

Performance of Waste Cooking Oil Esterification for Biodiesel Production Using Various Catalysts

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ABSTRACT

In this study, waste cooking oil (WCO) with high free fatty acid (FFA) content was esterified to produce biodiesel, and the catalysts' performance was investigated. Two deep eutectic solvents (DESs) were employed as the liquid catalysts (K₂CO₃-Gly and KOH-Gly), while the solid heterogeneous catalysts used were spent bleaching earth (SBE), KCC-1, and Na/KCC-1. DESs were prepared by mixing at reaction temperature and time of 80°C and 120 min, respectively. The American Standard Testing Method (ASTM) D974 determined the acid value. The catalysts were first screened for their catalytic activity in WCO esterification. The parameters investigated in this study were oil-to-methanol

molar ratio, catalyst loading, reaction time, and temperature. The highest conversion (94.7%) was obtained using Na/KCC-1. The performance of solid and liquid catalysts was evaluated using KOH-Gly and SBE for the reduction of FFA in WCO under different conditions of oil-to-methanol molar ratio (1:6–1:10), catalysts loading (0.2–2.0 g), reaction time (30–60 min), and temperature (40–100°C). The highest reduction of FFA in the esterification process for KOH-Gly and SBE as catalysts was 97.74% and 84.2%, respectively. Transesterification of the

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esterified oil shows a promising result (97%), and the process can potentially be scaled up. The GC-MS result shows that the produced oil has the highest percentage of hexadecanoic acid and methyl ester.

Keywords: Biodiesel, deep eutectic solvents, heterogeneous catalysts, waste cooking oil

INTRODUCTION

The requirement and demand for energy have been driven by fossil resource consumption, which negatively affects the environment and causes global warming issues (Aziz et al., 2017). Fossil fuels are known as limited energy sources due to the impact of climate change. Thus, renewable fuels are preferred to overcome the issue of increasing energy (Bobadilla et al., 2017; Japar et al., 2019; Rahman & Aziz, 2022). Biodiesel, produced from renewable feedstock, has received much attention worldwide in the energy sector (Nguyen et al., 2020; Aziz et al., 2019). Among the feedstock for biodiesel production includes animal fats, both edible and non-edible oils, as well as waste vegetable oils (Yusuff & Popoola, 2019; Rahman et al., 2019). High unsaturated fatty acid content is one of the main issues for most non-edible feedstock because two consecutive processes, namely esterification and transesterification, are required to deal with non-edible feedstock with high free fatty acid (FFA) content to produce biodiesel (Chuah et al., 2016., Azhar et al., 2021). Nowadays, waste cooking oil (WCO) has the economic advantage and potential to become the oil feedstock for biodiesel production. Reusing WCO is a good practice to prevent homes and restaurants from dumping WCO into wastewater (Razali et al., 2018; Razali et al., 2020).

Deep eutectic solvents (DESs) are mixtures of hydrogen bond donors with hydrogen bond acceptor materials. These mixtures have lower melting points than their constituting compounds (Shahbaz et al., 2013; Fatt et al., 2021). The development of DESs as low-cost and environmentally friendly solvents has several major advantages over conventional ionic liquids and organic solvents, such as sample preparation, low cost, low toxicity, and high biodegradability (Taslim et al., 2017; Ismail et al., 2019), and DESs have been used as biodiesel catalysts. Previous research revealed that various types of DESs were used in biodiesel production. Hayyan et al. (2014) utilized choline chloride (ChCl)-based DES as the catalyst to pretreat acidic crude palm oil in biodiesel synthesis. ChCl-based DESs were used to convert *Pongamia pinnata* into biodiesel (Kadapure et al., 2017; Isa et al., 2017; Dahawi et al., 2019).

The use of potassium carbonate (K_2CO_3)-based DESs have been applied for biodiesel synthesis, for example, in the biodiesel purification step (Manurung, Arief et al., 2018) and the extraction of minor components in palm methyl ester (Manurung & Liang, 2018). K_2CO_3 -based DES was utilized to purify palm biodiesel, where the purity of biodiesel of 98.6453% was achieved using a biodiesel-to-DES ratio of 1:3.5 (Manurung, Hutauruk et al.,

2018). Other than that, Sander et al. used K_2CO_3 -based DES to catalyze the deacidification of waste coffee grounds oil. A potassium-based DES was successfully used to extract FFA from waste coffee grounds oil (WCGO) and fresh coffee grounds oil (FCGO). The total acid number of WCGO and FCGO was lower than 1 mg KOH/g for 30 min reaction time using extractive deacidification with K_2CO_3 -based DES. The extraction efficiency ranged from 86.18% to 94.15% (Sander et al., 2020; Azahar et al., 2023). Recently, K_2CO_3 -based DES was used to purify waste cooking oil to avoid saponification during biodiesel synthesis. The total acid value decreased from 2.362 to 0.574 mg KOH/g in 30 min (Petračić et al., 2020).

Solid catalysts are a general type of heterogeneous catalyst, and their activity and selectivity determine their performance in catalyzing a reaction. Currently, many industries use heterogeneous catalysts that offer many advantages and are environmentally friendly, including non-corrosive, easily separated from the product through filtration, and can be used repeatedly over a long period (Sumarlan & Mentari, 2020; Mahmud et al., 2019). In a study of esterification of rapeseed oil fatty acids (RFA) using a carbon-based heterogeneous acid catalyst, biodiesel with an ester content of $\geq 96.5\%$ was successfully obtained from pure RFA under optimal esterification conditions (Malins et al., 2016). Spent bleaching earth (SBE) was previously used in biodiesel production (Petračić et al., 2020; Sumarlan & Mentari, 2020), but fewer studies of biodiesel production use SBE and KCC-1 as catalysts. Thus, using SBE and mesoporous silica KCC-1 as biodiesel catalysts provides an opportunity to explore biodiesel synthesis.

Therefore, this study investigates the performance of various catalysts in the esterification of waste cooking oil (WCO) for biodiesel production. This work reduced the FFA content in WCO via the esterification process using various DES and solid catalysts. The DESs used in this study were potassium carbonate-glycerol (K_2CO_3 -Gly) and potassium hydroxide-glycerol (KOH-Gly). Meanwhile, the solid catalysts used were KCC-1, modified KCC-1 (Na/KCC-1), and SBE. Free fatty acid conversion will be determined using titration in compliance with American Standard Testing Method (ASTM) D974. The transesterification process for the highest conversion from treated waste cooking oil will be performed with potassium hydroxide as a catalyst.

MATERIALS AND METHODS

Catalyst Preparation

Deep Eutectic Solvents. Potassium carbonate (K_2CO_3) and potassium hydroxide (KOH) were used to synthesize DESs using glycerol as a hydrogen bond donor. The DESs used in this work were synthesized following previous work (Herman, Isa et al., 2021; Chandraseagar et al., 2019). Glycerol was added to K_2CO_3 with a mass ratio of 20:1 and homogeneously mixed for 120 min at 80 °C until a clear colorless mixture formed. Similar procedures were repeated using KOH for DES synthesis. A vacuum desiccator was used to

store the resultant K_2CO_3 -Gly and KOH-Gly to preserve the physicochemical properties of the catalysts.

Solid Catalysts. The microwave-assisted hydrothermal method was used to synthesize parent KCC-1, as Hamid et al. (2018) reported, whereas Na/KCC-1 was prepared by our research collaborators (Hanif et al., 2021). KCC-1 and SBE were supplied by Universiti Teknologi Malaysia and used as received.

Characterization of Catalyst Samples. The following procedures explain the characterization of SBE. An X-ray diffractometer (Shimadzu 6000 XRD) was utilized to evaluate the crystalline phase of the samples. The measurements were performed using $Cu-K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of $20\text{--}80^\circ$ in 2θ at an accelerating voltage of 40 kV and an intensity of 30 mA. The data was collected at 0.02° intervals and a speed of 2° min^{-1} . A Perkin-Elmer Spectrum 65 spectrometer was used to analyze Fourier transform infrared (FTIR) spectroscopy and identify the functional groups introduced onto the catalysts. Hanif et al. (2021) reported the characterization of Na/KCC-1 in the previous study.

Esterification of Waste Cooking Oil. The WCO utilized in this process was collected from restaurants in Perlis, Malaysia. The conditions used for the esterification process are presented in Table 1. The sample size of WCO was kept constant at 40 g for every reaction of the experiment. The esterification reaction was performed in a 250 ml reaction flask equipped with a magnetic stirrer and thermometer. DESs as catalysts were dissolved in methanol and mixed with oil in the reaction flask. Meanwhile, the selected catalysts were added to the preheated oil for solid catalysts, and the mixture was stirred continuously at 600 rpm. Temperature was monitored using a thermometer. After the reaction, the liquid mixture was separated from the catalyst using a simple centrifuge.

Table 1
Conditions of solid and liquid catalysts in the esterification process

Parameter	Conditions
Oil-to-methanol molar ratio, OMMR	1:6, 1:8, and 1:10
Catalyst loading, CL (g)	0.8, 1.2, 1.6, and 2.0
Reaction time, RT (min)	30, 45, and 60
Temperature, T ($^\circ\text{C}$)	40, 60, 80, and 100

Titration was applied to determine the FFA content of the tested samples. The samples were titrated with 0.1 N KOH after they were dissolved in a mixture of isopropyl alcohol and phenolphthalein. The equation reported by Thoai et al. (2019) was employed to determine the FFA conversion and acid value. Experimental works were replicated three times.

Transesterification of Treated WCO. The SBE and KOH-Gly treated oils were used in the transesterification process catalyzed by KOH. The transesterification conditions

employed were oil-to-methanol molar ratio (1:6), catalyst loading (0.55 wt.%), reaction time (60 min), and temperature (65 °C). The KOH-based catalyst was first dissolved in methanol and stirred at room temperature for three minutes while treated oil was heated in a round bottom flask. When the treated oil reached the temperature of 65 °C, potassium methoxide was mixed into the oil for one hour of reaction time. After that, the mixture was poured into a separating funnel. The ester layer was separated by gravity and located at the upper layer. The glycerol, extra methanol and undesired products were removed in the lower layer. The ester layer was washed several times with a small amount of hot water until it met the requirements.

The ester layer was analyzed using gas chromatography-mass spectrometry to identify the ester component produced in the sample. The stoichiometry of the transesterification reaction requires 3 mol of alcohol per mol of triglyceride to yield 3 mol of alkyl ester biodiesel and 1 mol of glycerol. The biodiesel and reaction for FAME conversions were calculated using Equation 1 (Changmai et al., 2020).

$$\text{Yield of FAME (\%)} = \frac{\text{Weight of methyl ester (g)}}{\text{Weight of oil used in reaction (g)}} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Characteristics of Catalysts

Parent KCC-1 and Na/KCC-1 were characterized in the previous work of our research group and reported by Hanif et al. (2021). Figure 1 presents the results of the X-ray diffraction (XRD) analysis of SBE.

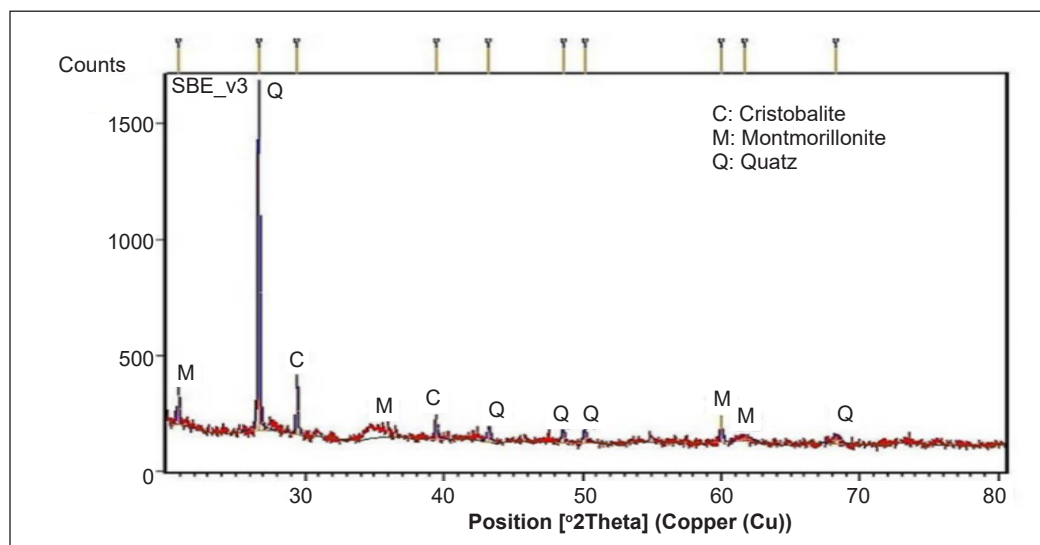


Figure 1. XRD pattern of SBE

A partially amorphous phase with ten obvious peaks of montmorillonite, cristobalite, and quartz can be seen in the SBE sample. Raw SBE mainly contains quartz that is obtained at the peak of the crystalline quartz impurities (SiO_2). The presence of montmorillonite in SBE proved that it could act as a relative catalyst to lower the FFA content in WCO esterification (Kanda et al., 2017; Ismail et al., 2021). The presence of montmorillonite in SBE patterns also aligns with the result of FTIR obtained (Figure 2).

Figure 2 shows the FTIR result consisting of various vibration and absorption bands. The vibration bands observed in SBE at 3214 cm^{-1} correspond to the O-H stretching of structural hydroxyl groups and hydration water molecules, respectively, indicating the possibility of the hydroxyl linkage. Also, a strong stretching vibration band of $\text{CH}_2\text{-CH}_3$ was observed at 2923 cm^{-1} in SBE, indicating saturated carbonaceous oil chains and FFAs in SBE. The broad band at 1464 cm^{-1} in the FTIR spectrum of SBE represents C-H bending, showing high oil content in SBE. A strong adsorption bank in the region of 1649 cm^{-1} in SBE indicates O-H bending vibrations of physisorbed water molecules, proving the presence of Brønsted acid sites in SBE due to hydration. Absorption bands Si-O and Si-O-Al at 969 cm^{-1} confirm the montmorillonite structure in SBE. The band at 643 cm^{-1} of SBE probably indicates the presence of Al-O impurities and out-of-the-plane Si-O coupling, also known as cristobalite (Kanda et al., 2017).

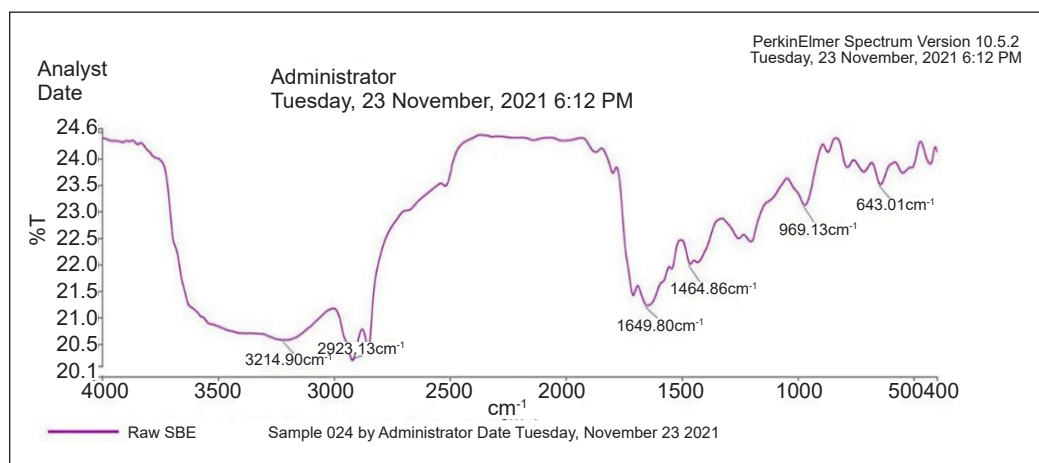


Figure 2. FTIR analysis of SBE

Effect of Solid and Liquid Catalysts on Waste Cooking Oil Esterification

Screening The Effect of Solid Catalysts in Waste Cooking Oil Esterification. Figure 3 shows the effect of the type catalyst used on the FFA conversion of WCO, where the oil-to-methanol molar ratio, reaction time, catalyst loading, and temperature were fixed at 1:10, 60 min, 2 g, and 60°C , respectively. The parameters were set according to the preliminary study in the laboratory and were found suitable for screening purposes. The FFA conversion was

obtained in the 76%–94% range. The lowest and highest conversions were obtained using KCC-1 (76.7%) and Na/KCC-1 (94.66%).

Although WCO esterification using solid catalysts has been reported in many studies (Sumarlan & Mentari, 2020; Malins et al., 2016; Aziz et al., 2017), the use of KCC-1 and Na/KCC-1 as catalysts for esterification is still new, and they offer interesting prospects to explore for the next study. The use of Na/KCC-1 in this study demonstrated the efficiency of the catalyst as the FFA conversion exceeded 90%. Although the combination of Na/KCC-1 showed a promising result, due to the limited sample of KCC-1, the comparison of solid and liquid catalysts with SBE as a catalyst was pursued. The combination of Na/KCC-1 will be investigated in the next study.

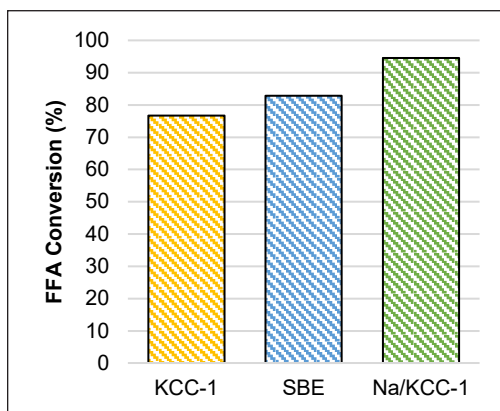


Figure 3. FFA conversion of WCO for screening of solid catalysts at 60 min, 60 °C, and 1:10 oil-to-methanol molar ratio (Replicated three times with standard deviation of 0.20–0.25)

Screening the Effect of DESs and Comparing the Performance of DESs and Solid Catalysts in WCO Esterification. The FFA conversion in WCO using DESs as catalysts with a constant loading of 2 g is shown in Figure 4. High FFA conversion was obtained using KOH-Gly (90.26%) compared to 87.65% using K_2CO_3 -Gly. The two layers of the final product were obtained from the esterification of WCO and DES. The separation of the product was easier compared to solid catalysts. It was reported that biodiesel yield increased in the presence of DESs (Kadapuri et al., 2017). K_2CO_3 -based DESs (Pourvusughi, 2012; Malins et al., 2016) and KOH-based DESs (Herman, Mukhrofut et al., 2021) were previously used in several studies for biodiesel production.

The performance of DESs and solid catalysts is shown in Table 2. Similar works from previous studies have proven the efficiency of reducing acid values using solid catalysts and DESs. A sulfonated carbon-based catalyst prepared using bamboo and palm kernel shell was used to

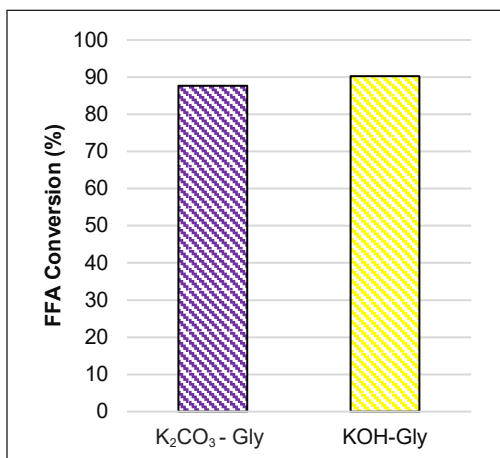


Figure 4. FFA conversion of WCO for screening of DESs at 60 min, 60°C, and 1:10 oil-to-methanol molar ratio (Replicated three times with standard deviation of 0.20–0.25)

esterify palm fatty acid distillate (PFAD), and the acid value obtained was lower than the maximum threshold (0.45 mg KOH/g) (Farabi et al., 2019). This study obtained the highest reduction using KOH-Gly and Na/KCC-1 with 0.81 and 0.45 mg KOH/g, respectively. KCC-1 recorded the lowest FFA reduction for this work.

Table 2
Acid value after WCO esterification

Sample	Catalyst	Acid Value (mg KOH/g)
WCO	Blank	8.42
	KCC-1	1.96
	SBE	1.43
	K ₂ CO ₃ -Gly	1.04
	KOH-Gly	0.81
	Na/KCC-1	0.45

Comparison of the Effect of SBE and DES as Catalysts

Effect of Catalyst Loading. Figure 5 shows the relationship between FFA conversion and catalyst loading, while the oil-to-methanol molar ratio, reaction time, and temperature were fixed at 1:10, 60 min, and 60°C, respectively. The FFA conversion using KOH-Gly and SBE increased from 34.32% to 83.49% and 78.62% to 79.57%, respectively, as the catalysts loading increased from 0.8 g to 2.0 g. The significant increase in the conversion shows that the amount of catalyst dosage influences the FFA conversion in this reaction process (Alhassan et al., 2015). The increase in fatty acid methyl ester (FAME) yield can be attributed to higher viscosity with higher CL, which reduces the diffusion of a three-phase system (methanol-oil-catalyst) (Ali et al., 2020). A similar trend in the esterification of PFAD was reported by Chongkhong et al. (2007).

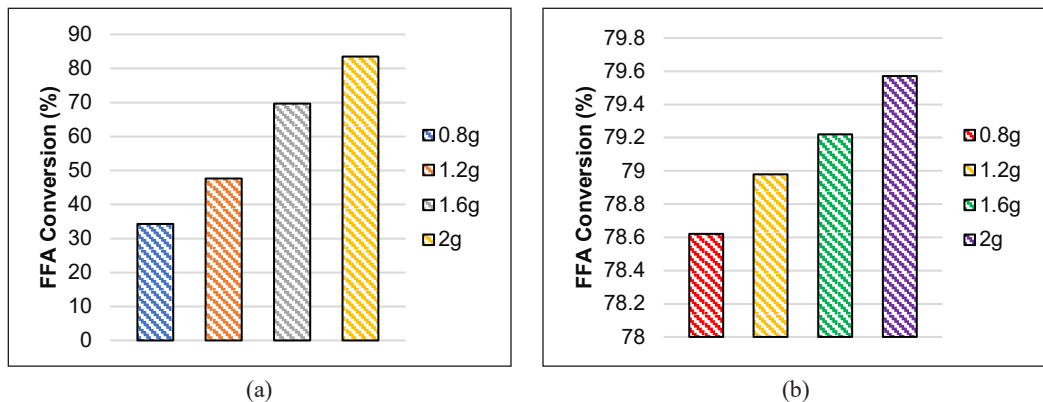


Figure 5. Effect of catalyst loading on FFA conversion at 60 min, 60°C, and 1:10 oil-to-methanol molar ratio using (a) KOH-Gly and (b) SBE catalysts (Replicated three times with standard deviation of 0.20–0.25)

Effect of Oil-to-Methanol Molar Ratio. Figure 6 illustrates the effect of the oil-to-methanol molar ratio on FFA conversion at 60 min and 60°C. Figure 6 shows high conversion is possible with a high oil-to-methanol molar ratio. The FFA conversion using

KOH-Gly increased at the ratio of 1:6 and continued to increase at the ratios of 1:8 and 1:10. The highest conversion for KOH-Gly was 97.74% at the ratio of 1:10. Meanwhile, the FFA conversion using SBE ranged between 78% and 83%. The Le Chatelier principle can be used to explain the upward trend in conversion. Increased methanol concentration resulted in a higher final conversion of FFA to methyl ester (Al-Sakkari et al., 2017). A previous study demonstrated that increasing the molar ratio to 1:18 increased the FFA conversion (Gan et al., 2009). Furthermore, increasing the oil-to-methanol molar ratio reduces the viscosity of the reaction mixture from a mass transfer standpoint. It improves the mixing of reactants and catalysts, resulting in a higher conversion in a given period due to the increasing mass transfer rate (Gan et al., 2010).

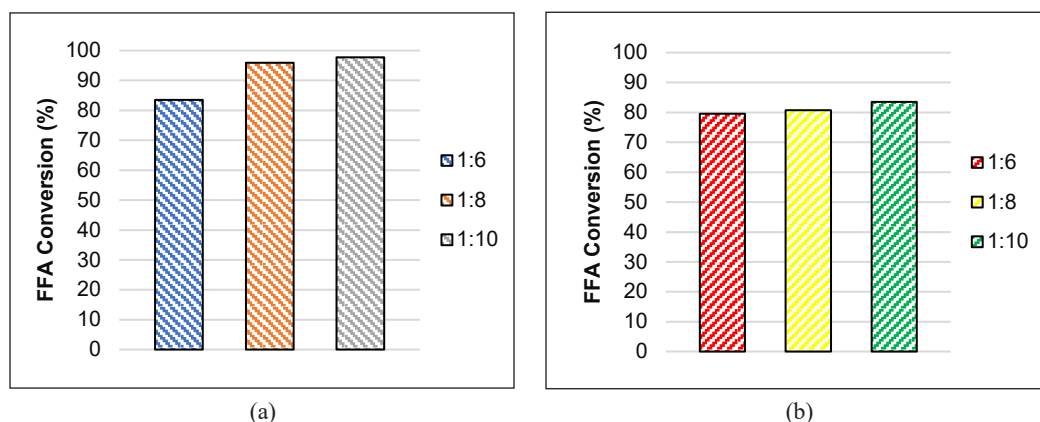


Figure 6. Effect of oil-to-methanol molar ratio on FFA conversion at 60 min, 60°C, and 2 g of catalyst loading using (a) KOH-Gly and (b) SBE catalysts (Replicated three times with standard deviation of 0.20–0.25)

Effect of Temperature. Figure 7 presents the study's results on the effect of temperature at 40, 60, 80, and 100°C for the oil-to-methanol molar ratio of 1:10 and reaction time of 60 min. From the Figure 7, higher FFA conversion rates are achieved at higher reaction times because esterification is endothermic (Bhatia et al., 2020). Furthermore, due to the agitation effect, a pseudo-homogeneous reaction mixture is produced after methanol droplets are broken.

Esterification should be conducted at a temperature lower than 65°C to avoid excessive methanol evaporation, which can induce the backward reaction and lower the conversion reaction (Al-Sakkari et al., 2020). A previous study did not observe a significant change in FFA conversion when the temperature was increased from 65°C to 85°C. The FFA conversion exceeded 90% at the optimized temperature of 65°C (Farabi et al., 2019). However, some studies have shown a similar trend to the current study, in which a higher conversion of FFA was obtained at a temperature of more than 65 °C. The dissolution follows the diffusion of FFA toward the catalyst in methanol. Subsequently, the penetration

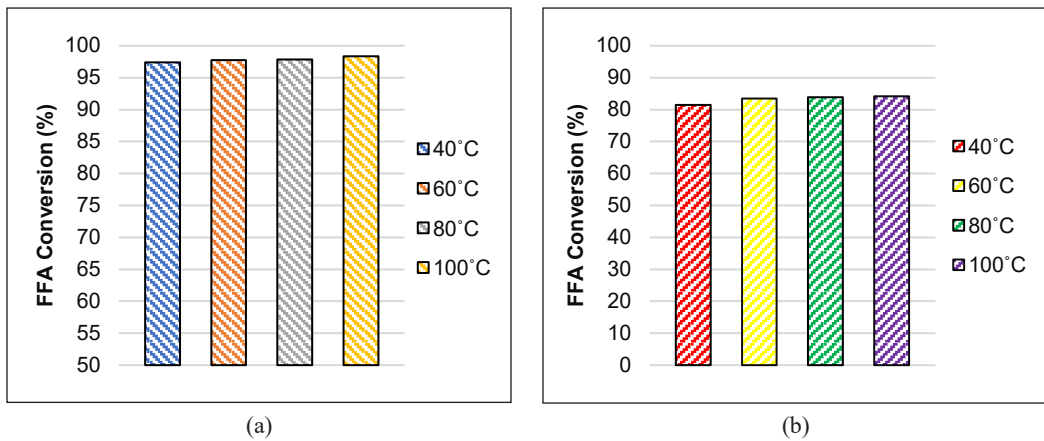


Figure 7. Effect of temperature on FFA conversion at 60 min, 1:10 oil-to-methanol molar ratio, and 2 g of catalyst loading using (a) KOH-Gly and (b) SBE catalysts (Replicated three times with standard deviation of 0.20–0.25)

of FFA inside the pores of the catalyst enables the FFA to undergo catalysis on the inner and outer surfaces (Boffito et al., 2013). As the viscosity of WCO drops, better mixing can be achieved between reactants and catalysts (Gan et al., 2010).

Effect of Reaction Time. The effect of reaction time on FFA conversion was studied by varying the reaction time from 30 to 60 min while other parameters were fixed. Figure 8 shows the FFA conversion of WCO. From the results, the FFA conversion increases with reaction time.

The oil-methanol immiscibility at the beginning of esterification influences the increase in FFA conversion with time (Rabie et al., 2019; Sofi et al., 2019). Hence, in this work, the maximum yields of 97.74% and 83.49% were obtained in 60 min at 100°C for the reaction

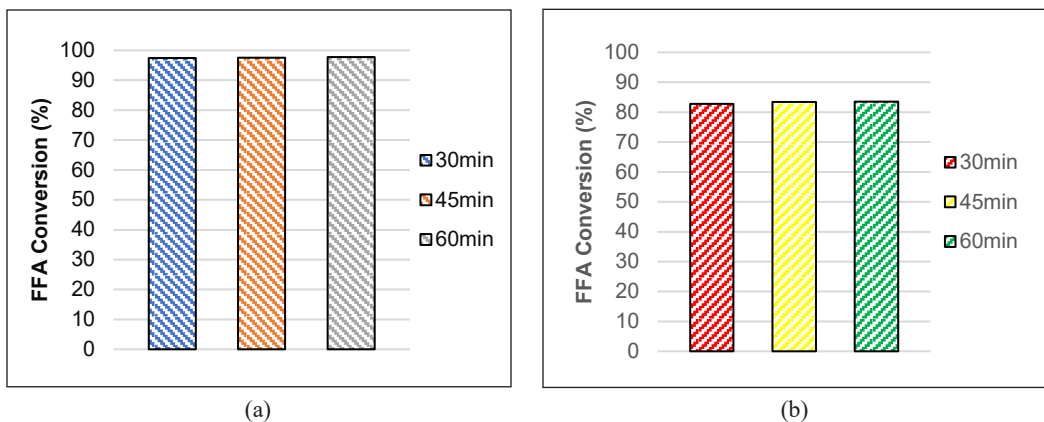


Figure 8. Effect of reaction time on FFA conversion at 60°C, 1:10 oil-to-methanol molar ratio, and 2 g of catalyst loading using (a) KOH-Gly and (b) SBE catalysts (Replicated three times with standard deviation of 0.20–0.25)

catalyzed by KOH-Gly and SBE, respectively. However, based on the results, 30 min is a suitable time for the esterification process because no significant increment was observed for FFA conversion of WCO at prolonged reaction times.

Transesterification of Treated WCO. The oil treated with KOH-Gly and SBE was used as the feedstock for biodiesel production via transesterification. The process was performed under similar conditions (1:6 oil-to-methanol molar ratio, 0.55 wt.% KOH, 1 h, and 65°C). High conversion of FAME was obtained in the 90%–97% range for KOH-Gly-treated oil and 80%–85% for SBE-treated oil.

Gas chromatography-mass spectrometry was utilized to identify the chemical composition of the biodiesel produced from the treated oil. Five main chemical compositions were analyzed: ester, acid, alcohol, ketone, and phenol. The analysis determined that the chemical composition of biodiesel from the treated oil using KOH-Gly was 98.54% ester, 0.22% acid, 0.03% alcohol, 0.02% phenol, 0.1% ketone, and 1.09% other compounds. Meanwhile, the biodiesel produced from the treated oil using SBE indicated 98.41% ester, 0.23% acid, 0.37% alcohol, 0.04% phenol, 0.11% ketone, and 0.84% other compounds. The composition of FAME produced from the treated oil using KOH-Gly and SBE is given in Table 3. Each biodiesel's highest fatty acid composition is hexadecanoic acid methyl ester, which is naturally present in crude palm oil and is the feedstock's source.

Table 3
Composition of FAME

Fatty Acid	Formula	Composition of Methyl Ester (%)	
		KOH-Gly Biodiesel	SBE Biodiesel
Dodecanoic acid, methyl ester	C ₁₃ H ₂₆ O ₂	0.56	0.64
Methyl tetradecanoate	C ₁₅ H ₃₀ O ₂	2.07	2.44
9-Hexadecenoic acid, methyl ester, (Z)-	C ₁₇ H ₃₂ O ₂	0.95	1.04
Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	60.24	58.78
Tetradecanoic acid, 2,3-dihydroxy propyl ester	C ₁₇ H ₃₄ O ₄	0.49	0.14
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C ₁₉ H ₃₄ O ₂	7.76	9.3
9-Octadecenoic acid, methyl ester	C ₁₉ H ₃₆ O ₂	18.16	17.47
Octadecanoic acid, methyl ester	C ₁₉ H ₃₈ O ₂	7.99	8.02
Eicosanoic acid, methyl ester	C ₂₁ H ₄₂ O ₂	0.29	0.27

CONCLUSION

This research is a forerunner for a novel process in which DESs and solid catalysts (KCC-1, Na/KCC-1, and SBE) were used as the pretreatment catalysts prior to biodiesel production. The results revealed that FFA conversion reached the highest at 94.66% and 90.38% using Na/KCC-1 and KOH-Gly, respectively. FFA reduction in WCO shows that

the samples can be potentially used as a feedstock to produce biodiesel. A further study of WCO esterification using KOH-Gly and SBE as catalysts was conducted. The highest conversion was achieved using KOH-Gly at 98.34%. Meanwhile, the conversion using SBE as a catalyst was lower than KOH-Gly with 84.2%. The transesterification process found that the conversion was 80%–97% using KOH-Gly and SBE-treated oil. The highest FAME for each biodiesel is hexadecanoic acid, a methyl ester that can improve the properties of biodiesel due to its higher cetane number. From a practical viewpoint, modified KCC-1 can be widely explored as a catalyst for WCO esterification and transesterification for biodiesel production.

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