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Original Article

Extraction and Optimization of Transesterification Process to Produce Pine Biodiesel Using Nano Catalyst

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Abstract *- This study focuses on the extraction and optimization of the transesterification process for converting pine oil into biodiesel using a nanocatalyst. The extraction of pine oil involves the efficient extraction of triglycerides from pine seeds, which are subsequently subjected to the transesterification process. In this process, a novel nanocatalyst is employed to enhance the reaction rate and product yield. The nano catalyst's unique properties, including its high surface area and reactivity, make it an ideal candidate for improving biodiesel production efficiency. To optimize the transesterification process, a comprehensive experimental design is undertaken, utilizing Response Surface Methodology (RSM) and Central Composite Design (CCD). The key process parameters, such as catalyst concentration, reaction time and retention temperature, are systematically varied and analysed to determine their impact on biodiesel yield and quality. The use of statistical tools allows for the development of predictive models and the identification of optimal conditions for pine biodiesel production. The yield of pine biodiesel has further increased using nano alumina, and cerium oxide catalysts added additional to the KOH catalyst. The results of this study contribute to the development of efficient and environmentally friendly biodiesel production methods, thereby fostering the utilization of pine as a valuable feedstock for the biofuel industry.*

Keywords *- Transesterification, Nanocatalyst, Optimization, Biodiesel, Pine oil.*

1. Introduction

With growing concerns about climate change, energy security, and the environmental impact of fossil fuels, the exploration of alternative and sustainable energy sources has become paramount. Biodiesel, a renewable and biodegradable fuel derived from triglycerides (commonly found in vegetable oils and animal fats), has emerged as a promising contender for mitigating these concerns [1]. Biodiesel not only reduces greenhouse gas emissions but also promotes energy independence. One of the most significant advantages of biodiesel is its potential to reduce greenhouse gas emissions.

Unlike conventional diesel fuels, biodiesel is derived from renewable sources such as vegetable oils, animal fats, and algae. When burned, biodiesel releases carbon dioxide (CO_2) into the atmosphere, but it is considered carbon-neutral because the CO_2 emissions are offset by the CO_2 absorbed during the growth of the feedstock crops [2-4]. This closed carbon cycle helps mitigate the effects of climate change. Biodiesel also offers a cleaner-burning alternative to traditional diesel fuels. It produces fewer harmful emissions, such as sulphur oxides (SOx), nitrogen oxides (NOx), and particulate matter. This leads to improved air quality, especially in urban areas, and reduced health risks associated with exposure to air pollution [5]. By diversifying our energy sources, biodiesel can enhance energy security. Relying less on fossil fuels, which are subject to geopolitical tensions and price fluctuations, reduces a nation's vulnerability to supply disruptions and price spikes. Biodiesel production often relies on crops like soybeans, pine, soap nut, mahua, pongamia, canola, and palm oil, as well as non-food sources like algae [6-8]. This creates an opportunity for sustainable agriculture and the development of non-food crop alternatives, reducing the pressure on food production and land use. The most common method for biodiesel production is transesterification. This chemical reaction involves combining a triglyceride (found in oils and fats) with an alcohol (usually methanol or ethanol) in the presence of a catalyst (typically sodium hydroxide or potassium hydroxide). This process breaks down the triglyceride into biodiesel and glycerine [9].

Fossil fuels are essential but limited, so renewable biofuels like biodiesel are important for sustainable energy. This review discusses biodiesel production from various sources using methods like transesterification and the benefits of nanocatalysts. Nanocatalysts improve production by increasing surface area and catalytic activity. Despite the progress, challenges like finding affordable feedstocks and optimizing production processes remain. Non-edible oils and microalgae show promise as better sources of biodiesel.

Researchers are continually exploring advanced techniques for biodiesel production, including enzymatic transesterification, supercritical transesterification, and microwave-assisted methods [10, 11]. These techniques aim to improve efficiency and reduce the environmental footprint of biodiesel production. The need for biodiesel as a sustainable and eco-friendly alternative to conventional diesel fuels is clear. It offers a range of benefits, from reducing greenhouse gas emissions and air pollution to enhancing energy security and promoting sustainable agriculture. To harness the full potential of biodiesel, it is crucial to continue developing and adopting efficient production methods that minimize environmental impact. As technology and research advance, biodiesel holds the promise of playing a significant role in a cleaner and more sustainable energy future.

Excessive use of petroleum fuels causes global warming and price instability, so renewable alternatives like biodiesel are needed. Biodiesel is a clean, renewable fuel made from waste oils and fats. It's produced using various catalysts, with nanocatalysts showing great promise due to their high efficiency and easy recovery. Despite their benefits, nanocatalysts need more research to address toxicity concerns. Overall, nanocatalysts can significantly improve biodiesel production and other bio-based products [10].

Biodiesel production involves transesterification using either homogeneous or heterogeneous catalysts. Homogeneous catalysts are efficient but challenging to purify and reuse, while heterogeneous catalysts are easier to manage and work well with various oils. Emerging nanocatalysts and biocatalysts offer eco-friendly alternatives but have limitations like slower reaction rates and higher costs. Research is focused on improving these catalysts for efficient, large-scale biodiesel production.

CCD, or Central Composite Design, is a statistical experimental design technique that is used to optimize processes in various fields, including biodiesel production. CCD allows for the systematic optimization of biodiesel production processes by varying multiple factors simultaneously [12]. This can lead to a more efficient use of resources, reduced experimentation time, and cost savings. CCD uses a relatively small number of experimental runs compared to a full factorial design, which reduces the time and resources required for experimentation. This is particularly valuable in biodiesel production, where multiple factors such as temperature, catalyst concentration, and reaction time can impact product quality and yield [13]. CCD helps identify the optimal combination of process variables that result in the highest biodiesel yield and quality. This ensures that production processes are not only efficient but also produce biodiesel that meets or exceeds quality standards. The quest for sustainable and environmentally friendly energy sources has led to significant advancements in biodiesel production. One crucial aspect of this process is the use of catalysts to facilitate transesterification, a chemical reaction that converts triglycerides into biodiesel.

In recent years, researchers have explored the incorporation of nanoparticle additives as catalysts, unlocking new possibilities for efficient and sustainable biodiesel production. Nanoparticles, tiny structures with dimensions on the nanoscale, have garnered attention for their unique properties and versatility. Researchers have discovered that certain nanoparticles, when used as additives in transesterification, can serve as highly efficient catalysts, offering several advantages. Nanoparticles possess an exceptionally high surface area-to-volume ratio.

This property enhances their catalytic activity, as a larger surface area allows for more active sites where the transesterification reaction can occur [14]. In this work, the transesterification process has been optimized using CCD by considering catalyst quantity, reaction temperature and retention time as factors and biodiesel yield as a response. Additionally, along with the KOH catalyst, Nano alumina and cerium oxide were added to the transesterification process to increase the yield.

2. Literature Review

Al-Widyan et al. (2002) studied making biodiesel from used vegetable oils. They showed that used oils can be turned into a good fuel similar to diesel. Aalam and Saravanan (2015) made biodiesel from mahua oil using a chemical process. They showed how important it is to choose the right chemicals to get good biodiesel. Ingle et al. (2020) and Bano et al. (2020) reviewed the use of very tiny particles, called nanocatalysts, to make biodiesel.

These tiny particles help make biodiesel faster and with less energy. Boudy and Seers (2009) studied how biodiesel's thickness and weight affect the fuel injection in engines. These properties are important for how the fuel is sprayed into the engine. Tziourtzioumis and Stamatelos (2012) looked at how using a lot of biodiesel (70%) changes how fuel injectors work, especially when the engine's speed changes. Raheman and Ghadge (2007) and Ozsezen and Canakci (2011) tested engines running on biodiesel made from mahua and waste palm oils.

They found that while biodiesel engines may have slightly less power, they have better lubrication, which reduces engine wear. Devan and Mahalakshmi (2009) studied engines using a mix of paradise oil and eucalyptus oil biodiesel. They found these mixes burned fuel better and used less fuel. Cheung et al. (2009) and Tuccar et al. (2014) studied the emissions from engines using biodiesel and biodiesel-methanol blends.

They found that biodiesel reduces harmful emissions like carbon monoxide (CO), hydrocarbons (HC), and particulate matter. However, it may slightly increase nitrogen oxides (NOx). Aalam et al. (2015, 2017) and Sadikbasha and Anand (2011) added tiny metal particles to biodiesel. These additives improved engine performance and reduced harmful emissions by helping the fuel burn better. Aalam et al. (2016) studied how increasing the fuel injection pressure affects engines running on mahua biodiesel blends. Higher pressure helped the fuel mix better with air, leading to more complete burning and fewer emissions.

3. Transesterification Process

Transesterification is a fundamental chemical reaction in biodiesel production, where triglycerides are converted into biodiesel and glycerol through the use of a catalyst, typically an alkali metal hydroxide. Two critical parameters that significantly influence the transesterification process are reaction temperature and reaction time. In this article, we explore how these factors play a pivotal role in biodiesel production and the delicate balance between achieving high efficiency and maximizing yield. Transesterification is a chemical reaction commonly used in the production of biodiesel and other ester-based compounds. In transesterification, the ester functional group in an ester compound reacts with an alcohol to form a new ester compound and an alcohol molecule as a byproduct. In this work, Methanol is used as the alcohol in transesterification reactions. Methanol serves as a reactant to replace the glycerol portion of the triglyceride, leading to the formation of ester molecules. In the presence of the KOH catalyst, the triglycerides react with the hydroxide ions (OH-) from the catalyst, leading to the hydrolysis of the ester bonds. This results in the formation of glycerol (a byproduct) and fatty acid anions.

Triglyceride + Hydroxide ion (OH-) → Glycerol + Fatty Acid Anions

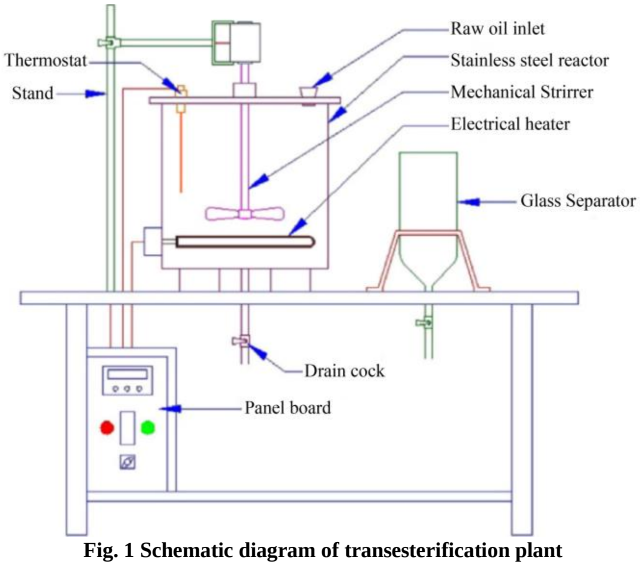

Fig. 1 Schematic diagram of transesterification plant

4. Optimization of Biodiesel Production

Optimizing the production of pine biodiesel is essential to maximize efficiency, minimize waste, and ensure the product's quality. CCD, a statistical experimental design technique, plays a pivotal role in achieving these goals. CCD starts with a systematic exploration of critical factors that influence the biodiesel production process. These factors might include reaction temperature, catalyst concentration, and reaction time, among others. CCD divides the experimental space into a series of data points, each representing a unique combination of the selected factors.

These data points are strategically chosen to capture the entire response surface and identify optimal conditions. Experiments are conducted at the selected data points, and the results are used to build a mathematical model that describes the relationship between the factors and the desired response variables, such as biodiesel yield or purity. With the response surface model in hand, CCD enables researchers to identify the optimal conditions that maximize the desired response while minimizing undesirable factors. This step helps fine-tune the production process for improved efficiency and quality.

The Predicted R^2 of 0.5756 is not as close to the Adjusted R^2 of 0.9288 as one might normally expect; i.e., the difference is more than 0.2. This could propose a massive block impact or a likely hassle together in conjunction with your model and/or information. Subjects to don't forget are version bargain, reaction transformation, outliers, and so forth. All empirical fashions ought to be examined with the resource of doing affirmation runs. Adeq Precision measures the sign-to-noise ratio. A ratio of more than four is suitable. Your ratio of 14.202 indicates the right enough signal. This model can be used to navigate the layout region.

Table 1 shows the details of ANOVA for the Quadratic model of pine biodiesel yield. The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant.

The intercept in orthogonal form is the overall common response of all runs. Coefficients are purely general transformations based on complex systems. The VIFs are 1 when the factors are orthogonal; VIFs greater than 1 indicate multi-co linearity, with a higher VIF indicating a stronger correlation between subjects. As a rough rule, pile VIFs of less than 10 tonnes are tolerable. Table 2 suggests coefficient information based on coded components.

By systematically exploring the experimental space, CCD helps researchers identify the most efficient conditions for biodiesel production, reducing resource consumption and waste. Figures 2 to 6 show the response surface of pine biodiesel yield with reaction temperature, Temperature and different percentages by weight of KOH catalyst. Totally 17 experiments were carried out depending upon the factors given by Box Behnken. The reaction temperature, retention time and percentage by weight of KOH catalyst are considered as factors in this design. The pine biodiesel yield was considered as a response. From the RSM, it is clear that the reaction temperature retention time plays a vital role in the production of pine biodiesel. The yield of biodiesel was found to be higher when the reaction temperature was 60 to 70°C. The addition of a KOH catalyst enhances the yield of biodiesel in the transesterification process. A 12.5% hike in biodiesel yield was found when the amount of catalyst was increased from 0.2 to 1% by weight.

Table 1. ANOVA for quadratic model

Std. Dev.	1.56	**R^2**	0.9689
Mean	77.71	**Adjusted R^2**	0.9288
C.V. %	2.01	**Predicted R^2**	0.5756
		Adeq. Precision	14.2023

Table 2. Coefficient in terms of coded factors

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	82.20	1	0.6980	80.55	83.85	
A-Temperature	3.25	1	0.5518	1.95	4.55	1.0000
B-Reaction time	2.88	1	0.5518	1.57	4.18	1.0000
C-Catalyst concentration	4.63	1	0.5518	3.32	5.93	1.0000
AB	0.7500	1	0.7803	-1.10	2.60	1.0000
AC	2.25	1	0.7803	0.4048	4.10	1.0000
BC	0.0000	1	0.7803	-1.85	1.85	1.0000
A^2	-3.85	1	0.7606	-5.65	-2.05	1.01
B^2	-0.6000	1	0.7606	-2.40	1.20	1.01
C^2	-5.10	1	0.7606	-6.90	-3.30	1.01

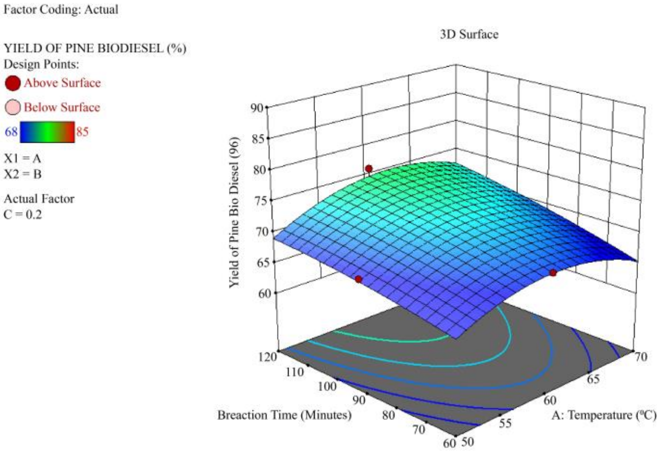

Fig. 2 Response surface of pine biodiesel yield with reaction temperature, retention time and 0.2% by weight of KOH catalyst

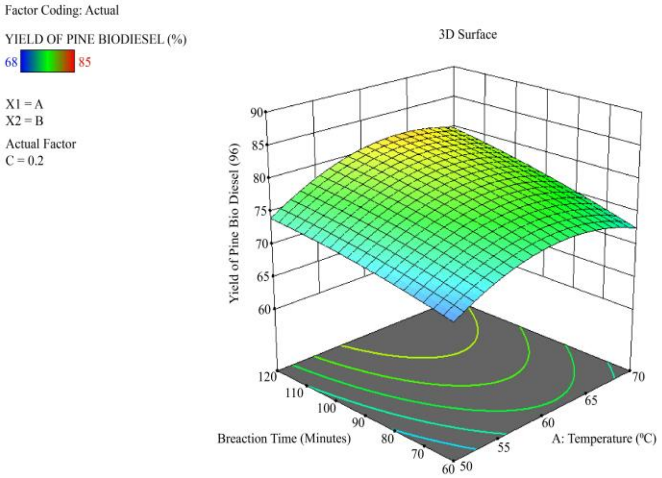

Fig. 3 Response surface of pine biodiesel yield with reaction temperature, retention time and 0.4% by weight of KOH catalyst

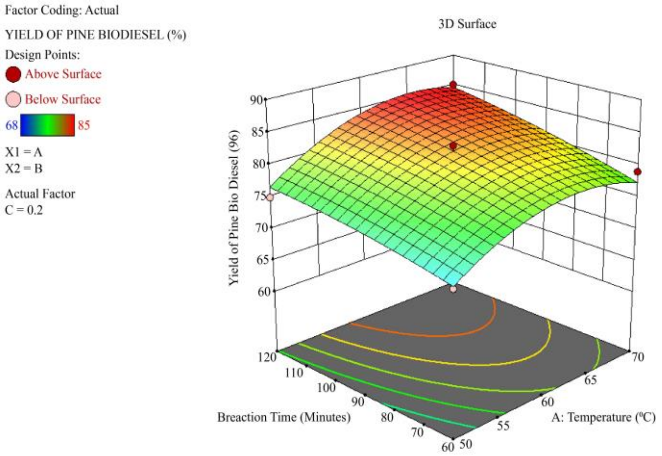

Fig. 4 Response surface of pine biodiesel yield with reaction temperature, retention time and 0.6% by weight of KOH catalyst

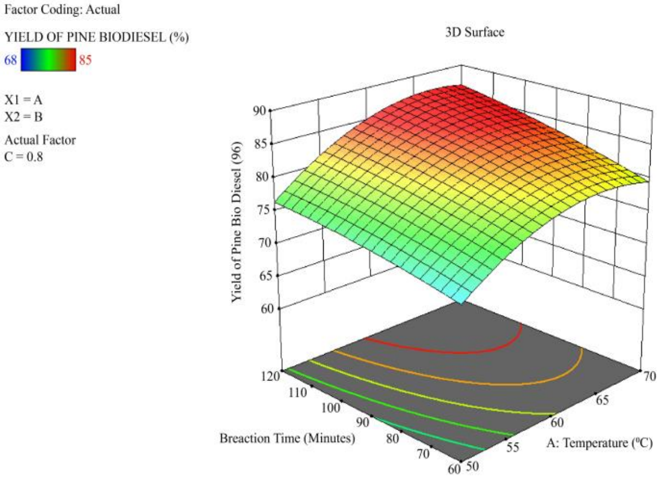

Fig. 5 Response surface of pine biodiesel yield with reaction temperature, retention time and 0.8% by weight of KOH catalyst

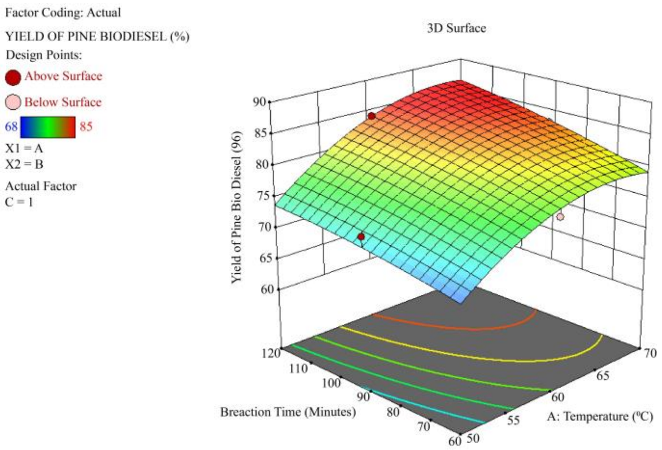

Fig. 6 Response surface of pine biodiesel yield with reaction temperature, retention time and 1% by weight of KOH catalyst

The Cube Image in Central Composite Design involves conducting a series of experiments based on the CCD. In this design, temperature, time, and catalyst quantity are systematically varied within predetermined bounds. The experiments are performed at various combinations of these factors to collect data on biodiesel production. These data are then analysed to build a predictive model that links the input factors to the response variables. Figure 7. Shows the Cube image of pine biodiesel yield with reaction temperature, Temperature and KOH catalyst. By influencing mathematical optimization techniques, this model was used in this work to determine the optimal conditions for maximum biodiesel yield and quality.

The Normal Plot of Residuals is a graphical technique used to assess the normality of residuals, which is a crucial assumption in many statistical models. Normality implies that the residuals follow a normal distribution, which is often a reasonable assumption when analysing data. This assumption is essential for various statistical analyses and modelling techniques, including analysis of variance (ANOVA) and linear regression. Ideally, the points on the plot should form a straight line.

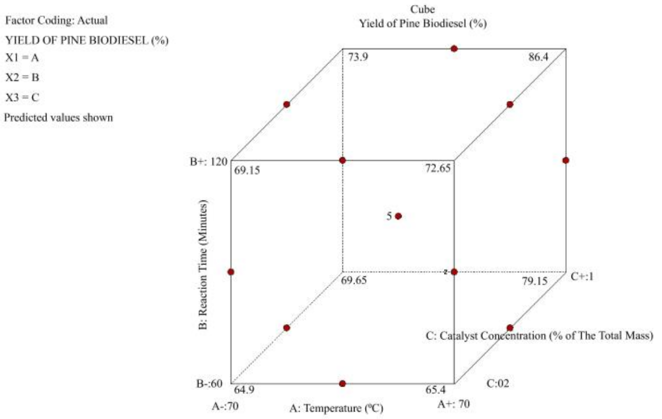

Fig. 7 Cube image of pine biodiesel yield with reaction temperature, and KOH catalyst

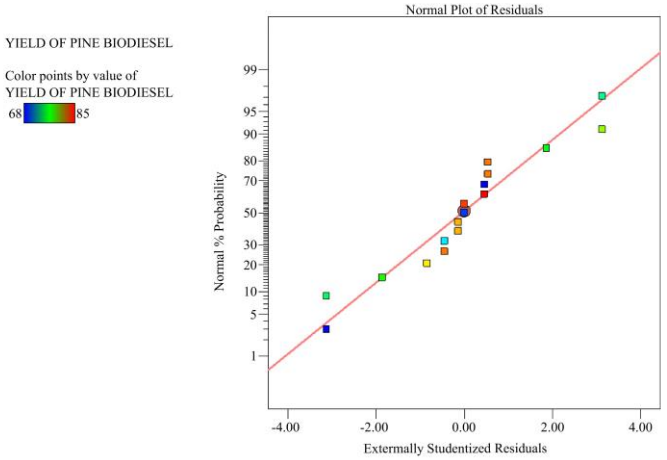

Fig. 8 Normal plot of residuals image of pine biodiesel yield with externally standardized residuals

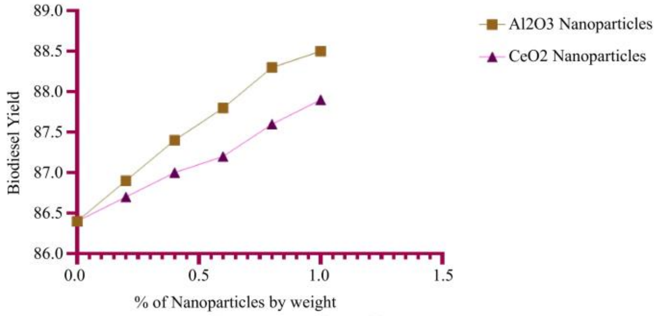

Fig. 9 Effects of Al_2O_3 and CeO_2 nanoparticles in biodiesel yield

A slight curvature may not be concerning. Outliers on the plot suggest significant deviations from normality. Identifying and addressing the underlying causes of these outliers is crucial to improving the biodiesel production process. Figure 8. Shows the image of a Normal Plot of Residuals yield with externally standardized residuals of pine biodiesel.

5. Effect of Nanoparticles on Biodiesel Yield

KOH is a widely used catalyst in transesterification, but it has certain limitations. Nanoparticles can improve catalytic efficiency by providing a high surface area for reactions to take place. Both alumina and cerium oxide nanoparticles possess catalytic properties that can promote the transesterification reaction, leading to higher biodiesel yields. Nanoparticles, owing to their small size and excellent dispersibility, facilitate better mixing of reactants. This ensures that the catalyst is evenly distributed throughout the reaction mixture, improving contact between the reactants and accelerating the reaction rate. Figure 9 shows the Effects of Al_2O_3 and CeO_2 nanoparticles in biodiesel yield.

From the results, it is clear that the addition of nanoparticles has increased the biodiesel yield. The yield was found to be higher when the quantity of Al_2O_3 and CeO_2 nanoparticles was increased. Compared with CeO_2, Al_2O_3 nanoparticles give a higher yield. This may be due to Alumina nanoparticles; in particular, they are known for their ability to neutralize acidic components in feedstocks, which can inhibit the transesterification process. By mitigating the acid content in the reactants, alumina nanoparticles help create more favourable conditions for the reaction to occur.

6. Conclusion

The alumina and cerium oxide nanoparticles with the traditional KOH catalyst in transesterification offer a promising approach to enhance biodiesel production. As the world seeks sustainable energy solutions, innovations like nanoparticle-enhanced transesterification may contribute to a greener and more sustainable future. From the results, it is concluded that

1. The yield of biodiesel increases with the addition of KOH catalyst and temperature. The optimum quantity of KOH catalyst was 7 to 8% by weight, and the optimum temperature was found as 60°C.
2. Similarly, the addition of alumina and cerium oxide nanoparticles further increases the yield by up to 2%. Compared with the cerium oxide, alumina was found effective in increasing the pine biodiesel yield.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper. The first author, *C Manikandan*, is the sole author of this research, and *C. Syed Aalam* has been added as a co-author due to their role as the project guide, with no influence from any secondary interests.

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