

Green Nanocatalysts From Biomass For Sustainable Biodiesel Production From Used Cooking Oil

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ABSTRACT

This study presents the development of an in-house sustainable nanocatalyst derived from rice husk and sugarcane bagasse for biodiesel production from used cooking oil. The esterification and transesterification processes were carried out to convert triglycerides in the used cooking oil into fatty acid methyl ester (FAME). The biocomposite nanocatalyst produced had a particle size (D90) of 5.42 nm. The results showed that the highest biodiesel conversion yield achieved was 97.7% under optimal operating parameters: a methanol-to-oil ratio (MTOR) of 12:1, a catalyst dosage of 6%, a temperature of 65°C, and a reaction time of 75 minutes. This catalyst demonstrated a higher conversion yield compared to similar green catalysts. Furthermore, the biodiesel quality conformed to the Indonesian National Standard SNI 7182:2005.

Keywords: biodiesel, nano-catalyst, rice husk, sugarcane bagasse, used cooking oil

INTRODUCTION

The combustion of fossil fuels has the potential to harm human health and cause environmental damage (Madziel et al., 2020). This issue underscores the urgent need for clean and sustainable alternative energy sources. Biodiesel has emerged as a promising medium- to long-term solution to replace fossil fuels like diesel. Research by (Alhikami et al., 2022) highlights several advantages of biodiesel, including its high flash point, high cetane number, low CO₂ emissions, and sulfur-free nature. Additionally, biodiesel can be used in diesel engines without modification (Riyadi et al., 2023), making it an attractive alternative to traditional fossil fuels.

Biodiesel is produced through transesterification, which involves mixing vegetable oils or animal fats with alcohol or methanol. Catalysts are often used to enhance the efficiency of this process, with homogeneous catalysts such as HCl, H₂SO₄, and NaOH being popular choices due to their high activity and affordability (Changmai et al., 2020). However, homogeneous catalysts have several drawbacks, including corrosiveness, environmental pollution, and a lack of reusability (Mukhtar et al., 2022).

To address these issues, research has shifted toward solid heterogeneous catalysts. Studies have investigated solid catalysts derived from materials such as CaO from animal bone waste (Hussain et al., 2021), zeolite (Alismaeel et al., 2022), and agricultural waste like rice husk (Khan et al., 2021) and sugarcane bagasse (Basumatary et al.,

2021). Nanocatalysts, with particle sizes on the nanoscale, have been shown to significantly enhance the transesterification reaction rate for converting vegetable oil into biodiesel (Sulaiman et al., 2024). Biocomposite technology also holds considerable promise; for example, studies by (Sulaiman et al., 2024) and (Aleman-Ramirez et al., 2022). Reported high biodiesel yields using biocomposite catalysts. Moreover, Mohamed et al. (2020) investigated the use of the RS-SO₃H catalyst, derived from rice husk through a sulfonation mechanism, for converting waste cooking oil into biodiesel. The resulting FAME achieved a high conversion rate of 97.71%. Additionally, other studies have reported the use of waste cooking oil as a feedstock for biodiesel production using green heterogeneous catalysts (Basumatary et al., 2021; Lin et al., 2020; Sahu, 2021)

Agricultural waste, such as rice husk and sugarcane bagasse, is rich in valuable minerals after calcination at moderate temperatures (Jittin et al., 2021). Rice husk, for instance, contains silica, which can enhance catalytic activity (Sulaiman et al., 2024). This study introduces an innovative approach by utilizing a biocomposite nanocatalyst made from a combination of rice husk and sugarcane bagasse to improve the efficiency of biodiesel production. The biodiesel produced was also tested for density, viscosity, and flash point to ensure compliance with the Indonesian National Standard for biodiesel (SNI 7182:2005).

METHOD

2.1 Experimental materials

The materials used in this research include rice husk waste and sugarcane bagasse sourced from local farms, methanol, KOH, distilled water, and H₂SO₄ (sulfuric acid) purchased from a local chemical store, as well as used cooking oil obtained from household waste.

The esterification, calcination, and transesterification reactions were conducted using the following equipment: a magnetic stirrer and hotplate, a thermometer, a three-necked flask with a condenser, a furnace, and an oven for the calcination process, measuring cylinders, beakers, separating funnels, spatulas, filter paper, and a desiccator. For catalyst and mineral content characterization, particle size analysis (PSA), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) were performed. Biodiesel testing included density, viscosity, flash point, and acidity evaluations.

2.2. Experimental procedures

To reduce the free fatty acid content of used cooking oil, the esterification process was conducted with a

methanol-to-oil ratio (MTOR) of 1:10, 4% sulfuric acid, at a temperature of 65°C for 75 minutes, based on the optimum esterification conditions from Farooq et al. (2018). Figure 1 illustrates the esterification process conducted in this study. The subsequent transesterification process, aimed at converting triglycerides in waste cooking oil into fatty acid methyl esters, was carried out using a green nanocatalyst made from rice husk and sugarcane bagasse. Figure 2 depicts the experimental setup for the transesterification process. Initially, the biomass was milled to a 200-mesh size and subjected to a calcination process at 500°C for 4 hours. The rice husk and sugarcane bagasse were combined to form a biocomposite material. The catalyst was tested using a particle size analyzer (PSA) to determine the particle size. The parameters varied during the transesterification process included methanol-to-oil ratios (MTOR) of 5:1, 9:1, and 12:1; catalyst dosages ranging from 2 to 6 wt.%; and an operating temperature of 65°C for 75 minutes, as outlined in the experimental design shown in Figure 3. Biodiesel yield resulting from the transesterification process was calculated using Equation 1.

$$\text{Biodiesel yields} = \frac{\text{Weight biodiesel (gram)}}{\text{Weight waste cooking (gram)}} \times 100 \quad (1)$$

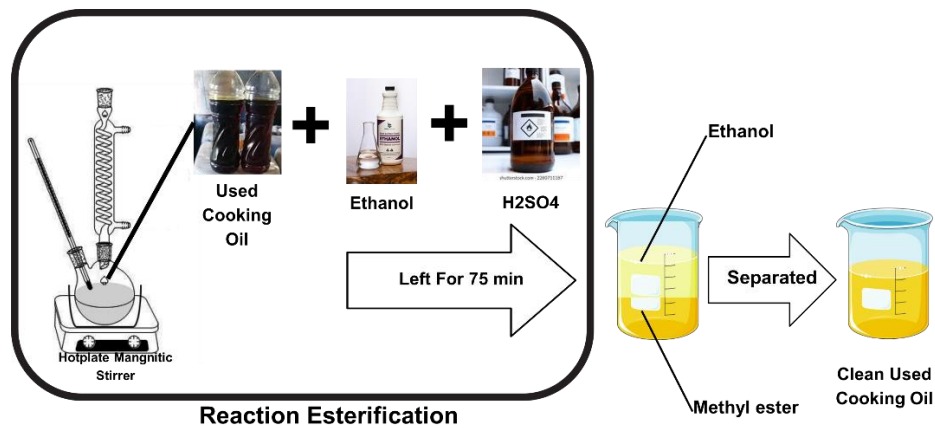


Figure 1. Esterification process to reduce free fatty acids in used cooking oil

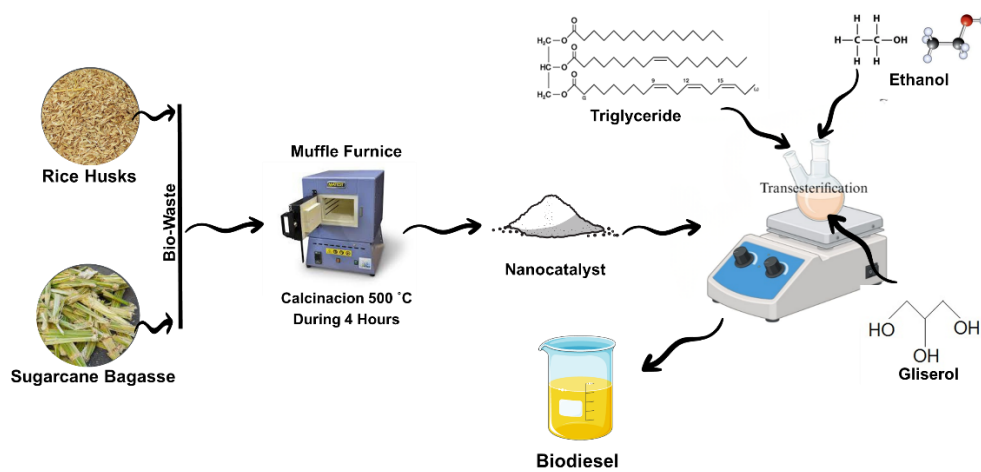


Figure 2. Nano-catalyst production and transesterifications process

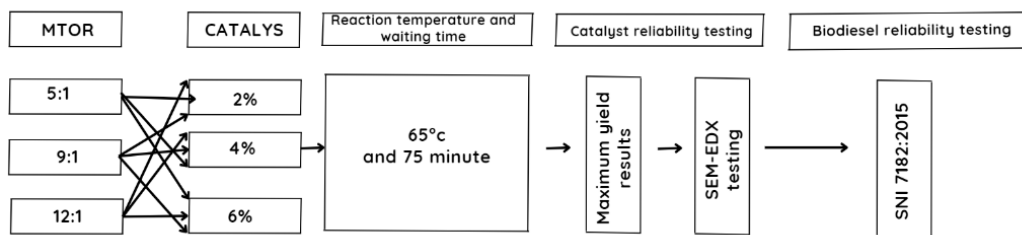


Figure 3. Experimental design of this study

RESULTS AND DISCUSSION

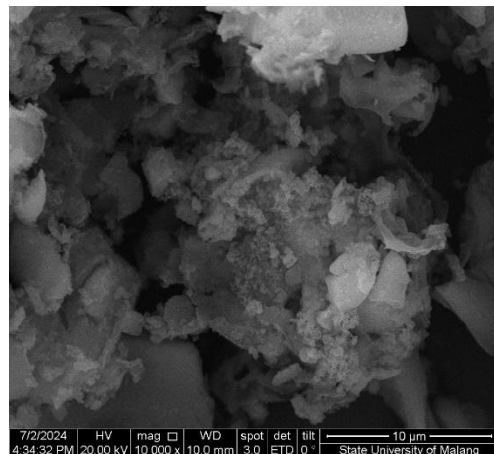
3.1 Surface morphology of nano-catalyst

The surface morphology and elemental compositions of the nanocatalyst were analyzed at a

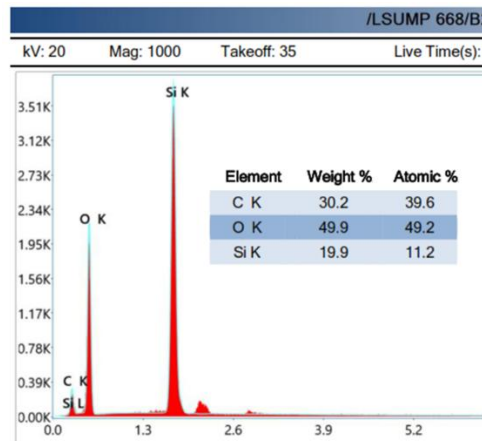
magnification of 10,000x, as shown in Figure 4. According to the SEM images, sugarcane bagasse exhibited a surface structure similar to that of rice husk. The elemental composition of both materials was comparable, with rice husk containing a slightly

higher silica (Si) content than sugarcane bagasse. Notably, silica is the primary element contributing to the transesterification process and has

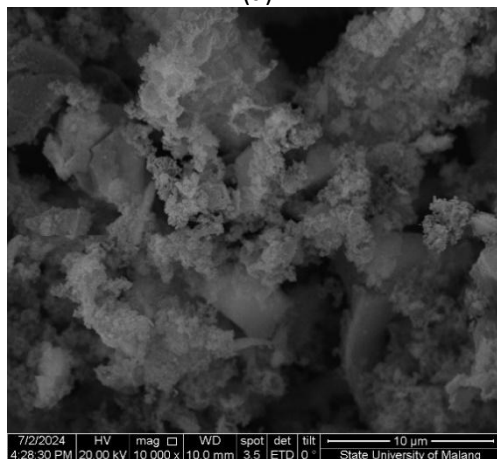
been shown to enhance the conversion of triglycerides into fatty acid methyl esters (FAME) (Sahu, 2021)



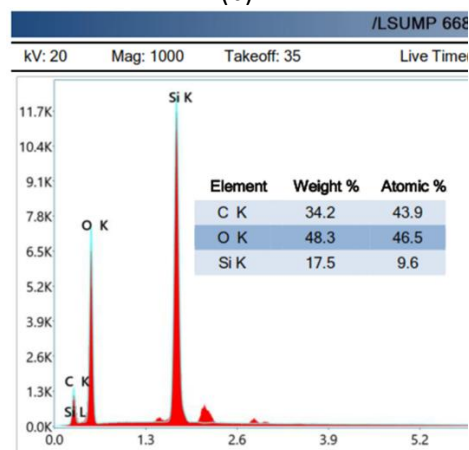
(a)



(b)



(c)



(d)

Figure 4. SEM images of rice husk (a), sugarcane bagasse (c), and EDX of rice husk (b), sugarcane bagasse (d).

3.2 Particle size analysis of nano-catalyst

Particle size analysis was conducted using the dynamic light scattering method to quantify the particle size at the nanoscale. This measurement was crucial for assessing the size of the catalyst. Notably, smaller catalyst particles increase the surface area,

which helps accelerate the reaction process during transesterification. It was observed that rice husk had a particle size range (D10–D90) of 2.08–5.79 nm, while sugarcane bagasse had a particle size range (D10–D90) of 2.22–5.42 nm. Both materials exhibited similar particle sizes.

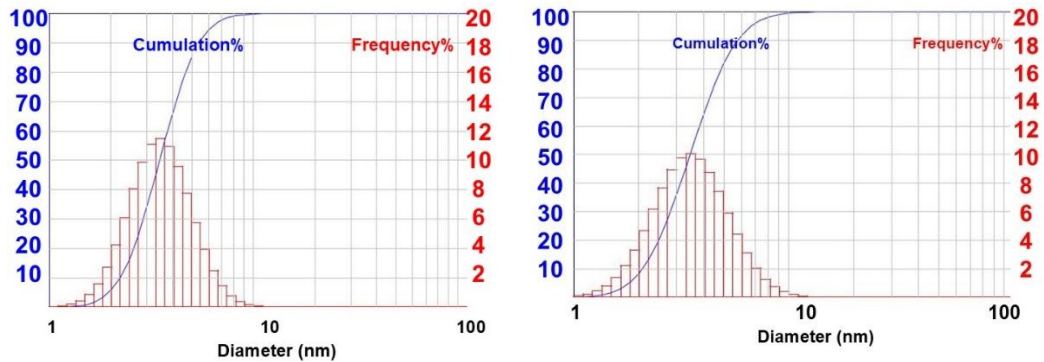


Figure 5. Particle size analysis of rice husk (a), and sugarcane bagasse (b).

3.3 Biodiesel yield

Table 1 presents the results of the transesterification process, which converts used cooking oil into fatty acid methyl esters (FAME) using a biocomposite nanocatalyst derived from rice husk and sugarcane bagasse. According to the SNI 7182:2005 national biodiesel standard, the acceptable density range for biodiesel is 0.850–0.890 g/cm³. The results indicate that three of the samples meet this standard at an MTOR of 12:1 across all catalyst dosage variants.

Moreover, the viscosity and free fatty acid (FFA) content of biodiesel products also conform to the SNI 7182:2005 standard, as summarized in Table 2. The biocomposite nanocatalyst achieved a high

biodiesel yield, reaching 97.7%. Additionally, the flash point and calorific value of biodiesel products comply with the SNI standard.

It is noteworthy that a higher methanol-to-oil ratio (MTOR) improves the quality of biodiesel. As shown in Table 1, an MTOR of 12:1 produced biodiesel with superior physical properties compared to lower ratios. The lowest biodiesel conversion was observed at an MTOR of 5:1 with a catalyst dosage of 2%. Furthermore, increasing the catalyst dosage produced biodiesel from used cooking oil more effectively. For example, at an MTOR of 12:1, increasing the catalyst dosage from 2% to 6% resulted in a yield increase from 95% to 97%.

Table 1. Physical properties of biodiesel at different parameters.

MTOR	Catalyst (%)	Yield (%)	Density g/cm ³	Viscosity (cSt)	FFA (%)
5:1	2%	64,9	0,809	7.63	0.26
5:1	4%	81,2	0,869	6.93	0.30
5:1	6%	81,7	0,811	6.14	0.17
9:1	2%	82,7	0,827	6.7	0.27
9:1	4%	93,1	0,847	6.81	0.22
9:1	6%	91,9	0,840	6.66	0.21
12:1	2%	95,5	0,851	8.81	0.16
12:1	4%	91,7	0,850	8.61	0.26
12:1	6%	97,7	0,856	8.38	0.23

Table 2. Properties of the highest biodiesel yield.

No.	Catalyst (wt)	Biodiesel yield (%)	Flashpoint (°C)	HHV (cal/g)
1.	6%	97,7%	127,8°C	10121.04208

3.4. Comparison study

The results of utilizing a bio composite nanocatalyst in this study were compared with findings from other literature, as tabulated in Table 3. The present work demonstrated comparable high biodiesel conversion rates relative to other catalysts. For example, a study by Sahu (Sahu, 2021) using rice husk alone achieved a biodiesel conversion of approximately 9

3.70%. Similarly, (Basumatary et al., 2021) A conversion rate of 92.84% was reported for sugarcane bagasse as a heterogeneous catalyst. In contrast, combining these two waste biomass materials, coupled with the reduced particle size of the catalyst, increased the biodiesel yield to 97.7%. This study confirms the superiority of combining rice husk and sugarcane bagasse into a single bio composite catalyst with nanoscale particle sizes, resulting in enhanced biodiesel production efficiency.

Table 3. Comparison study of different catalysts used for biodiesel production from used cooking oil

No	Authors	Type of catalyst	Catalyst dosage (wt.%)	Reaction temperature (°C)	Reaction time (hours)	MTOR	Yields (%)
1.	Lin et al. (2020)	Waste chicken eggshell	6	65	3	9:1	87.30
2.	Basumatary et al. (2021)	Sugarcane bagasse	10	65	4,75	9:1	92.84
3.	Sahu (2021)	Waste rice husk	3,5	65	2,5	15:1	93.70
4.	Parandi et al. (2022)	Lipase enzyme	5	40	30	4:1	96.00
5.	This work	Bio-composite rice husk and sugarcane bagasse	6	65	1.25	12:1	97.70

CONCLUSION

This paper investigated the use of a biocomposite nanocatalyst derived from rice husk and sugarcane bagasse as a heterogeneous catalyst for biodiesel production from used cooking oil. The oil conversion

process involved esterification and transesterification reactions using the nanocatalyst. The results showed that the highest biodiesel conversion achieved was 97.7%, with the quality of the biodiesel conforming to the SNI 7182:2005 national standard. A higher methanol-to-oil ratio (MTOR)

of 12:1 improved biodiesel yield and enhanced the physical properties, aligning them more closely with the national standard. Additionally, increasing the catalyst dosage led to a further 2% increase in biodiesel conversion. This study successfully demonstrated the production of biodiesel using a green nanocatalyst while confirming that the biodiesel met the quality requirements of the SNI 7182:2005 standard

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