and sustainable heterogeneous catalysts for biodiesel synthesis. These natural catalysts not only reduce the overall production cost but also offer a means of recycling agricultural waste. This study aims to evaluate the effectiveness of mango and banana peel powders as heterogeneous catalysts for the transesterification of WCO into biodiesel [5]. The research will compare their performance with that of potassium hydroxide (KOH), a commonly used homogeneous catalyst, to determine their efficiency in biodiesel yield and quality. Additionally, the study seeks to optimize reaction conditions to maximize biodiesel production while ensuring compliance with industry standards. By exploring the potential of fruit peel-derived catalysts, this research contributes to the development of a more sustainable, cost-effective, and environmentally friendly approach to biodiesel production.

2. Methodology

2.1. Materials, Reagents, and Equipment

Mango and banana peels served as heterogeneous catalysts, while KOH was employed as a homogeneous catalyst. Distilled water was utilized for rinsing the peels, beakers, and flasks. Waste cooking oil was the primary feedstock for biodiesel production, and ethanol was added as a blending agent. Phenolphthalein indicator was used to visually signal pH changes by altering its colour in acidic or basic conditions. Methanol functioned as the alcohol in the transesterification process. To expedite the mixing process, magnetic stirrers were applied. A hotplate was used both to heat the mixture for the fusion of materials and to facilitate water evaporation. Precise volumes of solutions were measured using a syringe, while flasks, beakers, and a burette were used for containing and transferring liquids. An electric grinder was employed to reduce the peels to a powder form, which was subsequently passed through a sieve to remove larger granules. Filter paper was used to separate the oil from the KOH catalyst, and a separatory funnel was utilized to partition the mixture into two distinct layers. Samples were accurately weighed using a balance. A reflux condenser was integrated into the process to cool and condense the generated vapours, thereby preventing solvent loss. Finally, a rotary evaporator was used to dry and purify the biodiesel by removing methanol and other impurities.

2.2. Feedstocks pre-treatment

2.2.1. Pre-treatment of waste cooking oil

Cooking oil waste needs to be processed before being used to remove any water because it includes water. Since water has a boiling point of 100 degrees Celsius, it needs to be heated to 120 degrees Celsius. This indicates that the waste cooking oil will boil to the point of 260 to 300 degrees Celsius, boiling all of the water within. The pre-treated waste cooking oil cools down and becomes dry and clean.

2.2.2. pre-treatment of banana peels and mango peels as catalysts

The process of pre-treating banana peels and mango peels as catalysts is illustrated in Figure1.

(1): washed mango peels and banana peels with distilled water.

(2): dried mango peels and banana peels in the oven at 80 C around 5 hours

(3): Mango powder and banana powder

Figure 1 preparation of banana and mango peels as catalysts

2.3. Experimental process

2.3.1. Acid value determination

The acid number, also known as the neutralization number, is a numerical measure of the amount of free fatty acids present in a freshly collected fuel sample and the total amount of free fatty acids and degradation products in older samples. The acid number is utilized to quantify the occurrence of mineral acids as acids, in the end, fuels, provided they are employed during manufacturing. The stoichiometric amount of potassium hydroxide (KOH) needed to neutralize one gram of fatty acid methyl ester (FAME) is measured in milligrams. Elevated acidity levels can severely erode the fuel feed system of an engine [7].

The acid value can be calculated using Equation (1), which considers the molecular weight of the chemical (KOH) and the mass of the sample.

$$\mathrm{AV\ (mg/g)} = (\mathrm{MW} \times \mathrm{N\ KOH} \times \mathrm{V\ KOH})/\mathrm{W} \quad (1)$$

$$\mathrm{AV} = (56.11 \times 0.1 \times 3.33)/20 = 0.934 \quad (2)$$

Combine 50 grams of ethanol with 20 grams of waste cooking oil in a 100-millilitre flask. Next, apply heat to the mixture and agitate it for 10 minutes at 50 degrees Celsius. Subsequently, add three drops of phenolphthalein indicator to the mixture. Perform a titration by adding the 0.1M KOH solution to the mix and shaking it until the colour transitions to pink. Measure the volume of the titration solution and compute the mean of the acid value. The procedure for determining the acid value using the titration method is illustrated in Figure 2.

(1) Mixture before titration
Mix 50 g of ethanol with 20 g of waste cooking oil in 100 ml flask

(2): Mixture after titration
drop 3 drops of phenolphthalein indicator to the Titration of the 0.1M KOH solution into the mixture

Figure 2 Titration method to determine the acid value

2.3.2. Free fatty acid determination

Free fatty acids (FFAs) were examined to identify the optimal approach for producing biodiesel. If the FFA content of the feedstock exceeds 5%, esterification is the optimal technique; however, if it is below 5%, transesterification is the most appropriate approach. The FFA is determined by utilizing the acid value obtained through experimental measurement [6].

Equation (3) shown below, is utilized to compute the Free Fatty Acid (FFA) by considering the acid value, KOH molecular weight, and oleic acid's molecular weight.

$$\mathrm{FA(\%)} = \mathrm{AV} \times \left(\frac{\mathrm{MW\ OF\ OLEIC\ ACID}}{\mathrm{MW\ OF\ KOH}}\right) \times \frac{1}{10} \quad (3)$$

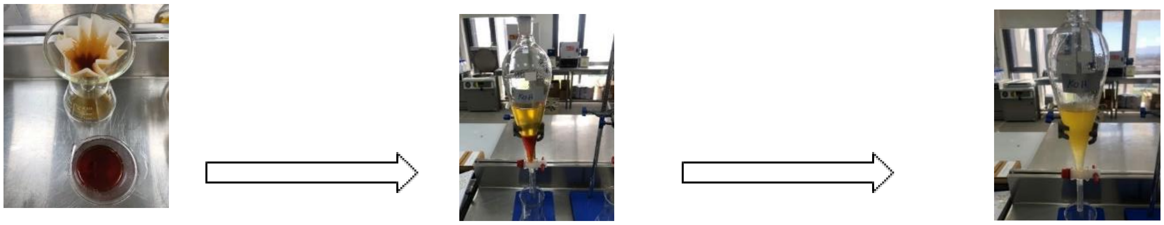
$$\mathrm{FA(\%)} = \frac{\mathrm{AV}}{2} \quad (4)$$

$$\mathrm{FFA}(\%) = \frac{0.934}{2} = 0.467\% \quad (5)$$

2.4. Transesterification reaction

2.4.1. Transesterification reaction of KOH catalyst

Figure 3 illustrates the sequential stages of the Transesterification reaction facilitated by the KOH catalyst. A solution including pre-treated waste cooking oil, methanol, and catalyst is prepared in a 250 ml separatory funnel. The stoichiometric ratio of oil to methanol is 6:1, with the addition of 2 grams of catalyst. To begin, combine methanol with 2 grams of catalyst and heat the mixture to 50 degrees Celsius for 20 minutes. Utilize a magnetic stirrer to ensure thorough mixing of the solution. Warm the oil to a temperature of 65 degrees Celsius for 1 hour, then combine it with the methanol and catalyst. The reaction mixture undergoes filter paper to separate the solid catalyst and any remaining impurities. Subsequently, the mixture was transferred to the separatory funnel and let it sit for 24 hours. Separate the glycerol component by distilling it after a full day. Next, perform three rounds of cleaning the biodiesel with distilled water. Ultimately, the biodiesel is generated at a temperature of 110 C for one hour to eliminate any moisture present, yielding a pure biodiesel sample**.**

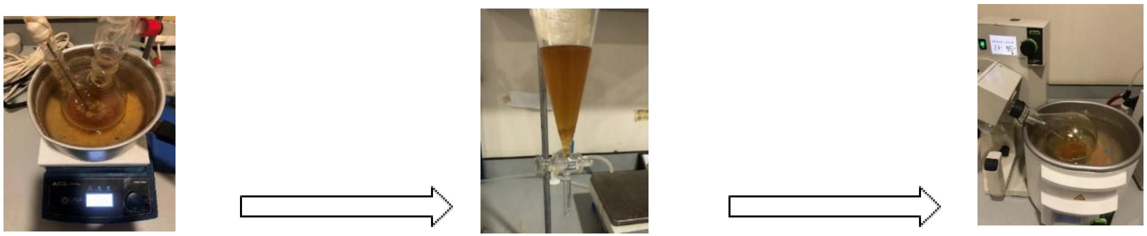


(1): filter the KOH mixture (2): reaction mixture of KOH catalyst (3): after washed the biodiesel with distilled water

Figure 3 transesterification reaction of KOH catalyst

2.4.2. Transesterification reaction of banana and mango catalysts

Figures 4 and 5 illustrate the sequential stages of the transesterification reaction using banana and mango catalysts. A solution comprising pre-treated waste cooking oil, methanol, and catalyst is prepared in a separatory funnel with a volume of 250 ml. The oil-to-methanol molar ratio is 6:1, with a catalyst mass of 2 g. To begin, combine methanol with 2g of catalyst and heat the mixture to 50°C for 20 minutes. Utilize a magnetic stirrer to ensure thorough mixing of the solution. Combine the mix with the oil and then move it to the reflux condenser to cool the produced vapours and transform them back into a liquid state. This process prevents the solvent from evaporating, extending the flask's heating duration to 65 C for 1 hour. Subsequently, transfer the mixture to the 250 ml separatory funnel and allow it to sit for 24 hours. To separate the glycerol component, distil it after a full day. Next, transfer the biodiesel to the rotary evaporator and allow it to undergo a drying and purification process for 1 hour. This process aims to remove methanol and other impurities from the biodiesel. Subsequently, the biodiesel was reintroduced into the separatory funnel for a thorough triple-washing process. Conclude the process by dehydrating the washed biodiesel using anhydrous sodium sulphate as a desiccant, resulting in the acquisition of a pure biodiesel sample.

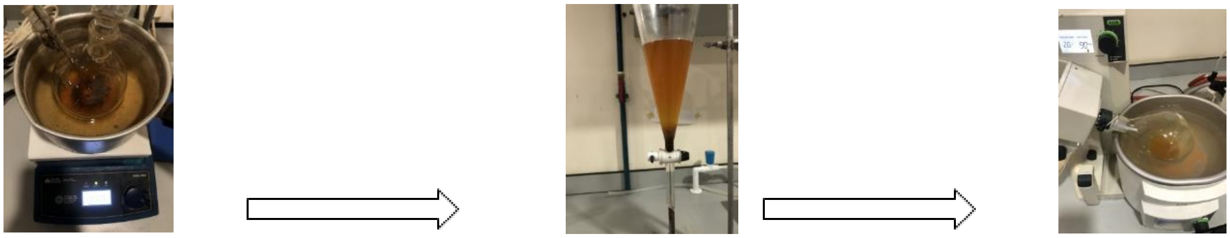


(1): the mixture of mango catalyst and methanol mix it with oil in the reflux condenser

(2): reaction mixture of mango catalyst

(3): mango biodiesel in the rotary evaporator

Figure 4 transesterification reaction of mango catalyst



(1): the mixture of banana catalyst and methanol mix it with oil in the reflux condenser

(2): reaction mixture of banana catalyst

(3): banana biodiesel in the rotary evaporator

Figure 5 transesterification reaction of banana catalyst

2.5. Biodiesel yield of the catalysts

The biodiesel yield was determined using equation (5).

$$\text{Biodiesel yield (\%)} = (\text{weight of biodiesel} / \text{weight of waste cooking oil}) \times 100 \quad (5)$$

$$\text{Biodiesel yield of KOH (\%)} = (45.06 / 100) \times 100 = 45.06\% \quad (6)$$

$$\text{Biodiesel yield of Mango (\%)} = (74.97 / 100) \times 100 = 74.97\% \quad (7)$$

$$\text{Biodiesel yield of Banana(\%)} = (63.44 / 100) \times 100 = 63.44\% \quad (8)$$

3. Result and discussion

The findings indicated that the mango catalyst exhibited the maximum biodiesel yield percentage of 74.97%, followed by the banana catalyst with 63.44%. The KOH catalyst had the lowest biodiesel yield percentage of 45.06%. Several factors contribute to these outcomes. Initially, as the temperature rises, the production of biodiesel also increases. This phenomenon was observed in the case of the mango and banana catalysts, which were subjected to a heating duration of one and a half hours. In contrast, the KOH catalyst was heated for only one hour. Moreover, extending the reaction duration will enhance biodiesel production for the mango and banana catalysts, which were allowed to react for four days. However, the KOH catalyst's reaction time was limited to only one day. All other parameters remain constant for all catalysts. As an illustration, the quantity of Catalyst present was merely 2 grams, the Molar ratio of oil to methanol was 1:6, and the FFA content was below 5%.

3.1. Catalyst characterization of mango powder and banana powder

3.1.1 FT-IR characterization of mango powder and banana powder before extraction of biodiesel

The beak for mango powder was at 1024.71 cm1 corresponds to C-O but for the banana powder was at 1010.76 cm1 corresponds to C-O carbohydrate. And all these peaks contributed to the catalyst being more active and reacting quickly. Mango peels [8] exhibit O-H, C-O, and CO_3 functional groups, contributing to catalytic activity. Wheat bran ash [9] contains

O-H, CH_2, C-O-C, and siloxane (O-Si-O) groups, enhancing its catalytic efficiency. Eggshell [10] features strong O-H and calcium-oxygen bonds, playing a role in carbonation. Snail shell [11] displays OH, Mg-OH, and oxide stretching modes, with significant metal oxide content. These catalysts, due to their unique functional groups, offer promising alternatives for biodiesel synthesis.

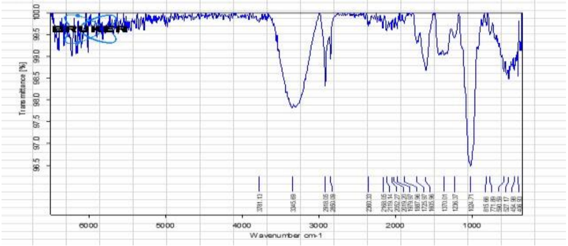


Figure 6 FT-IR for mango powder

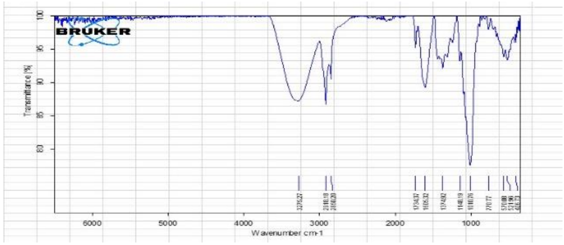


Figure 7 FT-IR for banana powder

3.1.2. SEM- EDS characterization of mango powder and banana powder before extraction of biodiesel

In SEM analysis showed that mango powder had a rough, non-porous surface, whereas banana powder was more porous In EDS confirmed that both catalysts contained high levels of carbon and oxygen, along with potassium and calcium in smaller quantities. Mango peel contains alkali and alkaline earth metals, enhancing catalytic activity [8]. Wheat bran ash has a dense, impermeable surface with fused microstructures [9]. Eggshell exhibits a rough, porous surface due to charge aggregation [10]. Snail shell features large pores for better fat absorption, with increased metal oxide content after calcination [11]. These materials show potential as efficient, sustainable catalysts.

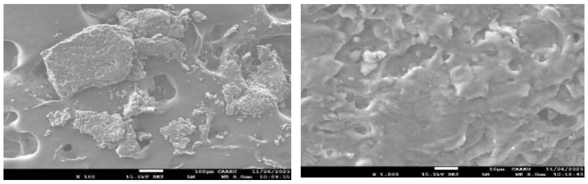


Figure 8 SEM for mango powder

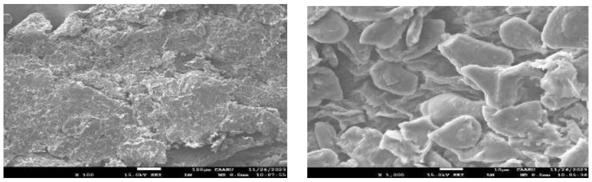


Figure 9 SEM for banana powder

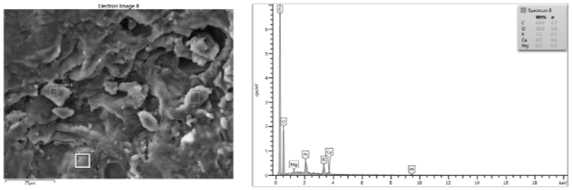


Figure 10 EDS spectrum 8 of mango powder

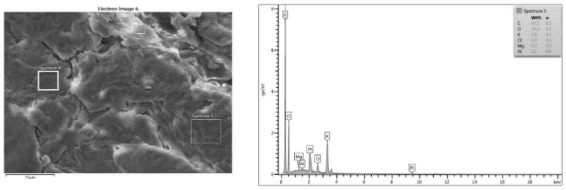


Figure 11 EDS spectrum3 for banana powder

3.1.3. XRD characterization of mango powder and banana powder before extraction of biodiesel

X-ray Diffraction (XRD) revealed crystalline structures with peak intensities varying between the two catalysts. Mango peel shows distinct crystalline peaks at multiple theta values [8]. Wheat bran ash contains silica, calcium oxide, and calcium carbonate, with characteristic peaks confirming its composition [9]. Eggshell exhibits peaks indicating its crystallographic structure, confirming its suitability as a catalyst [10]. These materials demonstrate potential for biodiesel production based on their structural properties.

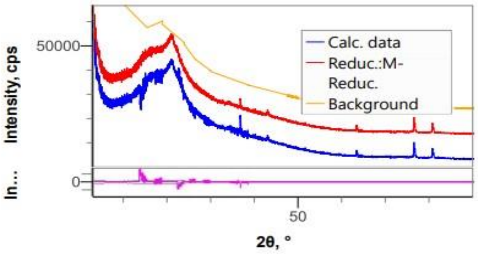


Figure 12 XRD for mango powder

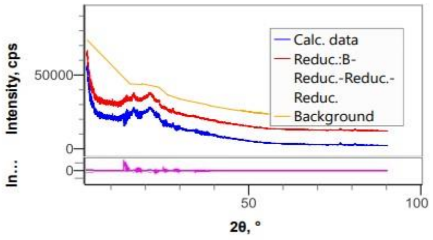
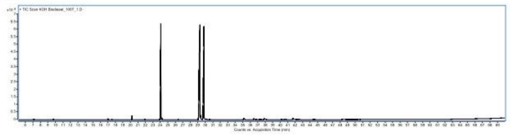


Figure 13 XRD for banana powder

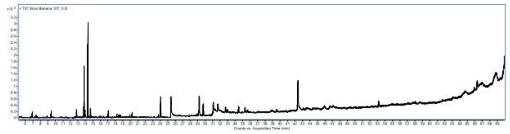
3.2. GC-MS characterization of biodiesel production from KOH, mango and banana as catalysts

GC-MS result showed that KOH is the most efficient catalyst for biodiesel production, but banana and mango peel catalysts still produce reasonable amounts of key biodiesel components, making them viable sustainable alternatives. Mango peel biodiesel contains various fatty acid methyl esters (FAMEs), including methyl octadecadienoate and methyl hexadecanoate [8]. Eggshell-based biodiesel meets ASTM and EU standards, with favorable saponification value, cetane number, and flash point, making it safer and stable [9]. Snail shell-based biodiesel contains key FAMEs like palmitoleic, stearic, oleic, and linoleic acid methyl esters, identified via GC-MS analysis [11]. These catalysts demonstrate strong potential for biodiesel production.

KOH Biodiesel:



Banana Biodiesel:



Mango Biodiesel:

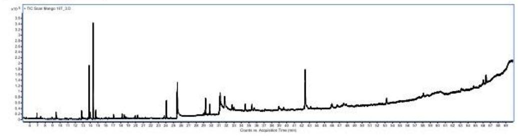
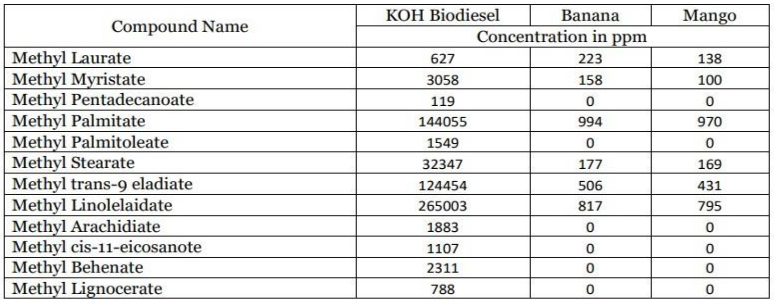


Figure 14 GC-MS biodiesel graphs

The table below presents the GC-MS (Gas Chromatography-Mass Spectrometry) analysis of biodiesel components produced using three different catalysts: KOH, banana peel, and mango peel. The data shows the concentration (in ppm) of various fatty acid methyl esters (FAMEs) found in the biodiesel samples. KOH Biodiesel has the highest concentrations of all major FAMEs, indicating its strong catalytic efficiency in producing biodiesel. Banana and Mango Peel Catalysts show lower FAME concentrations overall, suggesting a lower conversion efficiency compared to KOH. Methyl Palmitate and Methyl Linoleate are the dominant compounds in all biodiesel samples, indicating their importance in biodiesel composition. Banana and Mango biodiesel lack certain FAMEs in Methyl Arachidate, Methyl Behenate and Methyl Lignocerate, suggesting differences in catalytic performance and feedstock suitability.

Table 1 GC-MS biodiesel components



Compound Name	KOH Biodiesel	Banana	Mango
	Concentration in ppm		
Methyl Laurate	627	223	138
Methyl Myristate	3058	158	100
Methyl Pentadecanoate	119	0	0
Methyl Palmitate	144055	994	970
Methyl Palmitoleate	1549	0	0
Methyl Stearate	32347	177	169
Methyl trans-9 eladiate	124454	506	431
Methyl Linolelaidate	265003	817	795
Methyl Arachidiate	1883	0	0
Methyl cis-11-eicosanote	1107	0	0
Methyl Behenate	2311	0	0
Methyl Lignocerate	788	0	0

4. Conclusion

Biodiesel presents certain challenges in contemporary diesel engines; nevertheless, it remains a viable option for heavy-duty machinery and power generators, either in its neat form or blended with conventional diesel. Commercial adoption is hindered by high production costs, largely attributable to expensive raw materials (60–80% of total expenses). To mitigate these costs, waste oils—such as used cooking oil and animal fats—are often preferred feedstocks.

This study examines the performance of mango and banana powder as heterogeneous catalysts, utilizing SEM, FT-IR, XRD, and GC-MSMS for comprehensive characterization. Heterogeneous catalysts are advantageous over homogeneous counterparts due to their reusability and reduced environmental impact. In addition, producing biodiesel from waste oils helps address environmental issues like clogged drains and water pollution. As a renewable, biodegradable, and relatively safer alternative to petroleum diesel, biodiesel remains widely available and thus holds significant promise as a future fuel source.

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