

Waste Passion Fruit Peel as a Heterogeneous Catalyst for Room-Temperature Biodiesel Production

Juliati Br. Tarigan, Krishanjit Singh, Jenita S. Sinuraya, Minto Supeno, Helmina Sembiring, Kerista Tarigan, Siti Masriani Rambe, Justaman A. Karo-karo, and Eko K. Sitepu*



Cite This: *ACS Omega* 2022, 7, 7885–7892



Read Online

ACCESS |



Metrics & More

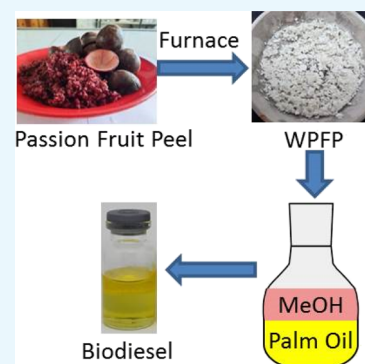


Article Recommendations



Supporting Information

ABSTRACT: A low-cost, green, and highly active catalyst which could transesterify oil under ambient conditions is required to reduce the biodiesel production cost. A novel heterogeneous catalyst derived from the waste agroproduct has been developed from passion fruit peel. The catalytic activity of calcined waste passion fruit peel (WFPF) which mainly contains potassium in the form of chloride and carbonate has been evaluated using factorial design to determine the interaction of molar ratio of oil to methanol, catalyst weight, and reaction time with three different reaction conditions such as 65, 45 °C, and room temperature. The transesterification of palm oil to biodiesel achieved a conversion of >90% for all variables determined at a reaction temperature of 45 and 65 °C, respectively, while a maximum biodiesel conversion of $95.4 \pm 2.8\%$ was obtained at room temperature and a reaction time of 30 min. The addition of certain amounts of the catalyst is required to reuse the catalyst as the leaching study showed the reduction of 22% of catalyst weight. The ability of calcined WFPF to catalyze transesterification at room temperature opens up the possibility to reduce biodiesel production cost.



INTRODUCTION

The competitiveness of biodiesel in the fuel market is quite low due to its higher price. The average prices of biodiesel were 10.2% more expensive than petrodiesel in the United States of America in July 2021.¹ A process model on biodiesel production cost showed that 75–88% of the total cost was used for purchasing the oil/lipid.^{2,3} Investigation on biodiesel production in Indonesia revealed that crude palm oil as input material consumed 85% of the total cost.⁴ The proposed solution through direct transesterification of oil-bearing materials to produce biodiesel could reduce the oil preparation cost.^{5,6} However, this suggested model has not been implemented elsewhere as the current biodiesel production industry platforms did not support it.

Another alternative solution is reducing consumables and energy requirement costs. Even though the catalyst particularly homogeneous base consumed only 1% of the total cost,⁴ the following procedure such as neutralization and purification of the biodiesel increases the production cost and requires a lot of water.^{7,8} To break the problem, the heterogeneous catalyst which is recoverable and recyclable has proved to catalyze the conversion of oil to biodiesel.^{9,10} Moreover, some heterogeneous compounds showed high catalytic activity and their performance is comparable to homogeneous base catalysts.¹¹ For instance, the coconut husk-derived catalyst could produce 97% of biodiesel from jatropha oil at 45 °C in 30 min reaction time.¹² Furthermore, the current biodiesel plant which operates at the boiling point of methanol consumes 9% of

the total cost mainly for electricity and steam.⁴ Therefore, converting the oil under ambient conditions is very desirable as it could reduce the energy input.

Recently, room-temperature biodiesel production using a heterogeneous substance as a catalyst has been developed. Compounds such as CaO, K₂O, CaSiO₃, or Na₂SiO₃ have been introduced to catalyze the transesterification reaction at ambient pressure and temperature with high biodiesel yield.^{13–22} Nanocrystalline CaO successfully converts all the soybean oil to biodiesel at room temperature in a 24 h reaction time.²² Furthermore, the reaction time becomes less using the same compound derived from the waste snail shell which has been previously calcined at 900 °C for 4 h to produce a biodiesel yield of 98% obtained in 7 h.¹⁸ Moreover, the transesterification rate has increased significantly and a completed conversion occurred only in 3 h when using calcined coconut husk which contains potassium in the form of carbonate, chloride, and oxide as a catalyst.¹² Other waste products which mainly contain potassium ions such as mango peel, tucuma peel, and *Brassica nigra* plant have been studied, and the reaction rates were high.^{13,15,16} In fact, the complete

Received: December 1, 2021

Accepted: February 3, 2022

Published: February 23, 2022



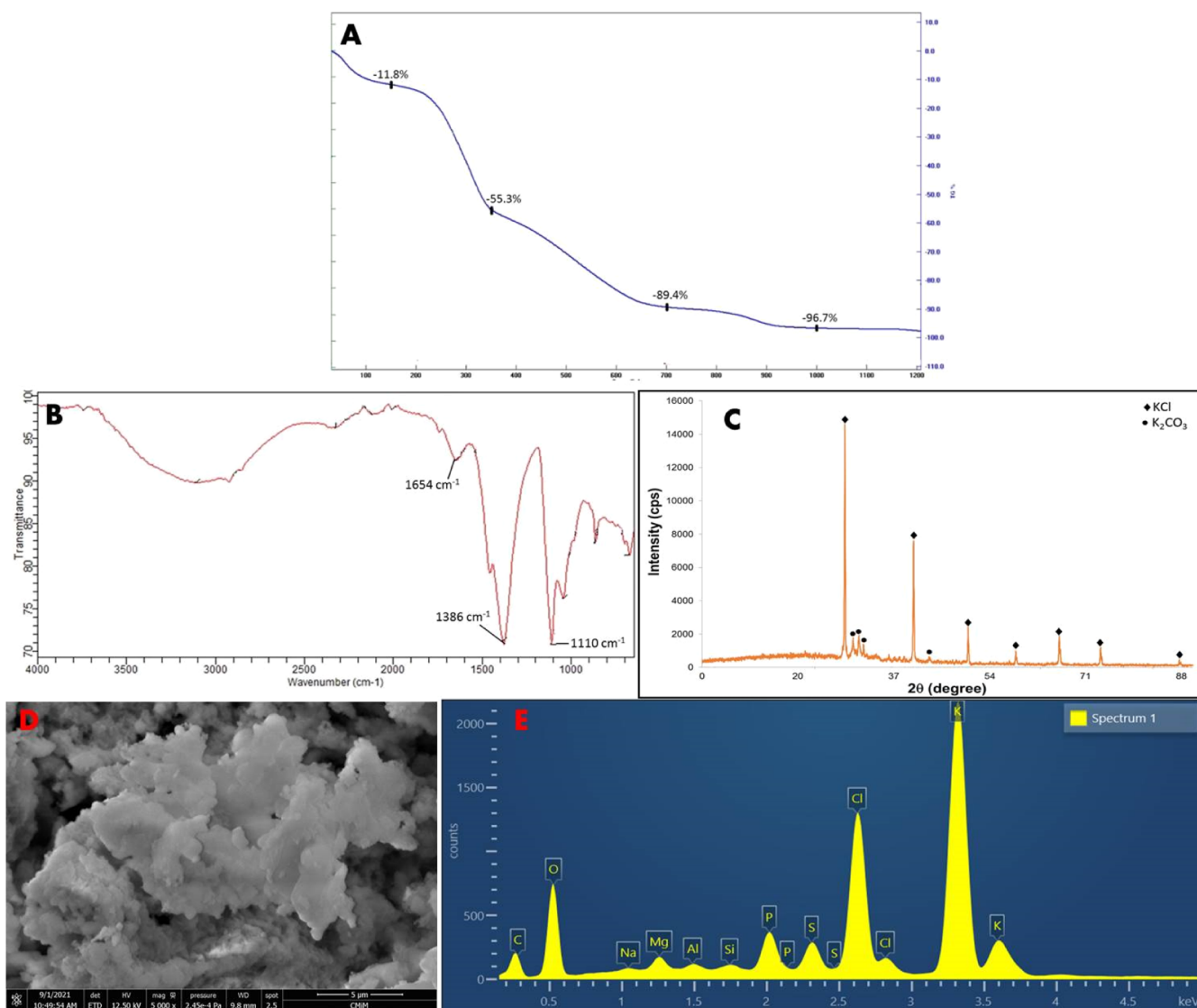


Figure 1. TGA pattern (A), FT-IR spectrum (B), XRD patterns (C), SEM image (D), and XRF spectrum (E) of calcined WPPF.

conversion of the transesterification reaction occurred in 75 min reaction time using waste *B. nigra plant* at room temperature.¹⁵ Based on this, the present study is aimed to investigate the performance of waste passion fruit peel (WPPF) as a heterogeneous catalyst for biodiesel production from palm oil. Passion fruit peel is a waste from a passion fruit syrup-manufacturing plant and is known to contain a high amount of potassium.²³ The passion fruit is easily grown in Indonesia with production in 2018 amounting to 59,270 tonnes,²⁴ in which 50% of them are passion fruit peel which has only been discarded into environments.²⁵ To date, the utilization of calcined WPPF as a heterogeneous catalyst in biodiesel production has not been studied. Therefore, the factorial design of the interaction between reaction temperature and a molar ratio of oil to methanol, catalyst weight, and reaction time was determined to establish the maximum biodiesel conversion and yield. The fatty acid (FA) extractions (mol %) of the four main fatty acids (FAs) such as palmitic, stearic, oleic, and linoleic acids were measured and compared with the raw material. The reusability of the heterogeneous catalyst was also determined. Furthermore, the WPPF was characterized by thermogravimetric analysis (TGA), X-ray

diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy coupled with energy-dispersive spectrometry (SEM–EDX), and Fourier transform infrared (FT-IR) spectroscopy.

RESULTS AND DISCUSSION

Catalyst Characterization. Figure 1A depicts the TGA pattern of calcined WPPF, which illustrated four main stages of weight loss. The TGA endothermic peak which occurred below 150 °C was attributed to the loss of free water molecules.²⁶ The second one in the range of 150–350 °C with an approximate weight loss of 43.5% resulted from the decomposition of dietary fibers.²⁵ The further decrease of 45.9% was observed at below 700 °C mainly due to the oxidation of the carbonaceous material present in the catalyst releasing carbon monoxide and carbon dioxide.¹⁶ The last degradation, 700–1001 °C, corresponds to a 7.3% weight loss apparently due to decomposition of the metal oxides.²⁷ Therefore, the calcination temperature of the WPPF was set to 400 °C as presumably pectic polysaccharide as the main component of WPPF (60–70%)²⁵ has decomposed and the carbonaceous compounds such as K_2CO_3 which have a similar

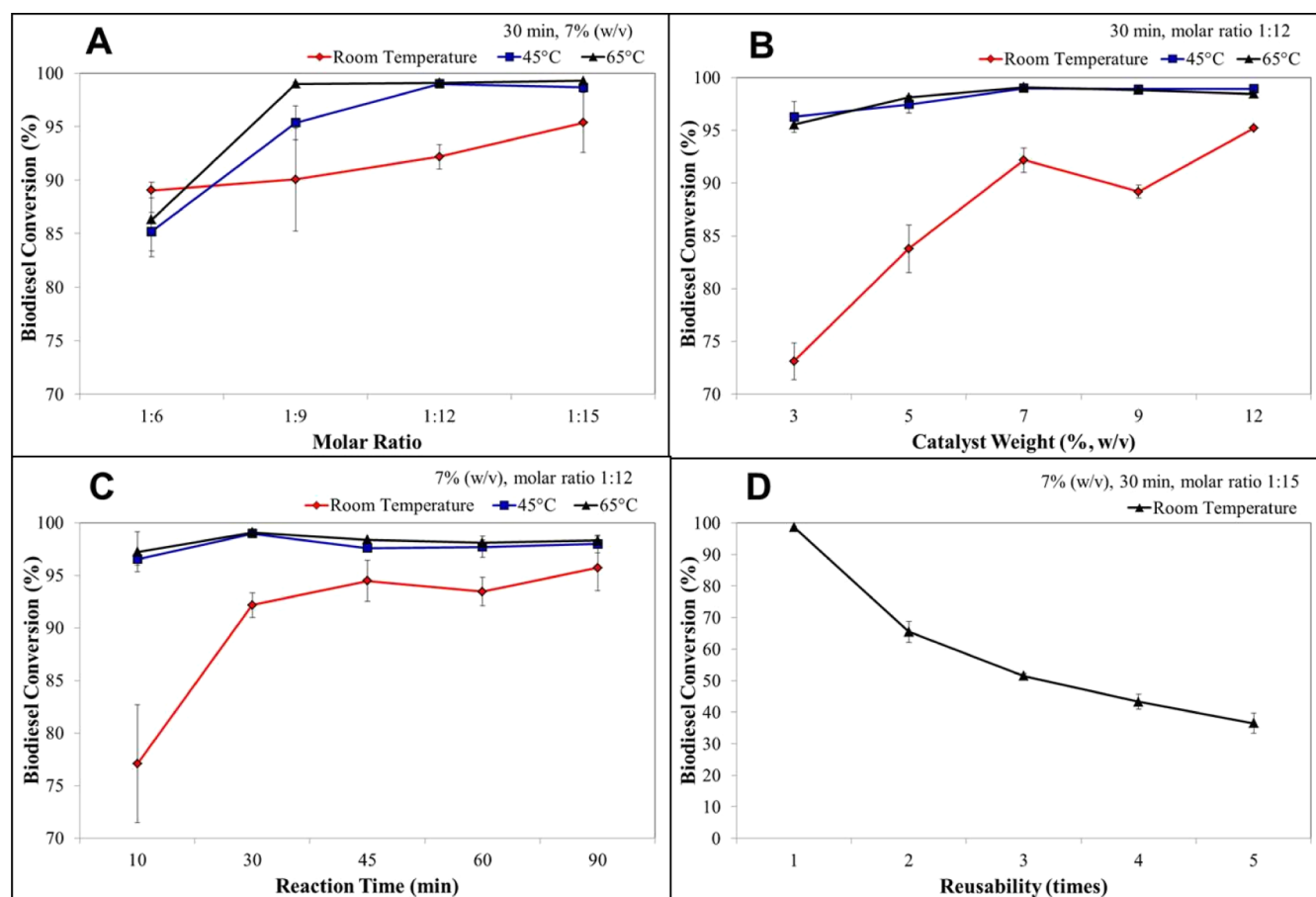


Figure 2. Effect of (A) molar ratio of palm oil to methanol; (B) catalyst concentration; (C) reaction time; and (D) reusability of catalyst on biodiesel conversion.

catalytic activity with the homogeneous basic catalyst reside in WFPF.²⁷ Furthermore, Vadery et al. (2014) concluded that calcination temperature above 400 °C did not affect the biodiesel conversion using calcined coconut husk ash as the catalyst.¹² The appearance of carbonate groups was identified by the FT-IR spectra (Figure 1B) which showed characteristic stretching and bending vibration of C–O from potassium carbonate at peaks of 1654, 1386, and 1110 cm^{-1} . The XRD pattern of calcined WFPF (Figure 1C) shows an amorphous structure mainly composed of potassium in the form of chloride and carbonate. The peaks at 28.34, 40.52, 50.18, 58.66, 66.36, 73.66, and 87.62° describe the presence of potassium chloride, while potassium carbonate was detected, corresponding to peaks of 29.78, 30.82, 31.64, and 43.34°.

The SEM image of WFPF as shown in Figure 1D displays an irregular shape and numbers of agglomerated structures with macropores. A similar SEM micrograph picture was obtained from calcined coconut husk ash which also contains potassium as the main element.¹² The elemental compositions of WFPF were determined using XRF, as displayed in Figure 1E. Potassium (K) is the major element present in WFPF which constitutes 44.4% of the total catalyst followed by chloride (16.6%) and carbon (7.9%), indicating that potassium is in the form of chloride and carbonate as revealed in the XRD spectra.

Effect of Molar Ratio. Stoichiometrically, the transesterification reaction involved 1 mol of triglyceride and 3 mol of methanol. However, due to the reversible reaction, more moles of methanol are required to push the reaction to

maximum biodiesel production.^{14,28} Commonly, a molar ratio of 1:6 is used in most transesterification reactions.³ Therefore, the molar ratio of palm oil to methanol ranges from 1:6 to 1:15 with an increase of 3 M being determined in three different reaction temperatures in this study. The experiments were conducted under a reaction condition of 7% (w/v) catalyst weight and a reaction time of 30 min. As predicted, the biodiesel conversions in the increasing molar ratio particularly at a molar ratio of 1:6 to 1:9 were detected to increase sharply from 85.2 ± 1.8 to $95.4 \pm 1.6\%$ and 86.3 ± 3.5 to $99.0 \pm 0.1\%$ for a reaction temperature of 45 and 65 °C, respectively, and remain constant in the addition of molar ratio (Figure 2A). As for the room-temperature reaction condition, the biodiesel conversion changes gradually and reached a peak at a molar ratio of 1:15, given a conversion of $95.4 \pm 2.8\%$. Furthermore, a similar line graph pattern occurred for the effect of molar ratio on biodiesel yield (Figure 3A). The highest biodiesel yields of 83.5 ± 1 , 93.6 ± 0.4 , and $95.2 \pm 0.5\%$ were obtained from a molar ratio of 1:12 for all the reaction temperatures. The Tukey test revealed that the significant effect is mainly driven by the molar ratio of 1:9, 1:12, and 1:15 either for biodiesel conversion or yield at a reaction temperature of 45 and 65 °C. Moreover, under the room-temperature condition, the molar ratio of 1:12 has a significant effect. These results match with the previous result which reported a plateau after a sharp increase in biodiesel yield.¹⁷ Mendonça et al. (2019) used *Astrocaryum aculeatum* Meyer peel as a heterogeneous catalyst in transesterification of soybean oil and reported that

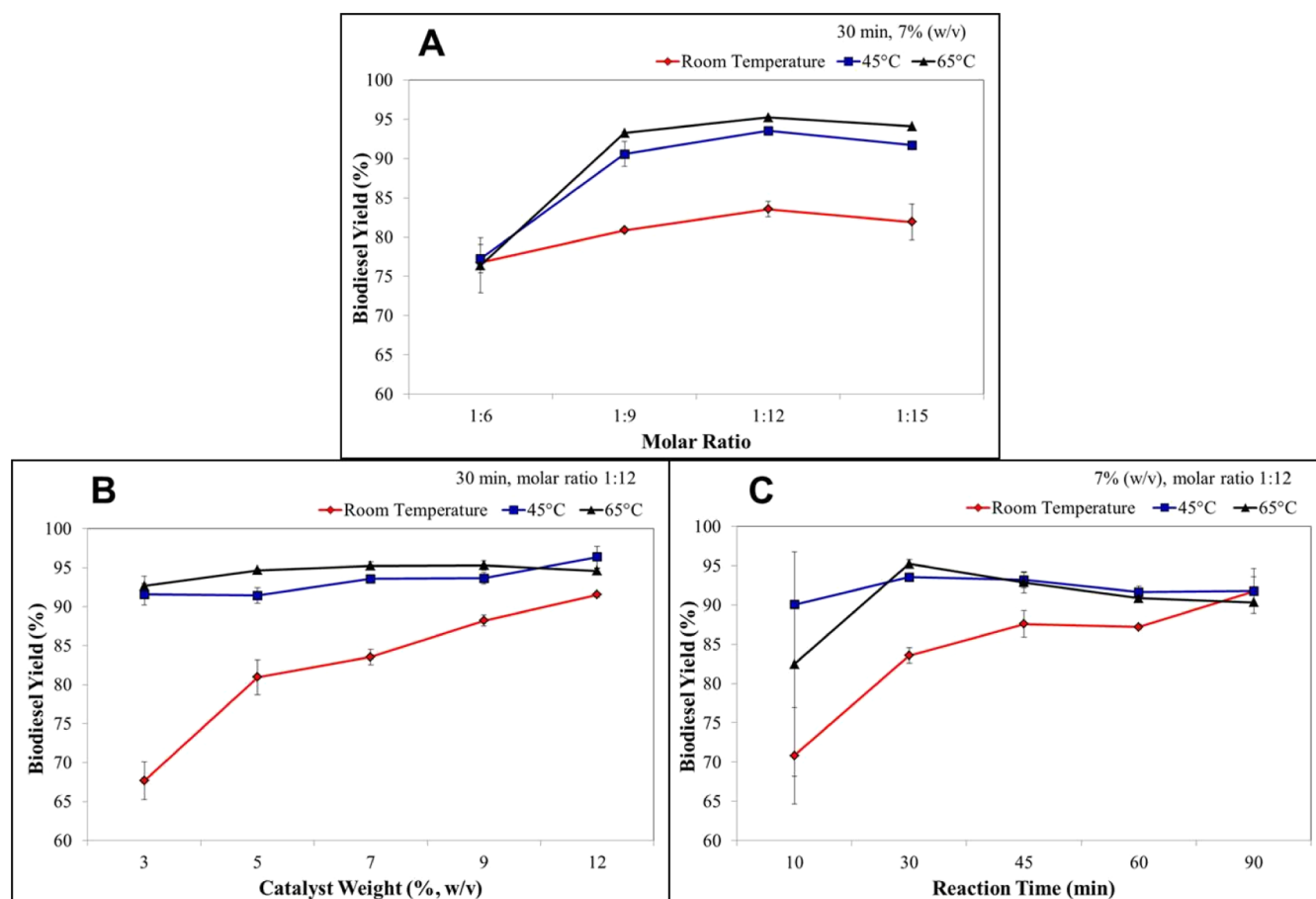


Figure 3. Effect of (A) molar ratio of palm oil to methanol; (B) catalyst concentration; and (C) reaction time on biodiesel yield.

the maximum biodiesel conversion was achieved at a molar ratio of 1:15 and remained constant in the increasing methanol volume.¹⁶

The molar ratio did not have a significant effect on FA extraction of $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, and $C_{18:2}$ (Figure 4A). The FA extraction of all fatty acids studied showed quite a similar value for all molar ratios and reaction temperatures. The average FA extractions of main fatty acids were 36.3, 36.4, and 36.1 mol % for $C_{16:0}$, 3.2 mol % for $C_{18:0}$, 48.0 mol % for $C_{18:0}$, and 10.6 mol % for $C_{18:2}$ for room temperature, 45°, and 65 °C reaction temperatures, respectively. It is noteworthy that FA extraction of $C_{18:1}$ from the biodiesel product exceeded 4.2, 4.1, and 4.3% from the raw material detected by GC.

Effect of Catalyst Weight. Catalyst concentration or weight is one important parameter that can affect the rate, conversion, and yield of biodiesel.^{3,29} The molar ratio of palm oil to methanol was set to 1:12 and reaction time of 30 min, while the catalyst weight of 3, 5, 7, 9, and 12% (w/v) was determined based on the different reaction temperatures. As shown in Figures 2B and 3B, the biodiesel conversion and yield routinely occurred at >90% at a reaction temperature of 45 and 65 °C, while it gradually increased from 73.1 ± 1.7 to $95.3 \pm 0.1\%$ and 67.7 ± 2.4 to $91.5 \pm 0.3\%$ under the room-temperature condition. The high biodiesel conversion and yield obtained at a reaction temperature of 45 and 65 °C showed that calcined passion fruit peel powder has high catalytic activity in the transesterification reaction. This high performance is due to the high basicity of the potassium ion which is the main compound contained in the catalyst.¹⁶ The

result in this study is in parallel with the previous study which uses waste mango peel as catalysts.¹³ Calcined coconut husk ash which contains 42.9% potassium ions also depicts a similar result in transesterification of jatropha oil.¹² The factorial ANOVA determined a significant effect of catalyst weight on both biodiesel conversion and yield which as stated by the Tukey test is mainly driven by a catalyst weight of 3–9% (w/v) and 3–7% (w/v) for 65 °C and room-temperature condition, respectively, and 12% (w/v) for 45 °C. The FA extraction of the biodiesel product routinely occurred quite similar to the palm oil composition. Furthermore, no significant effect was observed in catalyst weight on FA extraction of stearic, oleic, and linoleic acids, as shown in Figure 4B. However, a significant effect determined by ANOVA obtained for $C_{16:0}$ extractions is driven by low extraction efficiency (3.4%) compared to the palm oil fatty acid composition.

Effect of Reaction Time. It has been proved that reaction time has a positive correlation with biodiesel conversion.^{30,31} Therefore, the effect of reaction time was investigated at five different times such as 10, 30, 45, 60, and 90 min under the reaction condition of molar ratio of 1:12 and a catalyst weight of 7% (w/v) at three different reaction temperatures. As recorded, the biodiesel conversion of >90% occurred for all reaction times used at a reaction temperature of 45 and 65 °C with the highest conversion of 98.9 ± 0.1 and $99.1 \pm 0.2\%$, respectively, obtained in 30 min reaction time (Figure 2C). In contrast, the biodiesel conversion observed from room-temperature conditions showed a gradual increase and reached a peak of $95.7 \pm 2.2\%$ in 90 min reaction time. These results

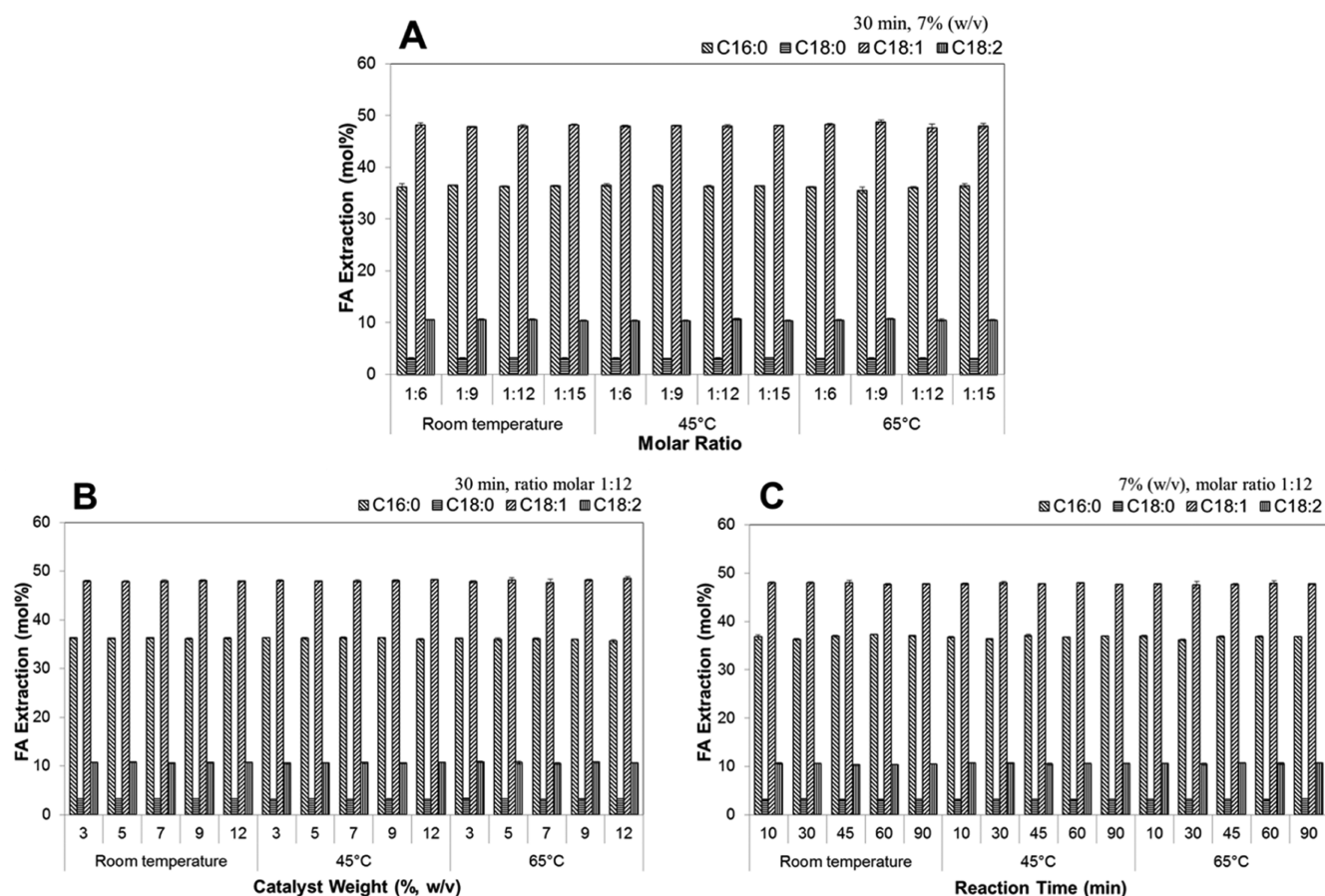


Figure 4. Effect of (A) molar ratio of palm oil to methanol; (B) catalyst concentration; and (C) reaction time on FA extraction (mol %).

are in agreement with previously published research which showed that the biodiesel conversion went up gradually and formed a plateau after reaching the peak in the esterification of fatty acid using heteropolyacid as a heterogeneous catalyst.³² Pathak et al. (2018) confirmed a similar result that the yield remained constant after the maximum conversion achieved in transesterification of soybean oil using calcined banana peel (*Musa acuminata*).³³ A quite identical line scheme was also obtained for the effect of reaction time on biodiesel yield, as depicted in Figure 3C. Similar to biodiesel conversion results, the highest biodiesel yield of 93.6 ± 0.4 and $95.3 \pm 0.5\%$ was obtained in 30 min reaction time at a reaction temperature of 45 and 65 °C, respectively, while it peaked at 91.7 ± 1.8 after 90 min reaction time for room-temperature experiment conditions. A confirmation on the significant effect of reaction time on biodiesel conversion and yield established by factorial ANOVA showed that it was mainly driven by low conversion and yield observed in reaction time of 10 min at room temperature ($77.1 \pm 5.6\%$ compared to 96.6 ± 0.6 and $97.3 \pm 1.9\%$ at the other reaction temperatures). As shown in Figure 4C, there was no significant effect of reaction time on FA extraction of main fatty acid components except palmitic acid under room-temperature conditions. This was due to the exceeding extraction of 1.1% after 60 min reaction time.

Comparison of Biodiesel Production Using Biobased Heterogeneous Catalysts. Table 1 summarizes processing parameters and outcomes achieved for biodiesel production using WPPF as a catalyst (this study) with data for other biobased catalysts. The biodiesel conversion routinely occurred >90 for all biobased heterogeneous catalysts with the complete

Table 1. Summary of the Maximum Condition for Biobased Heterogeneous Substances That Catalyze the Transesterification Reaction

biomass	potassium concentration (wt %)	reaction conditions (molar ratio oil: methanol, catalyst weight, temperature, and reaction time)	biodiesel conversion (%)	ref.
WPPF	44.4	1:15; 7 wt %; RT and 30 min	95.4	this study
banana pseudostem	26.2	1:14.9; 5.9 wt %; 65 °C and 178, 1 min	98	34
banana peduncle	70.1	1:9.2; 1.99 wt %; 65 °C and 60 min	98.7	35
tucuma peel	63.8	1:15; 1 wt %; 80 °C and 240 min	97.3	16
<i>Tectona grandis</i> leaves	53.3	1:6; 2.5 wt %; 60 °C and 180 min	100	36
cocoa pod husk	51.9	1:15; 4.5 wt %; 65 °C and 150 min	99	37
walnut shell	23.6	1:12; 5 wt %; 60 °C and 10 min	98	38
rice husk	5.7	1:12; 3 wt %; 65 °C and 180 min	97.7	39
coconut husk	55.8	1:12; 5 wt %; RT and 180 min	99.3	12
palm bunch ash	19.8	1:15; 3 wt %; 60 °C and 30 min	90	40

conversion occurring using *Tectona grandis* leaves. Potassium concentration in the biobased catalyst likely did not have a significant effect on biodiesel conversion. Calcined wood ash

which contains the lowest potassium ion in Table 1 showed a similar biodiesel conversion with banana peduncle which contains the highest potassium ion concentration. The catalyst weight used varied ranging from 1 to 7 wt % (this study). Only two studies were conducted at room temperature such as coconut husk and WFPF, while all others required reaction temperatures between 60 and 80 °C. For processing time, except for two studies reporting a reaction time of 10 and 30 min using walnut shell and palm bunch ash, respectively, other studies reported 2–8 times longer than the WFPF study. All studies used methanol higher than the stoichiometric amount which is necessary to move the equilibrium forward to biodiesel production. The molar ratio of oil to methanol used varied from 1:6 to 1:15. Based on the processing parameters, except for the calcined walnut shell, the WFPF showed better performance particularly in terms of reaction time and temperature compared to other studies.

Reusability and Stability of the Catalyst. Even though the catalyst consumed only 1% of total biodiesel production cost, recovery and reuse of the catalyst are necessary to avoid environmental pollution.⁹ Therefore, the reusability of the catalyst was studied under the reaction condition of molar ratio of 1:15, a catalyst weight of 7%, a reaction time of 30 min, and at room temperature. As shown in Figure 2D, the biodiesel conversion depreciated 34% after the first cycle and it remained decreased in the next sequent route. In total, the biodiesel conversion decreased by 63% after the fifth experiment. This was presumably due to the leaching of catalysts causing a reduction in the active site.^{26,27} To prove it, the leaching study had been conducted using 1 g of catalyst which was stirred at room temperature for 30 min with 20 mL of methanol. After filtration and drying, the catalyst weight reduced to $22 \pm 0.02\%$ proving that the catalyst was leached. This is presumably due to the hydrolysis of K_2O or KCl by methanol to form KOH .⁴⁰ Furthermore, the leached out filtrate was mixed with 10 g of palm oil and refluxed for 30 min. The biodiesel conversion was $92.4 \pm 1.6\%$ after separation, neutralization, and purification processes. This result was in agreement with the works of Vadery et al., who (2017) obtained a conversion of 96.1% using the leached out homogeneous catalyst in transesterification of jatropha oil.¹² In contrast, other published results showed that the filtrate did not show any catalytic activity, declaring the stability of wood ash and tucumã peel as biobased heterogeneous catalysts.^{16,41} The WFPF catalyst weight was observed to slightly reduce after the next cycle. In addition, XRF analysis was conducted to determine the leaching of active components in the WFPF catalyst. As shown in Table 2, the concentration of KCl

Table 2. XRF Analysis of Calcined WFPF Before and After the Leaching Test

WFPF	K_2O (wt %)	KCl (wt %)
calcined	44.4	17.1
after cycle 1	37.8	6.7
after cycle 2	35.4	3.3

decreased significantly (60.8%) after the first cycle, while that of K_2O slightly reduced (14.9%). A significant reduction of KCl concentration (50.8%) was also detected in the next cycle.

Based on this information, an additional certain amount of fresh catalyst is required to maintain high biodiesel conversion production. Another approach is to regenerate the catalyst

through washing and recalcination before the next cycles.¹¹ Furthermore, to avoid metal contamination in biodiesel products, washing and centrifugation of the biodiesel evidently could reduce the potassium concentration below the standard requirement.^{38,42,43}

CONCLUSIONS

WFPF has been successfully utilized as a heterogeneous catalyst in biodiesel production from palm oil. The calcined agrowaste contains potassium in the form of chloride and carbonate as main compounds. The biodiesel conversion and yield routinely obtained more than 90% for all parameters determined at a reaction temperature of 45 and 65 °C, while under room-temperature conditions, a high conversion of $95.4 \pm 2.8\%$ occurred after 30 min reaction time. The leaching study showed that the concentration of KCl reduced significantly after the subsequent cycle, while the concentration of K_2O reduced 14.9 and 6.4% after cycles 1 and 2, respectively.

EXPERIMENTAL SECTION

Materials. WFPF was collected from the local syrup plant in Tanah Karo, Sumatera Utara, Indonesia, and was washed, dried in an oven at 105 °C overnight, crushed using household spice grinders, and sieved using a 100 mesh sieve. The passion fruit peel powder was then calcined in a muffle furnace at 400 °C for 4 h and stored in a desiccator before use. The chemicals used in this study were purchased from a local chemical shop and were used without any pretreatment. The main components of palm oil used in this study are dominated by oleic and palmitic acids which consist of 46 and 37%, respectively, which was in agreement with the previous study.⁴⁴

Transesterification of Palm Oil. The transesterification of palm oil using WFPF as a heterogeneous catalyst was conducted using the reflux method. Different molar ratios of oil: methanol (1:6; 1:9; 1:12, and 1:15), catalyst weights (3, 5, 7, 9, and 12% based on oil weight), and reaction times (10, 30, 45, 60, and 90 min) were explored to determine the maximum biodiesel conversion for the transesterification process of palm oil. Briefly, 10 g of palm oil was mixed with an investigated volume of methanol and mass of the catalyst in a 150 mL round-bottom flask equipped with a condenser and magnetic heating stirrer. The reaction was conducted based on investigated time in three different reaction temperatures such as room temperature, 45, and 65 °C. The biodiesel product was then separated from the catalyst, leftover methanol, and glycerol using centrifugation. The weight of biodiesel was determined for yield calculation and it was stored in a desiccator before gas chromatography (GC) analysis.

Reusability and Leaching Test. The reaction condition which is producing the maximum biodiesel conversion was used to investigate the reusability test of the catalyst. After separation using centrifugation, the catalyst was used directly for subsequent cycles without any treatment to clean the catalyst. The reusability test was conducted for five cycles. In addition, the leaching test was also determined to study the catalyst stability following the previously published procedure with slight modification.¹⁶ For this assessment, only catalyst and methanol were used. A total of 1 g of catalyst was added to a 250 mL flask with 20 mL of methanol and was stirred at room temperature for 30 min. The catalyst was filtered using the Buchner funnel and Whatman filter paper no. 40. The filter

paper was dried in an oven at 40 °C until constant weight. The percentage of leached catalyst was calculated based on the weight difference of the catalyst before and after stirring. The depreciation of element amount was determined using XRF analysis.

Biodiesel Conversion and Yield Calculation. The biodiesel conversion was determined using GC analysis following the EN 14103:2011 standard which has been published elsewhere.^{45,46} The biodiesel obtained from experiments was weighted and recorded as w (g). Next, the internal standard was added to the aliquot and the mixture was injected into GC (Shimadzu type 2010) equipped with a capillary column (length 15 mm and ID of 0.25 mm) and flame ionization detector. The fatty acid methyl ester content in the biodiesel sample (expressed as C , in percentage) was then calculated using eq 1 based on concentration (C_s , in mg/mL), the volume of the internal standard (V_s , in mL), the mass of the sample (m , in mg), and the difference peak area between all fatty acid methyl esters (ΣA) and the internal standard (A_s). The mass of methyl ester was calculated using eq 2 by multiplying the concentration with the mass of the sample obtained (w). Finally, the yield in mass percentage was calculated by dividing the mass of methyl ester with the mass of palm oil used.

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

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

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

Catalyst Characterization. The calcined WFPF was characterized using TGA, FT-IR, and XRD. The XRD profile of the catalyst was determined using a Rigaku MiniFlex XRD. The FT-IR analysis used a Perkin Elmer 100 spectrophotometer with the wavelength recorded in the range of 4000–600 cm^{-1} . The scanning electron microscope is equipped with an EDX detector for morphological surface and elemental analysis of the catalyst.

STATISTICAL ANALYSIS

The factorial significance effect of molar ratio of palm oil to methanol, catalyst weight, and reaction time against reaction temperature was statistically analyzed using Statistica v13 with a significance level set to $\alpha = 0.05$. Furthermore, Tukey's test was conducted to compare the result means.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06785>.

ANOVA, Hartley–Cochran homogeneity test and Tukey post hoc test for all parameters tested on biodiesel conversion, yield, and fatty acid extraction (PDF)

AUTHOR INFORMATION

Corresponding Author

Eko K. Sitepu – Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia; orcid.org/0000-0003-3565-9027; Email: ekositepu@usu.ac.id

Authors

Juliati Br. Tarigan – Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia

Krishanjit Singh – Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia

Jenita S. Sinuraya – Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia

Minto Supeno – Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia

Helmina Sembiring – Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia

Kerista Tarigan – Department of Physics, Universitas Sumatera Utara, Medan 20155, Indonesia

Siti Masriani Rambe – Balai Riset dan Standarisasi Industri, Medan 20214, Indonesia

Justaman A. Karo-karo – Balai Riset dan Standarisasi Industri, Medan 20214, Indonesia

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.1c06785>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors wish to thank the Rector of Universitas Sumatera Utara for supporting this work.

REFERENCES

- (1) Bourbon, E. *Clean Cities Alternative Fuel Price Report*. July 2021; U.S. Department of Energy: Maryland, 2021.
- (2) Haas, M. J.; McAloon, A. J.; Yee, W. C.; Foglia, T. A. A process model to estimate biodiesel production costs. *Bioresour. Technol.* **2006**, *97*, 671–678.
- (3) Sitepu, E. K.; Heimann, K.; Raston, C. L.; Zhang, W. Critical evaluation of process parameters for direct biodiesel production from diverse feedstock. *Renew. Sustain. Energy Rev.* **2020**, *123*, 109762.
- (4) Harahap, F.; Silveira, S.; Khatiwada, D. Cost competitiveness of palm oil biodiesel production in Indonesia. *Energy* **2019**, *170*, 62–72.
- (5) Kim, B.; Heo, H. Y.; Son, J.; Yang, J.; Chang, Y.-K.; Lee, J. H.; Lee, J. W. Simplifying biodiesel production from microalgae via wet in situ transesterification: A review in current research and future prospects. *Algal Res.* **2019**, *41*, 101557.
- (6) Sitepu, E. K.; Jones, D. B.; Tang, Y.; Leterme, S. C.; Heimann, K.; Zhang, W.; Raston, C. L. Continuous flow biodiesel production from wet microalgae using a hybrid thin film microfluidic platform. *Chem. Commun.* **2018**, *54*, 12085–12088.
- (7) Mahlia, T. M. I.; Syazmi, Z. A. H. S.; Mofijur, M.; Abas, A. E. P.; Bilad, M. R.; Ong, H. C.; Silitonga, A. S. Patent landscape review on biodiesel production: Technology updates. *Renew. Sustain. Energy Rev.* **2020**, *118*, 109526.
- (8) Bateni, H.; Saraeian, A.; Able, C. A comprehensive review on biodiesel purification and upgrading. *Biofuel Res. J.* **2017**, *4*, 668–690.
- (9) Chua, S. Y.; Periasamy, L. A. P.; Goh, C. M. H.; Tan, Y. H.; Mubarak, N. M.; Kansedo, J.; Khalid, M.; Walvekar, R.; Abdullah, E. C. Biodiesel synthesis using natural solid catalyst derived from biomass waste - A review. *J. Ind. Eng. Chem.* **2020**, *81*, 41–60.
- (10) Wang, A.; Quan, W.; Zhang, H.; Li, H.; Yang, S. Heterogeneous ZnO-containing catalysts for efficient biodiesel production. *RSC Adv.* **2021**, *11*, 20465–20478.
- (11) Changmai, B.; Vanlalveni, C.; Ingle, A. P.; Bhagat, R.; Rokhum, S. L. Widely used catalysts in biodiesel production: a review. *RSC Adv.* **2020**, *10*, 41625–41679.
- (12) Vadery, V.; Narayanan, B. N.; Ramakrishnan, R. M.; Cherikkallinmel, S. K.; Sugunan, S.; Narayanan, D. P.; Sasidharan, S. Room temperature production of jatropha biodiesel over coconut husk ash. *Energy* **2014**, *70*, 588–594.

- (13) Laskar, I. B.; Gupta, R.; Chatterjee, S.; Vanlalveni, C.; Rokhum, L. Taming waste: Waste *Mangifera indica* peel as a sustainable catalyst for biodiesel production at room temperature. *Renewable Energy* **2020**, *161*, 207–220.
- (14) Laskar, I. B.; Deshmukhya, T.; Bhanja, P.; Paul, B.; Gupta, R.; Chatterjee, S. Transesterification of soybean oil at room temperature using biowaste as catalyst; an experimental investigation on the effect of co-solvent on biodiesel yield. *Renewable Energy* **2020**, *162*, 98–111.
- (15) Nath, B.; Das, B.; Kalita, P.; Basumatary, S. Waste to value addition: Utilization of waste *Brassica nigra* plant derived novel green heterogeneous base catalyst for effective synthesis of biodiesel. *J. Clean. Prod.* **2019**, *239*, 118112.
- (16) Mendonça, I. M.; Paes, O. A. R. L.; Maia, P. J. S.; Souza, M. P.; Almeida, R. A.; Silva, C. C.; Duvoisin, S.; de Freitas, F. A. New heterogeneous catalyst for biodiesel production from waste tucumã peels (*Astrocaryum aculeatum* Meyer): Parameters optimization study. *Renewable Energy* **2019**, *130*, 103–110.
- (17) Yang, X.-X.; Wang, Y.-T.; Yang, Y.-T.; Feng, E.-Z.; Luo, J.; Zhang, F.; Yang, W.-J.; Bao, G.-R. Catalytic transesterification to biodiesel at room temperature over several solid bases. *Energy Convers. Manage.* **2018**, *164*, 112–121.
- (18) Laskar, I. B.; Rajkumari, K.; Gupta, R.; Chatterjee, S.; Paul, B.; Rokhum, S. L. Waste snail shell derived heterogeneous catalyst for biodiesel production by the transesterification of soybean oil. *RSC Adv.* **2018**, *8*, 20131–20142.
- (19) Piker, A.; Tabah, B.; Perkas, N.; Gedanken, A. A green and low-cost room temperature biodiesel production method from waste oil using egg shells as catalyst. *Fuel* **2016**, *182*, 34–41.
- (20) Baig, R. B. N.; Verma, S.; Nadagouda, M. N.; Varma, R. S. Room temperature synthesis of biodiesel using sulfonated graphitic carbon nitride. *Sci. Rep.* **2016**, *6*, 39387.
- (21) Sun, H.; Duan, J.; Chen, P.; Lou, H.; Zheng, X. Room temperature transesterification of soybean oil to biodiesel catalyzed by rod-like Ca SiO₂ solid base. *Catal. Commun.* **2011**, *12*, 1005–1008.
- (22) Venkat Reddy, C. R.; Oshel, R.; Verkade, J. G. Room-Temperature Conversion of Soybean Oil and Poultry Fat to Biodiesel Catalyzed by Nanocrystalline Calcium Oxides. *Energy Fuels* **2006**, *20*, 1310–1314.
- (23) Salgado, J. M.; Bombarde, T. A. D.; Mansi, D. N.; Piedade, S. M. d. S.; Meletti, L. M. M. Effects of different concentrations of passion fruit peel (*Passiflora edulis*) on the glicemic control in diabetic rat. *Food Sci. Technol.* **2010**, *30*, 784–789.
- (24) Statistics Indonesia. *Statistics of Annual Fruit and Vegetable Plants Indonesia*; BPS—Statistics Indonesia, 2019.
- (25) Guo, R.; Tian, S.; Li, X.; Wu, X.; Liu, X.; Li, D.; Liu, Y.; Ai, L.; Song, Z.; Wu, Y. Pectic polysaccharides from purple passion fruit peel: A comprehensive study in macromolecular and conformational characterizations. *Carbohydr. Polym.* **2020**, *229*, 115406.
- (26) Rajkumari, K.; Rokhum, L. A sustainable protocol for production of biodiesel by transesterification of soybean oil using banana trunk ash as a heterogeneous catalyst. *Biomass Convers. Biorefin.* **2020**, *10*, 839–848.
- (27) Madai, I. J.; Chande Jande, Y. A.; Kivevele, T. Fast Rate Production of Biodiesel from Neem Seed Oil Using a Catalyst Made from Banana Peel Ash Loaded with Metal Oxide (Li-CaO/Fe₂(SO₄)₃). *Adv. Mater. Sci. Eng.* **2020**, *2020*, 1–11.
- (28) Mumtaz, M. W.; Adnan, A.; Mukhtar, H.; Rashid, U.; Danish, M. Chapter Fifteen - Biodiesel Production Through Chemical and Biochemical Transesterification: Trends, Technicalities, and Future Perspectives. In *Clean Energy for Sustainable Development*; Rasul, M. G., Azad, A. k., Sharma, S. C., Eds.; Academic Press, 2017; pp 465–485.
- (29) Wong, K. Y.; Ng, J.-H.; Chong, C. T.; Lam, S. S.; Chong, W. T. Biodiesel process intensification through catalytic enhancement and emerging reactor designs: A critical review. *Renew. Sustain. Energy Rev.* **2019**, *116*, 109399.
- (30) Ma, G.; Hu, W.; Pei, H.; Jiang, L.; Ji, Y.; Mu, R. Study of KOH/Al₂O₃ as heterogeneous catalyst for biodiesel production via in situ transesterification from microalgae. *Environ. Technol.* **2015**, *36*, 622–627.
- (31) Jazzar, S.; Olivares-Carrillo, P.; Pérez de los Ríos, A.; Marzouki, M. N.; Ación-Fernández, F. G.; Fernández-Sevilla, J. M.; Molina-Grima, E.; Smaali, I.; Quesada-Medina, J. Direct supercritical methanolysis of wet and dry unwashed marine microalgae (*Nannochloropsis gaditana*) to biodiesel. *Appl. Energy* **2015**, *148*, 210–219.
- (32) de Godói Silva, V. W.; Laier, L. O.; Silva, M. J. d. Novel H₃PW₁₂O₄₀: Catalysed Esterification Reactions of Fatty Acids at Room Temperature for Biodiesel Production. *Catal. Lett.* **2010**, *135*, 207–211.
- (33) Pathak, G.; Das, D.; Rajkumari, K.; Rokhum, S. L. Exploiting waste: towards a sustainable production of biodiesel using *Musa acuminata* peel ash as a heterogeneous catalyst. *Green Chem.* **2018**, *20*, 2365–2373.
- (34) Niju, S.; Janaranjani, A.; Nanthini, R.; Sindhu, P. A.; Balajii, M. Valorization of banana pseudostem as a catalyst for transesterification process and its optimization studies. *Biomass Convers. Biorefin.* **2021**, DOI: 10.1007/s13399-021-01343-x.
- (35) Balajii, M.; Niju, S. Banana peduncle - A green and renewable heterogeneous base catalyst for biodiesel production from *Ceiba pentandra* oil. *Renewable Energy* **2020**, *146*, 2255–2269.
- (36) Gohain, M.; Laskar, K.; Phukon, H.; Bora, U.; Kalita, D.; Deka, D. Towards sustainable biodiesel and chemical production: Multi-functional use of heterogeneous catalyst from littered *Tectona grandis* leaves. *Waste Manag.* **2020**, *102*, 212–221.
- (37) Olatundun, E. A.; Borokini, O. O.; Betiku, E. Cocoa pod husk-plantain peel blend as a novel green heterogeneous catalyst for renewable and sustainable honne oil biodiesel synthesis: A case of biowastes-to-wealth. *Renewable Energy* **2020**, *166*, 163–175.
- (38) Miladinović, M. R.; Zdujčić, M. V.; Veljović, D. N.; Krstić, J. B.; Banković-Ilić, I. B.; Veljković, V. B.; Stamenković, O. S. Valorization of walnut shell ash as a catalyst for biodiesel production. *Renewable Energy* **2020**, *147*, 1033–1043.
- (39) Chen, G.-Y.; Shan, R.; Shi, J.-F.; Yan, B.-B. Transesterification of palm oil to biodiesel using rice husk ash-based catalysts. *Fuel Process. Technol.* **2015**, *133*, 8–13.
- (40) Boey, P.-L.; Ganesan, S.; Lim, S.-X.; Lim, S.-L.; Maniam, G. P.; Khairuddean, M. Utilization of BA (boiler ash) as catalyst for transesterification of palm olein. *Energy* **2011**, *36*, 5791–5796.
- (41) Sharma, M.; Khan, A. A.; Puri, S. K.; Tuli, D. K. Wood ash as a potential heterogeneous catalyst for biodiesel synthesis. *Biomass Bioenergy* **2012**, *41*, 94–106.
- (42) Chouhan, A. P. S.; Sarma, A. K. Biodiesel production from *Jatropha curcas* L. oil using *Lemna perpusilla* Torrey ash as heterogeneous catalyst. *Biomass Bioenergy* **2013**, *55*, 386–389.
- (43) Atadashi, I. M. Purification of crude biodiesel using dry washing and membrane technologies. *Alex. Eng. J.* **2015**, *54*, 1265–1272.
- (44) Montoya, C.; Cochard, B.; Flori, A.; Cros, D.; Lopes, R.; Cuellar, T.; Espeout, S.; Syaputra, I.; Villeneuve, P.; Pina, M.; et al. Genetic Architecture of Palm Oil Fatty Acid Composition in Cultivated Oil Palm (*Elaeis guineensis* Jacq.) Compared to Its Wild Relative *E. oleifera* (H.B.K) Cortés. *PLoS One* **2014**, *9*, No. e95412.
- (45) Atabani, A. E.; Shobana, S.; Mohammed, M. N.; Uğuz, G.; Kumar, G.; Arvindnarayan, S.; Aslam, M.; Al-Muhtaseb, A. a. H. Integrated valorization of waste cooking oil and spent coffee grounds for biodiesel production: Blending with higher alcohols, FT-IR, TGA, DSC and NMR characterizations. *Fuel* **2019**, *244*, 419–430.
- (46) Torres, A.; Fuentes, B.; Rodríguez, K. E.; Brito, A.; Diaz, L. Analysis of the Content of Fatty Acid Methyl Esters in Biodiesel by Fourier-Transform Infrared Spectroscopy: Method and Comparison with Gas Chromatography. *J. Am. Oil Chem. Soc.* **2020**, *97*, 651–661.