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Fly Ash (FA) Nanoparticles as Heterogeneous Catalysts for Efficient Biodiesel Production from Rapeseed Oil

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ABSTRACT

The global energy crisis is driven by the depletion of fossil fuel reserves, coupled with rapid population growth in developing countries. Additionally, fossil fuels are environmentally harmful, contributing to global warming, high toxicity, and non – biodegradability, making them unsustainable energy sources. This study investigates the effectiveness of fly ash nanoparticles as a heterogeneous catalyst in the trans – esterification of rapeseed oil for biodiesel production. The physical and chemical characteristics of fly ash were analysed using scanning electron microscopy (SEM) and X-ray fluorescence (XRF). The crude rapeseed oil was purified and trans – esterified, with fly ash applied as a catalyst in varying concentrations from 0.1 wt% to 1.0 wt%. The biodiesel's pour point, flash point, and fire point were measured. SEM analysis revealed irregular particles with a porous texture, while X-ray diffraction (XRD) indicated the presence of crystalline quartz with a hexagonal structure. XRF results confirmed that silicon dioxide (SiO_2) was the primary component of fly ash. The highest biodiesel yield, 96.11%, was achieved with 0.3 wt% fly ash. The pour point, flash point, and fire point of the biodiesel were recorded at 7°C, 146°C, and 109°C, respectively, all within ASTM biodiesel standards. The findings demonstrate that fly ash has significant potential as a heterogeneous catalyst for biodiesel production from rapeseed oil through trans-esterification.

Keywords: Fly ash nanoparticles, Heterogeneous catalyst, Biodiesel production, Rapeseed oil trans-esterification, Renewable energy.

INTRODUCTION

Biodiesel has emerged as a highly promising renewable energy source, offering a viable alternative to fossil fuels. Its rise in prominence is driven by its many advantages, including the availability of renewable feedstocks, its biodegradable nature, lower toxicity, sulphur-free emissions, and physical and chemical properties that closely resemble those of conventional fossil fuels. As concerns over the environmental impact and the finite nature of fossil fuels grow, biodiesel has gained attention as an ecologically and economically sustainable energy source. One of the key advancements in biodiesel production is the use of catalysts, which have proven to significantly enhance both the efficiency and quantity of biodiesel produced.

Catalysts, in general, are substances that accelerate the rate of chemical reactions by lowering the

activation energy required for the process [1-15]. These substances, even when added in minimal amounts compared to the reactants, are not consumed during the reaction. Rather, they facilitate the process and can often be reused, making them indispensable in various chemical conversions. Catalysts are also known to influence the selectivity of reactions, ensuring that the desired products are produced more efficiently. However, catalysts can either participate directly in the reaction or, in some cases, function by altering surface characteristics, thereby accelerating the process without being consumed themselves [2].

Catalysis plays a central role in fostering environmentally friendly and commercially feasible chemical reactions. The use of catalysts in biodiesel production not only improves efficiency but also supports the development of green technologies by reducing the energy input required in chemical processes. One type of catalyst that has been particularly impactful is the heterogeneous catalyst, which differs from homogeneous catalysts in that it exists in a different phase from the reactants. In biodiesel production, the reactants – typically feedstock oil and methanol – are in liquid form, while the heterogeneous catalyst is in a solid state. This phase difference enables easier separation of the catalyst from the reaction mixture, offering numerous practical and economic advantages [1].

In traditional biodiesel production, homogeneous catalysts such as potassium hydroxide (KOH), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl) have been widely used. These catalysts, along with food-grade feedstocks like soybean oil, palm oil, and sunflower oil, have dominated commercial biodiesel production. However, the rising cost of these food-grade oils, which contribute more than 70% of the total cost of biodiesel production, has rendered this approach increasingly unsustainable [13,18]. Additionally, the use of homogeneous catalysts poses several challenges, such as difficulties in post-reaction purification and the need for significant amounts of water to wash out the catalysts from the biodiesel, which in turn increases production costs and environmental impacts.

In recent years, heterogeneous catalysts have garnered substantial attention in both scientific research and industrial applications due to their economic and environmental benefits. The primary advantage of heterogeneous catalysts in biodiesel production lies in their ability to be separated from the reaction mixture through simple physical processes, such as filtration or centrifugation [13]. This not only simplifies the production process but also allows the catalyst to be reused multiple times, thus reducing the overall cost of biodiesel production [19-30]. Furthermore, the use of heterogeneous catalysts can mitigate the problem of dissolved metals or other impurities in the biodiesel, which is often a concern with homogeneous catalysts.

The growing interest in heterogeneous catalysts, particularly solid catalysts, is driven by their potential to resolve many of the technical issues associated with traditional biodiesel production. By reducing the need for post-reaction washing, improving biodiesel yield, and enhancing process efficiency, these catalysts represent a significant step forward in making biodiesel production more sustainable and cost-effective [14]. In addition, the use of solid catalysts reduces the environmental impact of biodiesel production, aligning it more closely with the principles of green technology [22].

This research focuses on the conversion of rapeseed oil to biodiesel using fly ash as a

heterogeneous catalyst. Fly ash, a waste product that is typically disposed of in landfills, is readily available and can be repurposed for biodiesel production. Its catalytic properties enable the efficient conversion of the high free fatty acid (FFA) content in rapeseed oil to fatty acid methyl esters (FAME) under moderate reaction conditions. Utilizing rapeseed oil as a feedstock addresses food security concerns associated with the use of food-grade oils in biodiesel production, while also significantly reducing the overall cost of biodiesel production due to its lower price.

The main objective of this study is to explore the current state of heterogeneous catalysts in biodiesel production, particularly the potential of fly ash as an environmentally friendly and economically viable option. By using fly ash as a catalyst, the research aims to demonstrate how waste materials can be effectively repurposed to produce sustainable energy, thereby contributing to a greener, more cost-effective biodiesel production process. This approach not only reduces the reliance on expensive food-grade oils but also promotes the use of waste products in industrial applications, further aligning biodiesel production with sustainable development goals.

METHODOLOGY

X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) characterization of the fly ash sample was carried out at the Central Laboratory of Umaru Musa Yar'adua University in Katsina, using the ARL QUANT'X EDXRF Analyzer (S/N 9952120). During the process, incoming X-rays from the XRF machine eject electrons from the inner orbitals of atoms, causing the atoms to become excited. This excitation leads to the emission of high-energy radiation, such as photons, protons, and electrons. The emitted radiation is then detected and analysed, with the intensity of the emitted lines varying based on the element. Finally, the intensity levels of these detected lines are converted into corresponding elemental concentrations.

Scanning Electron Microscopy (SEM)

The surface morphology of the fly ash nanoparticles was examined using a multipurpose Scanning Electron Microscope (SEM), model PHENOM PROX MVE016477830, at Umaru Musa Yar'adua University, Katsina. A small amount of the sample powder was placed on a carbon tape attached to a sample holder. To ensure only fine particles remained on the tape, any excess powder was carefully blown off using an air gun. The prepared sample was then placed into the SEM chamber for analysis. The microscope was operated at 10kV, and an image of the sample was captured at a magnification of X100.

Infrared Spectral Analysis

Fourier Transform Infrared (FT-IR) spectroscopy was used to identify the functional groups present in the sample. For the FT-IR analysis, the liquid sample was prepared as a thin film and inserted between two potassium bromide (KBr) discs, which were made from single crystals. A drop of the liquid sample was placed on one disc, and the second disc was placed on top, spreading the liquid into a thin film. The analysis was conducted at the National Research Institute for Chemical Technology (NARICT) in Zaria.

Sample Purification

The purification of the oil sample was carried out through the following steps: First, 200 ml of the

oil was measured using a measuring cylinder and preheated to 70°C on a hot magnetic stirrer equipped with a thermometer. Next, 1.5 ml of citric acid was measured and added to the heated oil, and the mixture was continuously stirred and heated for 15 minutes at 70°C. Following this, 4 ml of 8% NaOH solution (prepared by dissolving 8 g of NaOH in 100 ml of distilled water) was added to the oil, and the stirring and heating continued for another 15 minutes at the same temperature.

The mixture was then transferred to a vacuum oven, where it was heated at 85°C for 30 minutes. Afterward, it was returned to the hot magnetic stirrer, heated to 70°C, and 2 g of silicon reagent was added while the mixture was stirred and heated for 30 minutes. The temperature was then increased to 85°C, and 4 g of activated carbon was added to every 100 ml of the oil sample. The mixture was heated and stirred for 30 minutes before being separated using filter paper.

Trans – esterification

Sixty grams (60 g) of crude oil was placed in a 250 ml conical flask and heated while stirring on a hot magnetic stirrer plate until the temperature reached 60 – 65°C. Meanwhile, 0.6 g of NaOH was accurately measured using an electronic scale and dissolved in 21 ml of methanol. This solution was then added to the conical flask and heated for 60 minutes while continuing to stir on the hot plate. After one hour of consistent stirring and heating at 65°C, the mixture was carefully transferred into a separating funnel using a glass funnel. It was allowed to cool for approximately 40 minutes, during which two distinct liquid layers formed. The upper layer, which contained biodiesel, was separated from the lower layer, which consisted of triglyceride fatty acids and other byproducts.

Nano – fluids Preparation

The fly ash nanoparticles powder was sourced from the environment and is reported to be dispersible, according to the manufacturer's specifications. The preparation of nanofluids involves a two-step process. Various volume concentrations of powdered nanoparticles were created, specifically 0.2%, 0.4%, 0.6%, 0.8%, and 1%, and a purified sample oil respectively. To enhance the stability and dispersion of the nanoparticles, each sample was stirred for 3 – 4 hours with a magnetic stirrer before being subjected to analysis.

Measurement of Pour Point

The pour point of the crude sample oils was determined using a cylindrical test tube, thermometer, ice bath, and retort stand. The crude oil was poured into the cylindrical test tube up to the 5 ml mark, which was then secured to a retort stand that held the thermometer. This assembly was placed in an ice bath and allowed to cool to 3°C. The pour point of the crude oil was recorded as the lowest temperature at which movement was observed within the oil in 5 seconds. This procedure was similarly applied to the purified and trans – esterified oil samples using fly ash as a catalyst.

Measurement of Flash Point

Crude sample oil was poured into a 100 ml conical flask up to the 10 ml mark and then heated on a hot magnetic plate at a rate of 14 to 17 ºC per minute until the temperature reached 56 ºC. The heating rate was subsequently decreased to 5 to 6 ºC per minute, and a test flame was applied at every 2 ºC increment until the oil ignited. The flash point was recorded as the lowest temperature at which the application of the flame test caused the vapor above the sample to ignite. This method

for measuring the flash point of crude sample oil was also applied to the purified oil, as well as the trans – esterified oil and the trans – esterified oil with the catalyst.

Measurement of Fire Point

Crude sample oil was poured into a 100 ml conical flask up to the 10 ml mark and heated on a hot magnetic plate at a rate of 14 to 17 ºC per minute until it reached 56 ºC. The temperature increase was then slowed to 5 to 6 ºC per minute, and a test flame was applied at every 2 ºC increment until the oil burned for at least 5 seconds. The fire point was recorded as the lowest temperature at which the application of the flame test caused the vapor above the sample to sustain combustion for 5 seconds. This procedure was also utilized to measure the fire point of the purified oil, as well as the trans – esterified oil and the trans – esterified oil with the catalyst.

RESULTS AND DISCUSSIONS

XRF of Fly Ash

Table 1 presents the X-ray fluorescence (XRF) analysis of the fly ash. The primary component of the ash is silicon dioxide (SiO_2), accounting for 66.43 wt%. This high concentration suggests that the fly ash has substantial silicate content, a characteristic that can enhance its utility as a catalyst due to the ability of silica to provide a large surface area and facilitate chemical reactions. followed by aluminium oxide (Al_2O_3) at 24.10 wt%. The presence of Al_2O_3 is significant as it is often associated with catalytic activity, particularly in heterogeneous catalysis. The combination of SiO_2 and Al_2O_3 in substantial amounts positions the fly ash as a potentially effective catalyst in various chemical processes.

Table 1: XRF of Fly Ash

Chemical Constituents	SiO_2	Al_2O_3	TiO_2	Cr_2O_3	Fe_2O_3	MnO	NiO	MgO	CaO	Na_2O	K_2O	P_2O_5	BaO	LOI
Oxides (wt%)	66.43	24.10	0.92	0.02	2.71	0.84	0.01	1.39	0.76	0.22	0.37	0.02	0.04	0.41

While the remaining oxides present in smaller quantities, their presence may still influence the catalytic properties and behaviour of the fly ash. For instance, Fe_2O_3 and TiO_2 can enhance catalytic activities, while the alkali and alkaline earth metals (MgO, CaO, Na_2O, K_2O) can impact the catalytic efficiency and stability under various reaction conditions.

SEM of Fly Ash

Figure 1 displays the scanning electron microscope (SEM) image of the fly ash, revealing that the ash possesses an irregular shape and a porous texture.

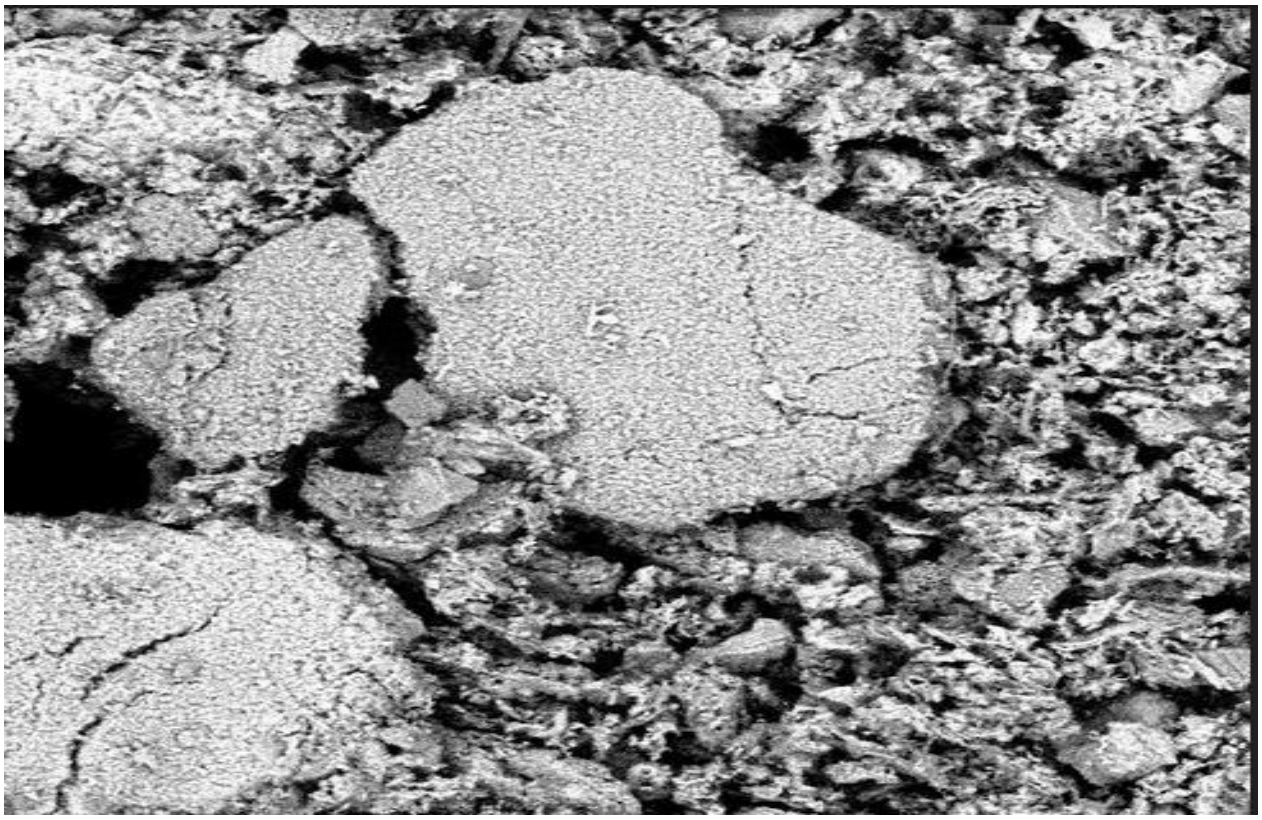

Figure 1: SEM of Fly Ash (Magnified ***1500X****)*

Percentage of Biodiesel Yield

The data presented in the table 2 outlines the relationship between the amount of catalyst used (in weight percentage) and the corresponding biodiesel yield achieved. Notably, as the catalyst concentration increases from 0.00 wt% to 0.30 wt%, there is a significant rise in biodiesel yield, peaking at 96.11% when 0.30 wt% of catalyst is utilized. This indicates that the catalyst is playing a crucial role in enhancing the transesterification process, which is essential for converting oil into biodiesel.

Table 2: Percentage of biodiesel Yield

Amount of catalyst use (wt%)	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
Percentage of biodiesel yield (%)	68.15	81.93	84.23	96.11	73.62	64.01	60.97	54.26	49.82	43.39	40.10

However, beyond the optimal concentration of 0.30 wt%, a noticeable decrease in biodiesel yield occurs as the catalyst concentration continues to rise, with yields plummeting to 40.10% at 1.00 wt%. This decline can be attributed to several factors. For example, an excessive amount of

catalyst may result in the formation of soap due to the strong intermolecular interactions that generate significant thermodynamic forces. This soap formation can impede the separation of biodiesel from glycerol, ultimately lowering the overall yield [31]. Furthermore, the increased viscosity of the reaction mixture at higher catalyst levels can hinder mass transfer and reaction kinetics, further complicating the biodiesel production process.

Table 3: Pour Point, Flash Point, and Fire Point

S/No	Sample	Pour point (^{O}C)	Flash point (^{O}C)	Fire Point (^{O}C)
1	Crude rapeseed Oil	20	195	146
2	Purified rapeseed Oil	15	189	137
3	Trans – esterified rapeseed Oil	10	167	128
5	Trans - esterified (0.1w% FA)	9	158	120
7	Trans - esterified (0.2w% FA)	8	151	114
9	Trans - esterified (0.3w% FA)	7	146	109
10	Trans - esterified (0.4w% FA)	11	172	126
11	Trans - esterified (0.5w% FA)	12	176	133
12	Trans - esterified (0.6w% FA)	14	179	138
13	Trans - esterified (0.7w% FA)	15	182	143
14	Trans - esterified (0.8w% FA)	16	184	150
15	Trans - esterified (1.0w% FA)	17	188	155
16	Trans - esterified (0.9w% FA)	19	190	161
17	Biodiesel standard	-15 to 10	100 to 170	>130
18	Diesel standard	-15 to 5	60 to 80	60 to 80

Pour Point

The pour point is defined as the lowest temperature at which a fuel sample remains fluid when its container is tilted. The temperature at which the sample ceases to flow for approximately five seconds is recorded as its pour point. For the trans-esterified oil with the addition of 0.3 wt% catalyst, the pour point was observed at 7°C (as shown in Table 3), which falls within the acceptable biodiesel standard range of -15°C to 10°C. Oxidation of biodiesel and its blends can degrade fuel quality by increasing the acid number, viscosity, and pour point [22]. Therefore,

higher oxidative stability prolongs the storage life of biodiesel blends without compromising engine performance.

Lee et al. [24] suggested that the presence of monoglycerides may influence the pour point, although this was not observed in the results. Additionally, the cis double bond in the erucic acid of rapeseed oil was found to hinder a significant reduction in the pour point of esters. The nature of the fatty acid chains in the original oil also plays a role in determining the pour point.

During the biodiesel synthesis process, an excess of sodium hydroxide was used to ensure complete conversion, requiring the biodiesel to be washed to remove the excess catalyst. Water traces in the oil, along with the excess lye, likely contributed to saponification. The experiments demonstrated that waste rapeseed oil can be effectively used for biodiesel production, provided it is properly filtered and heated to eliminate impurities and water. Removing water is critical as its presence can hinder the transesterification reaction and lead to soap formation, which can significantly reduce process efficiency.

Flash Point

The flash point of biodiesel is the temperature at which the fuel forms a vapor that ignites when exposed to a spark or flame, and this is closely linked to the amount of residual methanol present. Flash point is a critical property that can be correlated with the composition of biodiesel. Specifically, it is influenced by the level of unconverted triacylglycerides or a low concentration of mono – alkyl esters. A higher flash point ensures greater safety in fuel handling and storage, with ASTM D93 specifying a minimum flash point of 130°C. For instance, rapeseed oil biodiesel has a flash point of 146°C (as shown in Table 3), which is higher than that of conventional diesel fuel. This makes biodiesel safer than fossil diesel due to its higher flash point.

Flash point is a key parameter for assessing biodiesel safety during handling, transport, and storage. Additionally, the presence of residual alcohol in biodiesel lowers the flash point, making it a useful measure for monitoring biofuel purity [23]. The Initial Boiling Point (IBP) can also indicate biodiesel purity, as contaminants like glycerine – resulting from incomplete separation during transesterification – or solvents from possible adulterations can affect the IBP and boiling point range. Since glycerides have much higher boiling points than biodiesel or diesel, their presence can lead to carbon deposits in the engine, potentially causing durability issues.

Fire Point

Table 3 presents the fire point results for crude rapeseed oil, purified oil, and trans – esterified oil. The fire point decreases as the temperature rises. Specifically, the fire point for crude oil was recorded at 146°C, for purified oil at 137°C, for trans – esterified oil without nanoparticle addition at 128°C, and for trans – esterified nanofluid with 0.3 wt% fly ash (FA) at 109°C. The lowest fire point was observed with the addition of 0.3 wt% FA. This reduction in fire point values for biodiesel can be attributed to a decrease in the content of saturated fatty acid alkyl esters, as

unsaturated fatty acid alkyl esters tend to have lower melting points than their saturated counterparts.

The addition of nanoparticles to biodiesel also reduces viscosity, density, and flash point, while increasing the oxygen content of the blend. Some studies [11], indicate that nanoparticle additives are favoured due to their low cost and the availability of synthesis equipment. As nanoparticle concentration increases, a corresponding rise in fire point values has been observed, which may be due to the molar mass and long carbon chains of the nanoparticles. Edith [25] suggests that the fatty acid composition of esters and the presence of minor components like monoglycerides and steryl glycosides also contribute to an increase in fire point values.

CONCLUSION

This research investigated the effects of fly ash nanoparticles as heterogeneous catalysts for biodiesel production from rapeseed oil. The physical and chemical properties of the fly ash nanoparticles were analysed using X-ray fluorescence (XRF) and scanning electron microscopy (SEM), revealing that the fly ash is porous with silica as its main component. Optimal results were achieved for the pour point, fire point, and flash point, with values of 7°C, 146°C, and 109°C respectively, at 0.3 wt% fly ash nanoparticle addition. It was found that even a small amount of 0.3 wt% fly ash could significantly enhance the physical properties of biodiesel. This improvement is attributed to the reduction in saturated fatty acid alkyl esters, as unsaturated fatty acid alkyl esters have lower melting points. The addition of nanoparticles lowered the pour point, flash point, and fire point of the biodiesel, while increasing the oxygen content of the blend. Nanoparticle additives are often used in biodiesel production due to their low cost and the ease of synthesis, as supported by other studies.

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