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Utilization of waste banana peels as heterogeneous catalysts in room-temperature biodiesel production using a homogenizer†

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Banana peels as agro-waste residues contain potassium oxide as the main component after calcination. The calcined waste banana peels (WBPs) successfully transesterified palm oil to biodiesel at room temperature using a homogenizer. The catalyst was characterized by TGA, SEM, XRD and XRF. The catalytic activity of calcined WBPs was determined using parameters of the molar ratio of palm oil to methanol, catalyst weight, reaction time and rotational speed of the homogenizer. The highest biodiesel conversion of $97.7 \pm 0.6\%$ was achieved with a molar ratio of 1 : 15, catalyst weight of 7 wt%, reaction time of 30 min and rotational speed of 6000 rpm. Unfortunately, the calcined WBP cannot be reused unless some fresh catalyst is added to defend its catalytic activity, as the concentration of K_2O decreases after the reaction. However, the catalyst showed better performance as the transesterification reaction could be carried out at room temperature in a short reaction time using a homogenizer compared with other methods.

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1. Introduction

Regardless of some advantages of homogeneous catalysts including their high catalytic activity in biodiesel production, the process requires neutralization and purification of products.^{1,2} These post-production processes commonly use an excessive volume of water, which therefore raises another problem regarding wastewater treatment before release to the environment. The volume of water required to wash 1 L of biodiesel products is 3–10 L.³ Even though the homogeneous catalyst consumes only 1% of the total biodiesel production cost,⁴ those additional steps had increased the overall cost. Hence, it is reducing biodiesel competitiveness in the fuel market against petro-diesel. Other disadvantages of using a homogeneous catalyst include non-reusability and requirement of refined oil with free fatty acid content below 2%, which have also limited the utilization.^{5,6}

To overcome the disadvantages of homogeneous catalysts, heterogeneous substances are used as catalysts. Currently, many solid base or acid catalysts are developed either as a single compound or in combination with other compounds to increase their activity.⁷ Notwithstanding the ability of the heterogeneous catalyst to recover and recycle, its catalytic activity remained lower than that of the homogeneous catalyst. Bitire *et al.* (2021) concluded that KOH has better catalytic activity than that of

calcined chicken bone in the transesterification of parsley seed oil.⁸ This is attributable to a different phase of heterogeneous substance with methanol and oil, which limited mass transfer and hence resulted in a lower reaction rate.⁵ However, presently, some solid catalysts, particularly which contain potassium element, show a similar catalytic activity to homogeneous base catalysts.⁹ The waste of *Brassica nigra* plant which contains 56.13 wt% potassium was used as a catalyst in the transesterification of soybean oil and a biodiesel yield of 98.78% was obtained in a reaction time of 25 min at 65 °C.¹⁰ The result is comparable when sodium hydroxide was used as a catalyst.^{11,12} This heterogeneous catalyst emerged abundantly in agricultural wastes such as banana peels,¹³ banana peduncles,¹⁴ tucuma peel (*Astrocaryum aculeatum* Meyer),¹⁵ walnut shell,¹⁶ coconut husk,¹⁷ palm bunch ash,^{2,18–20} and passion fruit peel.²¹

Furthermore, the agricultural waste biomass-derived catalyst could catalyse the transesterification reaction at room temperature. The calcined waste of passion fruit peels showed excellent performance in the transesterification of palm oil at room temperature. The biodiesel conversion of $95.4 \pm 2.8\%$ was achieved in a reaction time of 30 min.²¹ The transesterification reaction time could be shortest when using a reaction-intensified device such as a microwave and homogenizer. Falowo *et al.* (2019) calcined the husk of an elephant-ear tree pod at 700 °C for 4 h to form a solid catalyst that contains 50.01% of potassium element.²² The heterogeneous catalyst showed higher catalytic activity with a biodiesel yield of $98.77 \pm 0.16\%$ achieved in 5.88 min under microwave irradiation.²² Our previous work has successfully demonstrated that palm bunch ash (containing 35.9% K_2O) could catalyse palm oil to

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biodiesel using a homogenizer. The biodiesel conversion of 98.9% was achieved under operational parameters of a homogenizer at a speed of 4000 rpm and a reaction time of 10 min.²

The objectives of this research are to determine the performance of WBPs (*Musa paradisiaca* var. *sapientum*) as heterogeneous catalysts for biodiesel production from palm oil using a homogenizer. Banana peels are known to contain a high amount of potassium element,^{23,24} and hence, have the potential to be used as catalysts. Banana is very abundant in Indonesia with the production amounting to 8.74 million tons in 2021.²⁵ Banana fruit consists of 40% peels.²⁶ Therefore, there are 3.5 million tons of banana peels and their utilization remains limited as a fertilizer. Homogenizer equipment has been proven to facilitate biodiesel production at atmospheric temperature and pressure.²⁷ However, to date, the utilization of calcined WBPs as solid catalysts using a homogenizer has not been studied. The effects of some factors such as the molar ratio of palm oil to methanol, catalyst weight, reaction time and rotational speed on the biodiesel conversion and yield were investigated. Furthermore, the reusability and leaching study of the catalyst was also determined.

2. Experimental

2.1 Materials

The palm oil was purchased from a local market. The fatty acid profile of palm oil is dominated by palmitic acid (36.86%) and oleic acid (46.03%). The total saturated fatty acid is 42.07%, monounsaturated fatty acid is 46.36% and polyunsaturated fatty acid is 11.57%. All the chemicals used were purchased from a local distributor and used as received without further purification.

2.2 Catalyst preparation and characterization

The WBP was collected from a banana flour plant in Yogyakarta, Indonesia, washed several times, dried in an oven at 110 °C overnight and then crushed and sieved using a 100 mesh sieve. The WBP powder was calcined in a furnace at 600 °C for 2 hours. The calcined WBP was characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray fluorescence (XRF). The TGA thermogram was recorded using a Shimadzu DTG-60, while XRD and XRF patterns were acquired using a Shimadzu XRD-7000 and a Rigaku Supermini-200, respectively. The surface morphology of the calcined WBP was observed using a SEM equipped with a JEOL JSM-6510LA energy-dispersive X-ray (EDX) spectrometer.

2.3 Biodiesel production

The transesterification reaction was carried out in a 500 mL homogenizer vessel. The homogenizer apparatus consists of a rotor-stator (diameter of 25 and 35 mm), and it was operated at room temperature. The operating parameters of the homogenizer were varied in the range of 3000–7000 rpm with an increment of 1000 rpm for rotational speed, reaction times of 5, 10, 20, 30 and 40 min, molar ratios of palm olein to methanol of 1 : 9 to 1 : 21 and catalyst weights of 5% to 15% based on oil. 80 mL of palm olein, and prescribed amounts of methanol and catalyst were dispersed in a homogenizer vessel with the

assigned rotational speed and reaction time. After the reaction, biodiesel and the leftover methanol and catalyst were separated by centrifugation at 7000 rpm for 10 min. Three layers were formed after centrifugation. The upper layer was biodiesel, followed by the mixture of methanol and glycerol, and the WBP catalyst. The biodiesel product was collected and stored in a desiccator for yield and conversion analysis.

2.4 Biodiesel conversion determination and yield calculation

The biodiesel conversion was determined by gas chromatography (GC) analysis following the procedure reported in previously published studies.^{2,21,28} The biodiesel product was weighted (w) and the aliquot was added with methyl heptadecanoate as the internal standard. Then, 1 μ L of the sample was injected into a GC Shimadzu type 2010 equipped with a capillary column and flame ionization detector with helium as the carrier gas. The temperature of the injection port and flame ionization detector was set at 260 °C and that of the column oven at 90 °C. The biodiesel conversion (C) was calculated based on the difference in the peak area of all fatty acid methyl ester ($\sum A$) and the internal standard (A_s) multiplied by the concentration (C_s) and volume (V_s) of internal standard and divided by the mass of the sample (m), as shown in eqn (1). Further, the mass of biodiesel was calculated using eqn (2). The biodiesel yield in percentage was achieved by dividing the mass of biodiesel by the mass of palm oil used as follows (eqn (3)):

$$C = \frac{\sum A - A_s}{A_s} \times \frac{C_s V_s}{m} \times 100\% \quad (1)$$

$$\text{Mass of methyl esters} = C \times w \quad (2)$$

$$\text{Yield} = \frac{\text{mass of methyl esters}}{\text{mass of palm oil}} \times 100\% \quad (3)$$

2.5 Leaching and reusability of the calcined WBP catalyst

The calcined WBP contains some active species that can be leached into the reaction medium causing contamination of the biodiesel product and could further decrease the catalytic activity. The concentration of potassium as the main element in the calcined WBP was detected by the EDS analysis before and after the dispersion. Hence, the leaching test of the catalyst was conducted under a reaction condition of 4 gram catalyst homogenized in 80 mL of methanol at a rotational speed of 4000 rpm for 30 min reaction time. Upon completion, the catalyst was filtered and dried in an oven at 40 °C overnight and stored in a desiccator for EDS analysis. For the reusability study, the catalyst separated from the reaction mixture through filtration was directly used for the subsequent cycle and the biodiesel product was collected for GC analysis.

2.6 Statistical analysis

The experiment data were obtained from 3 replications, and are presented as means \pm standard deviation of the mean. One-way

analysis of variance (ANOVA) was performed to identify statistically significant differences between parameters using Statistica v13. Tukey's post-hoc test ($P < 0.05$) was used to determine the significant difference between specific means.

3. Results and discussion

3.1 Catalyst characterization

The TGA analysis for the WBP is illustrated in Fig. 1A. The weight losses obtained from the TGA measurement curve showed three stages. The first one is related to the water evaporation of the WBP at 100–200 °C followed by the decomposition of the organic compound contained in the WBP at 200–400 °C.²¹ The final stage occurred at 400–600 °C due to the decomposition of carbonaceous compounds into carbon monoxide and carbon dioxide-producing metal oxide compounds.¹⁶ Furthermore, above 600 °C, the thermogram showed an insignificant weight loss; hence, that temperature was set as the calcination temperature. The result is similar to that of Fan *et al.*'s (2019) study, which reported that metal oxide compounds were composed after calcination at 600 °C.¹³ The SEM image of calcined WBP is shown in Fig. 1B. The surface morphology of the catalyst was recorded at 10 μm magnification. The magnified photo displayed an irregular shape and

agglomerated structure with some pores. A similar SEM image was reported in a study by Betiku *et al.* (2016), in which banana peels were calcined at 700 °C for 4 hours.²⁹ Other researchers also notified similar morphology images after the calcination of banana peels at 600 °C for 2 hours.¹³

The XRD pattern of the catalyst is shown in Fig. 1C, which displays some major inorganic compounds contained in the calcined WBP. The diffractogram showed potassium in the form of oxide as the main component followed by SiO_2 , P_2O_5 and CaO . This result was further corroborated by the XRF analysis result. As shown in Fig. 1D, K_2O is the major component present in the calcined WBP. Further, the EDS analysis clarifies the presence of the K_2O element with a concentration of 47.01 wt%. However, this result is considerably lower than that reported by a previous researcher who obtained 65.11 wt% of K_2O .³⁰

3.2 Effect of the molar ratio of palm olein to methanol

An additional mole of methanol above the stoichiometric value is usually required in the transesterification reaction to drive the reaction forward to the biodiesel product.^{2,21} Some biodiesel production studies have observed that optimum biodiesel production occurred using a molar ratio of oil to methanol of 1 : 9.^{2,31,32} Therefore, the effect of the molar ratio of palm olein to methanol was determined using the ratio of 1 : 9 to 1 : 21 with

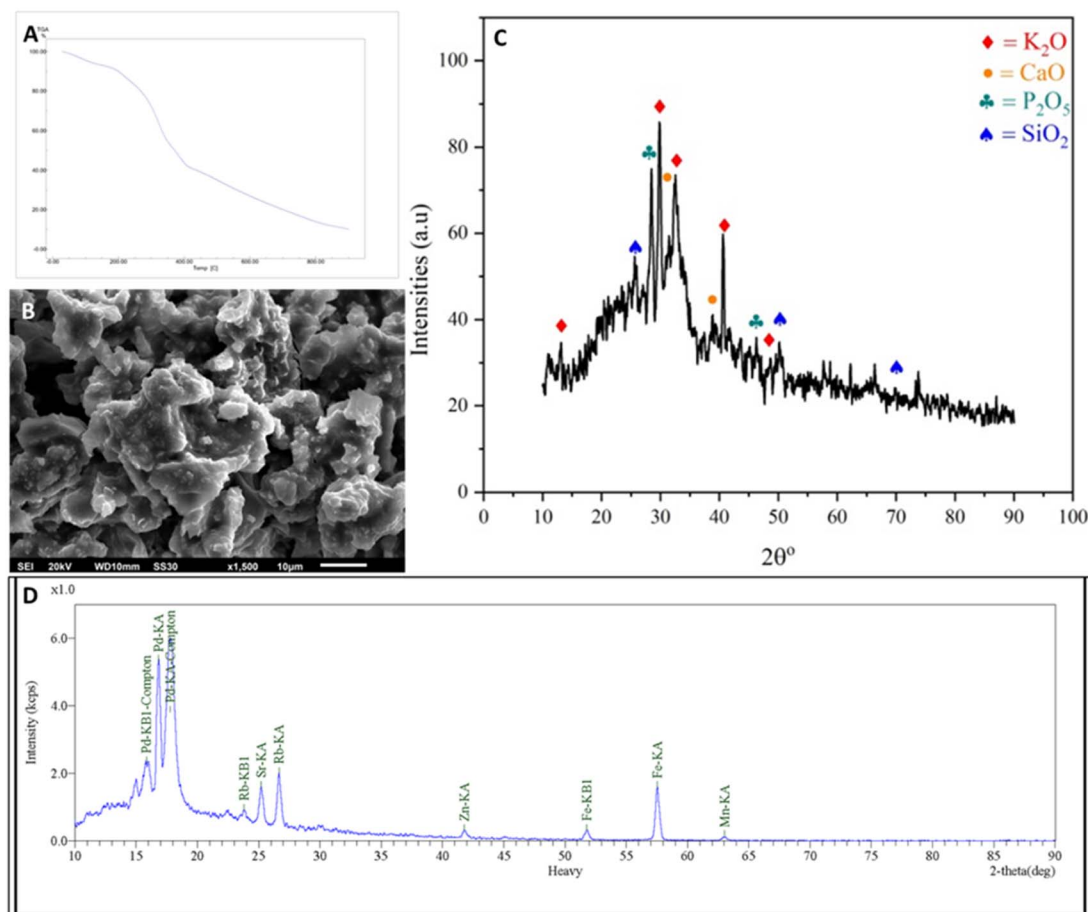


Fig. 1 Calcined WBP characterization: (A) TGA thermogram; (B) SEM image; (C) XRD spectra; and (D) XRF spectra.

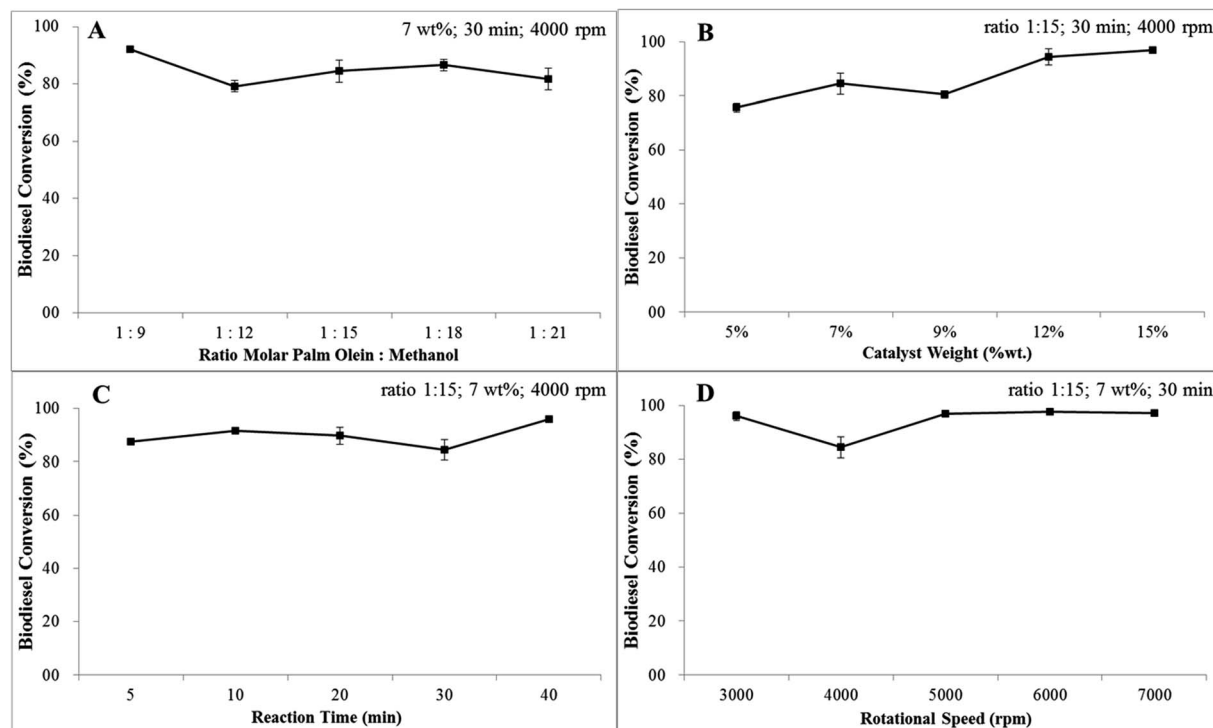


Fig. 2 Effect of (A) molar ratio of palm olein to methanol, (B) catalyst weight, (C) reaction time, and (D) rotational speed on biodiesel conversion.

an increment of 3 molars. The reaction condition set up for this study was a catalyst weight of 7 wt%, a reaction time of 30 min and a rotational speed of 4000 rpm. The average biodiesel

conversion of 85% was achieved with the highest conversion of $92 \pm 0.8\%$ at a molar ratio of 1:9, as shown in Fig. 2A. The maximum biodiesel yield of $85.8 \pm 3.7\%$ (Fig. 3B) was also

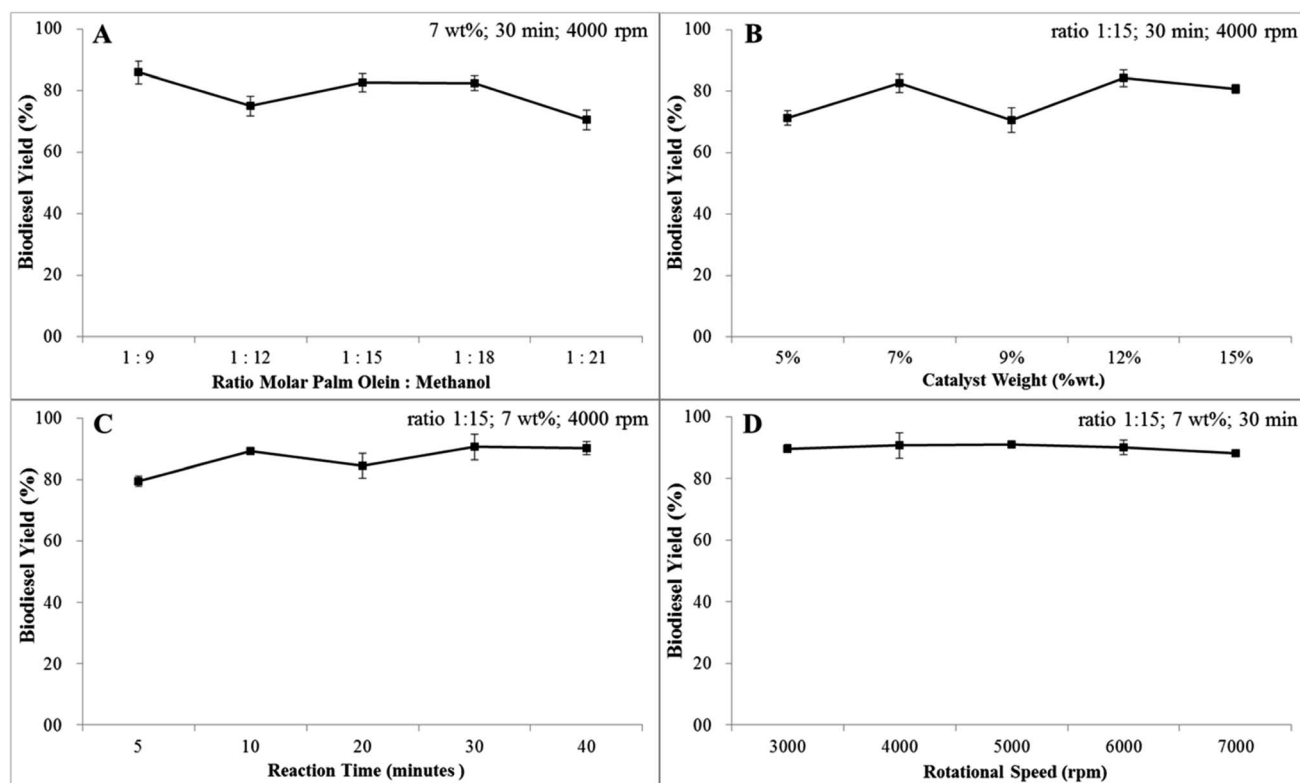


Fig. 3 Effect of (A) molar ratio of palm olein to methanol, (B) catalyst weight, (C) reaction time, and (D) rotational speed on biodiesel yield.

achieved at a molar ratio of 1 : 9. However, this result differs from previous research results, which achieved an optimum biodiesel yield using a molar ratio of 1 : 7.6 in the transesterification of Napoleon's plume seed oil with the WBP.²⁹ In contrast, our earlier study in homogenizer-intensified biodiesel production using palm bunch ash as a catalyst achieved a maximum biodiesel conversion at a molar ratio of 1 : 15,² which is a slightly higher ratio than that obtained in this study. Further, the analysis of variance revealed that the molar ratio of palm oil to methanol has a significant effect both on biodiesel conversion and yield. Tukey's test emphasizes the significance driven by molar ratios of 1 : 9 and 1 : 21 for biodiesel conversion and yield, respectively.

3.3 Effect of the catalyst weight

In the catalytic–transesterification reaction method, the catalyst weight or concentration plays a vital role in biodiesel conversion or yield.³³ Increasing catalyst weight could increase the biodiesel conversion up to the maximum peak before gradually decreasing.²⁸ This is presumably due to the increased viscosity of the reactant mixture, which decreases the active site of the heterogeneous catalyst.^{34,35} Therefore, the catalyst weight was investigated under reaction conditions of a molar ratio of 1 : 15, a reaction time of 30 min and a rotational speed of 4000 rpm. As recorded in Fig. 2B the biodiesel conversion was increased with the increase in catalyst weight reaching the highest conversion of $96.8 \pm$ at 15 wt%. This result is in agreement with the previous findings of researchers who reported a similar pattern.²⁷ Similarly, our result for the utilization of the homogenizer-enhanced transesterification reaction using palm bunch ash showed increasing biodiesel conversion with the increase in catalyst weight (from 88.3% using 5 wt% to 97.8% using 15 wt%).² In contrast, the biodiesel yield (Fig. 3B) did not show a similar pattern. The catalyst weight did not affect the yield with the highest value of 84.3 ± 2.7 achieved at 12 wt%. One-way ANOVA depicted that the catalyst weight has a significant effect on both biodiesel conversion and yield. This significant effect was driven by all the parameters tested based on Tukey's post hoc test.

3.4 Effect of the reaction time

Choosing an appropriate reaction time is necessary to avoid incomplete or backward reactions as transesterification is a reversible reaction. Hence, the homogenizer-facilitated transesterification reaction of palm oil to biodiesel using the calcined WBP as a catalyst was performed in reaction times of 5, 10, 20, 30 and 40 min. To study this parameter, all the reactions were conducted under the reaction condition of a molar ratio of 1 : 15, a catalyst weight of 7 wt% and a rotational speed of 4000 rpm. An average biodiesel conversion of 90% was obtained for all experiments, as shown in Fig. 2C, with the lowest concentration of $84.5 \pm 3.9\%$ achieved at a reaction time of 30 min and the highest concentration of $95.8 \pm 1.1\%$ at a reaction time of 40 min. Equivalently, the biodiesel yield showed a similar pattern with an average yield of 86.8% (Fig. 3C). In contrast to biodiesel conversion, the highest biodiesel yield of

$90.6 \pm 4.2\%$ was achieved at a reaction time of 30 min, while the lowest ($79.5 \pm 1.7\%$) was obtained at a reaction time of 5 min. Previous studies on the transesterification of soybean oil using a homogenizer and CaO as a catalyst³⁶ observed similar results to this study. However, the present result is lower than our previous result obtained using biomass containing potassium element as a catalyst and homogenizer in the transesterification of palm oil.² The significant effects of changing the reaction time on both the biodiesel conversion and yield were detected by ANOVA. Further, using Tukey's post hoc test, we identified that the significance was driven by all parameters tested for biodiesel conversion, while a short reaction time of 5 min significantly affected the biodiesel yield.

3.5 Effect of the rotational speed

The transesterification reaction rate increases with the increase in the mixing speed of the reactant.³⁷ A different phase of oil, methanol and heterogeneous catalyst has to limit diffusion between them, and hence, requires mixing intensity to increase the interaction and mass transfer.³⁸ Accordingly, a molar ratio of palm oil to methanol of 1 : 15, a catalyst weight of 7 wt% and a reaction time of 30 min were chosen for homogenizer-intensified biodiesel production using the calcined WBP as the heterogeneous catalyst with different rotational speeds ranging from 3000 to 7000 rpm (with an increment of 1000 rpm). Biodiesel conversion >95% routinely occurred for all the parameters tested; except for the rotational speed of 4000 rpm (Fig. 2D). This result indicated that high turbulence, provided by the homogenizer, could intensify the intermolecular interaction.^{39,40} The highest biodiesel conversion of $97.7 \pm 0.6\%$ was obtained using a rotational speed of 6000 rpm. Furthermore, Fig. 3D shows a plateau line of biodiesel yield, indicating that increasing rotational speed did not affect the yield. An average yield of 89.8% was achieved with the lowest yield of $88.1 \pm 1.0\%$ obtained at a rotational speed of 7000 rpm and the highest yield of $90.9 \pm 0.7\%$ at 5000 rpm. This result supports the previously reported result obtained using palm bunch ash as a catalyst in homogenizer-intensified biodiesel production at room temperature.² Similarly, other published research studies also reported that increasing rotational speed did not have a significant effect on the biodiesel yield after the maximum yield was achieved.³⁶ They concluded that high rotational speed produces super cavitation, which reduces the intermolecular interaction due to the collapse of cavities.³⁶ Using a single ANOVA, we determined the significant effect of the rotational speed on the biodiesel conversion and yield. The significance was driven by the low

Table 1 Reusability and leaching test of the catalyst

| Cycle | Biodiesel conversion (%) | Concentration of K ₂ O (wt%) |
|-------------|--------------------------|-----------------------------------------|
| Raw/cycle 1 | 97.4 ± 0.2 | 47.01 |
| Cycle 2 | 72.3 ± 1.9 | 17.47 |
| Cycle 3 | 46.1 ± 1.1 | 13.2 |
| Cycle 4 | 16.2 ± 0.7 | — |
| Cycle 5 | 6.9 ± 0.5 | — |

Table 2 Summary of banana bio-based catalyzed biodiesel production

| Banana parts/species | Potassium concentration (wt%) | Calcined temperature (°C) and time (h) | Reaction condition | Biodiesel conversion (%) | Ref. |
|-------------------------------------|-------------------------------|----------------------------------------|-------------------------------------|--------------------------|------------|
| Pseudotem/ <i>Musa acuminata</i> | 26.2 | 700; 4 | 1 : 14.9; 5.9 wt%; 65 °C; 178.1 min | 98 | 24 |
| Peduncle/ <i>Musa</i> spp. | 68.37 | 700; 4 | 1 : 9.2; 1.99 wt%; 65 °C; 60 min | 98.7 | 45 |
| Trunk/ <i>Musa acuminata</i> | 23.45 | NA | 1 : 6; 7 wt%; RT; 360 min | 98.39 | 42 |
| Peel/ <i>Musa paradisiaca</i> | 37.23 | 700; 4 | 1 : 9; 7 wt%; 65 °C; 120 min | 76.87 | 43 |
| Peels/ <i>Musa acuminata</i> Colla | 74.4 | 650; 3 | 1 : 8; 1.7 wt%; 60 °C; 53 min | 98.8 | 41 |
| Peels/ <i>Musa sapientum</i> | 56.22 | 600; 2 | 1 : 15; 4 wt%; 65 °C; 120 min | 98.91 | 46 |
| Peels/— | n.a. | 700; 4 | 1 : 0.8 (v/v); 4 wt%; 65 °C; 65 min | 99.5 | 47 |
| Peels/— | n.a. | 600; 2 | 1 : 15; 1.5 wt%; 65 °C; 60 min | 95.1 | 13 |
| Peels/ <i>Musa balbisiana</i> Colla | 41.37 | 700; 4 | 1 : 9; 2 wt%; 60 °C; 80 min | 96.3 | 48 |
| Peels/ <i>Musa</i> 'Gross Michel' | 99.73 | 700; 4 | 1 : 30; 2.75 wt%; 65 °C; 69.02 min | 98.5 | 29 |
| Peels/ <i>Musa paradisiaca</i> | 47.01 | 600; 2 | 1 : 15; 7 wt%; RT; 30 min | 97.7 | This study |

conversion at a rotational speed of 4000 rpm, while Tukey's post hoc test did not detect the significance for the biodiesel yield.

3.6 Reusability and leaching test of the calcined WBP

To establish the reusability information of the calcined WBP, the reaction condition was set to a molar ratio of 1 : 15, a catalyst weight of 7 wt%, a reaction time of 30 min and a rotational speed of 6000 rpm. Upon completion of each cycle, the remaining catalyst was separated and directly used as a catalyst for the subsequent cycle. As shown in Table 1, the biodiesel conversion gradually decreased in the subsequent cycles. The conversion declined 25% from cycle 1 to cycle 2 and 93% from cycle 1 to cycle 5. This is presumably due to the leaching of the catalyst. Furthermore, to clarify this issue, the leaching test was performed using the EDS analysis to determine the concentration of potassium oxide. The concentration of K₂O sharply decreased amounting to 62.8% after the first cycle, and it continued to decrease for the next cycle. Hydrolysis of K₂O to form KOH was presumably the reason that either biodiesel or potassium oxide concentration was reduced.^{2,21,41,42} Vadery *et al.* (2014) demonstrated the transesterification of jatropha oil using the leached-out catalyst achieving 96.1% biodiesel conversion.¹⁷ Therefore, the calcined WBP catalyst cannot be re-used unless it is refreshed by adding some fresh catalysts to maintain its catalytic activity.

3.7 Comparison of biodiesel production using the banana residue-derived bio-based catalyst

Most of the studies on the utilization of banana residue as a heterogeneous catalyst used peels, and they are summarized in Table 2. In all the cases of calcined waste banana residue-catalyzed transesterification reactions, the biodiesel conversion routinely reached >95% except for a study by Ma'arof *et al.* (2021) who obtained a conversion of 76.87%.⁴³ All the banana residues contain potassium element as the main component. However, the concentration of potassium did not significantly affect the biodiesel conversion. The banana pseudostem, which contains the lowest potassium concentration²⁴ as indicated in Table 2, showed a high biodiesel conversion, which is comparable with that of the banana peels,²⁹ which contain the

highest concentration of potassium ion. The reaction parameters such as the molar ratio of oil to methanol and catalyst weight do not have a significant effect on biodiesel conversion. The molar ratio used varied from 1 : 6 to 1 : 30 and the catalyst weight ranged from 1.5 to 7 wt%. Interestingly, two studies reported biodiesel production at room temperature. Rajkumari and Rokhum (2020) used a banana trunk that was burnt to ash as a heterogeneous catalyst in the transesterification of soybean oil to biodiesel.⁴² The reaction was conducted at ambient temperature and achieved a biodiesel conversion of 98.39% after 360 min of reaction time. In contrast, this study showed that the calcined WBP could catalyze biodiesel production in a reaction time of 30 min at room temperature. In fact, among all calcined studies that used banana residues as heterogeneous catalysts, a reaction time of 30 min was the shortest while the longest was 360 min. However, this shortest reaction time was achieved using a homogenizer apparatus that provides large turbulence enhancing the mass transfer rate of the reactants.^{2,44}

4. Conclusion

In this investigation, WBPs were calcined and successfully used as heterogeneous catalysts in the homogenizer-facilitated transesterification of palm oil to biodiesel. Potassium oxide was the main element in the calcined WBP with a concentration of 47.01 wt%. The highest biodiesel conversion and yield of 97.7 ± 0.6% and 90.0 ± 2.3% respectively were achieved under reaction conditions of a molar ratio of palm oil to methanol of 1 : 15, a catalyst weight of 7 wt%, a reaction time of 30 min and a rotational speed of 6000 rpm. The reusability and leaching study showed that the addition of a fresh catalyst is necessary to maintain the catalytic activity as the concentration of potassium element is decreased after every reaction cycle. However, this study was conducted at room temperature for a short reaction time compared with other methods that require heating at methanol boiling point and a long reaction time.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 I. M. Atadashi, *Alexandria Eng. J.*, 2015, **54**, 1265–1272.
- 2 E. K. Sitepu, Y. Sembiring, M. Supeno, K. Tarigan, J. Ginting, J. A. Karo-karo and J. B. Tarigan, *S. Afr. J. Chem. Eng.*, 2022, **40**, 240–245.
- 3 H. Bateni, A. Saraeian and C. Able, *Biofuel Res. J.*, 2017, **4**, 668–690.
- 4 F. Harahap, S. Silveira and D. Khatiwada, *Energy*, 2019, **170**, 62–72.
- 5 Y. Zhang, L. Duan and H. Esmaeili, *Biomass Bioenergy*, 2022, **158**, 106356.
- 6 P. R. Yaashikaa, P. S. Kumar and S. Karishma, *Fuel*, 2022, **316**, 123379.
- 7 M. Jayakumar, N. Karmegam, M. P. Gundupalli, K. Bizuneh Gebeyehu, B. Tessema Asfaw, S. W. Chang, B. Ravindran and M. Kumar Awasthi, *Bioresour. Technol.*, 2021, **331**, 125054.
- 8 S. O. Bitire, T.-C. Jen and M. Belaid, *ACS Omega*, 2021, **6**, 25124–25137.
- 9 A. Alagumalai, O. Mahian, F. Hollmann and W. Zhang, *Sci. Total Environ.*, 2021, **768**, 144856.
- 10 B. Nath, B. Das, P. Kalita and S. Basumatary, *J. Cleaner Prod.*, 2019, **239**, 118112.
- 11 G. Vicente, M. Martínez and J. Aracil, *Bioresour. Technol.*, 2004, **92**, 297–305.
- 12 B. Changmai, C. Vanlalveni, A. P. Ingle, R. Bhagat and L. Rokhum, *RSC Adv.*, 2020, **10**, 41625–41679.
- 13 M. Fan, H. Wu, M. Shi, P. Zhang and P. Jiang, *Green Energy Environ.*, 2019, **4**, 322–327.
- 14 M. Balajii and S. Niju, *Energy Convers. Manage.*, 2019, **189**, 118–131.
- 15 I. M. Mendonça, O. A. R. L. Paes, P. J. S. Maia, M. P. Souza, R. A. Almeida, C. C. Silva, S. Duvoisin and F. A. de Freitas, *Renewable Energy*, 2019, **130**, 103–110.
- 16 M. R. Miladinović, M. V. Zdujić, D. N. Veljović, J. B. Krstić, I. B. Banković-Ilić, V. B. Veljković and O. S. Stamenković, *Renewable Energy*, 2020, **147**, 1033–1043.
- 17 V. Vadery, B. N. Narayanan, R. M. Ramakrishnan, S. K. Cherikkallinmel, S. Sugunan, D. P. Narayanan and S. Sasidharan, *Energy*, 2014, **70**, 588–594.
- 18 H. Husin, T. M. Asnawi, A. Firdaus, H. Husaini, I. Ibrahim and F. Hasfita, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2018, **358**, 012008.
- 19 Z. Yaakob, I. S. B. Sukarman, B. Narayanan, S. R. S. Abdullah and M. Ismail, *Bioresour. Technol.*, 2012, **104**, 695–700.
- 20 P.-L. Boey, S. Ganesan, S.-X. Lim, S.-L. Lim, G. P. Maniam and M. Khairuddean, *Energy*, 2011, **36**, 5791–5796.
- 21 J. B. Tarigan, K. Singh, J. S. Sinuraya, M. Supeno, H. Sembiring, K. Tarigan, S. M. Rambe, J. A. Karo-karo and E. K. Sitepu, *ACS Omega*, 2022, **7**, 7885–7892.
- 22 O. A. Falowo, M. I. Oloko-Oba and E. Betiku, *Chem. Eng. Process. Process Intensif.*, 2019, **140**, 157–170.
- 23 E. A. Olatundun, O. O. Borokini and E. Betiku, *Renewable Energy*, 2020, **166**, 163–175.
- 24 S. Niju, A. Janaranjani, R. Nanthini, P. A. Sindhu and M. Balajii, *Biomass Convers. Biorefin.*, 2021, 1805–1818.
- 25 B.-S. Indonesia, *Statistics of Horticultural 2021*, BPS-Statistics Indonesia, Jakarta, 2021.
- 26 J. A. Serna-Jiménez, F. Luna-Lama, Á. Caballero, M. d. I. Á. Martín, A. F. Chica and J. Á. Siles, *Biomass Bioenergy*, 2021, **155**, 106279.
- 27 M. Sánchez-Cantú, M. Morales Téllez, L. M. Pérez-Díaz, R. Zeferino-Díaz, J. C. Hilario-Martínez and J. Sandoval-Ramírez, *Renewable Energy*, 2019, **130**, 174–181.
- 28 J. B. Tarigan, R. Anggraini, R. P. Sembiring, M. Supeno, K. Tarigan, J. Ginting, J. A. Karo-karo and E. K. Sitepu, *RSC Adv.*, 2022, **12**, 2094–2101.
- 29 E. Betiku, A. M. Akintunde and T. V. Ojumu, *Energy*, 2016, **103**, 797–806.
- 30 G. Pathak, D. Das, K. Rajkumari and L. Rokhum, *Green Chem.*, 2018, **20**, 2365–2373.
- 31 R. Kasirajan, *S. Afr. J. Chem. Eng.*, 2021, **37**, 161–166.
- 32 S. X. Tan, S. Lim, H. C. Ong and Y. L. Pang, *Fuel*, 2019, **235**, 886–907.
- 33 Y.-C. Lin, K. T. T. Amesho, C.-E. Chen, P.-C. Cheng and F.-C. Chou, *Sustainable Chem. Pharm.*, 2020, **17**, 100310.
- 34 S. Y. Chua, L. A. P. Periasamy, C. M. H. Goh, Y. H. Tan, N. M. Mubarak, J. Kandedo, M. Khalid, R. Walvekar and E. C. Abdullah, *J. Ind. Eng. Chem.*, 2020, **81**, 41–60.
- 35 W. Xie and L. Zhao, *Energy Convers. Manage.*, 2014, **79**, 34–42.
- 36 S. Joshi, P. R. Gogate, P. F. Moreira and R. Giudici, *Ultrason. Sonochem.*, 2017, **39**, 645–653.
- 37 M. Tabatabaei, M. Aghbashlo, M. Dehghani, H. K. S. Panahi, A. Mollahosseini, M. Hosseini and M. M. Soufiyan, *Prog. Energy Combust. Sci.*, 2019, **74**, 239–303.
- 38 M. A. Bashir, S. Wu, J. Zhu, A. Krosuri, M. U. Khan and R. J. Ndeddy Aka, *Fuel Process. Technol.*, 2022, **227**, 107–120.
- 39 M.-C. Hsiao, S.-S. Hou, J.-Y. Kuo and P.-H. Hsieh, *Energies*, 2018, **11**, 2622.
- 40 V. Vikash, K. D. P. Nigam and V. Kumar, *Chem. Eng. Sci.*, 2021, **232**, 116296.
- 41 I. J. Madai, Y. A. Chande Jande and T. Kivevele, *Adv. Mater. Sci. Eng.*, 2020, **2020**, 1–11.
- 42 K. Rajkumari and L. Rokhum, *Biomass Convers. Biorefin.*, 2020, **10**, 839–848.
- 43 N. A. N. B. Ma'arof, N. Hindryawati, S. N. M. Khazaai, P. Bhuyar, M. H. A. Rahim and G. P. Maniam, *Appl. Nanosci.*, 2021, 871–882.
- 44 M. Kwak, D. Kim, S. Kim, H. Lee and Y. K. Chang, *Renewable Energy*, 2020, **149**, 1395–1405.

- 45 M. Balajii and S. Niju, *Renewable Energy*, 2020, **146**, 2255–2269.
- 46 J. Jitjamnong, C. Thunyaratchatanon, A. Luengnaruemitchai, N. Kongrit, N. Kasetsoomboon, A. Sopajarn, N. Chuaykarn and N. Khantikulanon, *Biomass Convers. Biorefin.*, 2020, 2795–2811.
- 47 V. O. Odude, A. J. Adesina, O. O. Oyetunde, O. O. Adeyemi, N. B. Ishola, A. O. Etim and E. Betiku, *Waste Biomass Valorization*, 2019, **10**, 877–888.
- 48 M. Gohain, A. Devi and D. Deka, *Ind. Crops Prod.*, 2017, **109**, 8–18.