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SYNTHESIS OF BIODIESEL FROM USED FRYING OIL USING MODIFIED BANANA PEEL WASTE AS A HETEROGENEOUS CATALYST

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ABSTRACT

In this study, biodiesel was synthesised from a transesterification reaction of used frying oil (UFO) catalysed by modified banana peel waste (Modified-BPW). The catalyst properties were characterised using Fourier Transform Infrared Spectrometer (FTIR) and Scanning Electron Microscopy (SEM) analyses. The reaction parameters were varied to evaluate the optimal reaction parameters that could influence the biodiesel yield, such as methanol to oil molar ratio, catalyst loading amount and water content presence in the UFO at a fixed reaction time of 2 hours and a reaction temperature of 65°C. The catalytic activity resulted in the reaction condition of 12:1 of methanol to oil molar ratio, 1 wt.% of catalyst dosage and 0.5 wt.% water content in UFO, obtaining the highest biodiesel yield of 88.7%. The results indicated that the Modified-BPW could be a promising catalyst for biodiesel synthesis from UFO.

***Keywords**: Biodisel, transesterification, used frying oil, banana peel waste and modified heterogeneous catalyst*

INTRODUCTION

Used frying oil (UFO) was known as an economical biodiesel feedstock because it was abundant [1], and the waste did not contradict the food crops issues. Moreover, recycling UFO as a selected feedstock for biodiesel production would avoid the problem of their final disposal as waste [2], reducing their environmental impact and taking advantage of the energy they contain. However, typically, UFO has free fatty acid (FFA) and water contents above the recommended values for direct use in a homogeneous base-catalysed transesterification reaction. Furthermore, this type of catalyst produces soaps as by-products, requiring additional processing technologies for proper disposal.

Thus, a heterogeneous base-catalysed transesterification reaction was a good alternative to overcome those limitations [3]-[4]. This type of catalyst had many advantages, including high catalytic activity, high water tolerance, and a simplification characteristic of the biodiesel purification stages to obtain the final biodiesel product and reusable [5]. Moreover, applying heterogeneous catalysts in transesterification to produce biodiesel can address the drawbacks of sludge generation after the reaction process and, later, reduce biodiesel production's overall operation cost.

Agricultural waste-derived catalysts have gained enormous attention in recent years as it held as an effective waste management. Several researchers successfully utilised agricultural waste-derived catalysts for biodiesel production, especially from waste oils. Bananas became a significant cash crop widely cultivated worldwide [6]. The waste produced from this fruit was tremendous, and the disposal of the peels was costly [7]. Therefore, using peels that can contribute to increasing economic security was beneficial. Banana peels are rich in minerals and other trace elements, which will produce a highly effective catalyst for biodiesel synthesis at a specific temperature over a given period.

In this study, the banana peel waste (BPW) catalyst was prepared with a modification by activation

with potassium hydroxide (KOH) to enhance the characteristics of the catalyst. Additionally, to be fitted with the application as a catalyst for biodiesel synthesis from UFO. FTIR spectroscopy and SEM analyses were used to characterise the catalyst properties. The parameters effects (methanol to oil volume ratio, amount of catalyst loading, and amount of water present in UFO) affecting the biodiesel yields were studied with a correlation with the catalyst properties.

EXPERIMENTAL

Material and Chemicals

BPW was collected from a nearby fruit stall near Gambang, Pahang. They also obtained UFO from a nearby local restaurant. Potassium hydroxide, KOH (99.99%), was purchased from Sigma-Aldrich. Methanol, CH_3OH (99.98%) where QRec supplied it. All chemicals used were in analytical grade.

Preparation of Catalyst

The banana peel waste (BPW) was initially dried in an oven at 105°C for 24 hours. Then, the dried BPW was crushed into small pieces. After that, the ground BPW were soaked in 1M KOH solution for 30 minutes and stirred for 2 hours at 300 rpm without heat. Lastly, the mixture was filtered and calcined in a muffle furnace at 550°C for 2 hours with a ramping rate of 4°C/min under an air environment and labelled as a Modified-BPW catalyst.

Characterisation of Catalyst

Fourier-transformed infrared (FTIR) spectroscopy analysis was done using a single-reflection of attenuated total reflectance (ATR) technique in IR Tracer-100 spectrophotometer with a resolution of 4 cm^{-1} in the 4000-400 cm^{-1} IR range.

The morphology and elemental analysis of the catalyst were observed by SEM using a FEI Model Quanta 450 microscope equipped with an energy-dispersive x-ray (EDX) analyser operated at 15 kV.

Catalytic Activity

Transesterification reactions were carried out in a three-neck round bottom glass flask (250 mL) equipped with a reflux condenser, a thermometer and a digital hot plate with a magnetic stirrer. Firstly, methanol to UFO molar ratio (3:1, 6:1, 9:1, 12:1, 15:1), amount of catalyst loading ((1, 2, 3, 4, 5) wt.%), and amount of water content present in UFO ((0.25, 0.5, 0.75, 1) wt.%) were varied in a fixed reaction mixture at 65°C for 2 hours. The mixture was mixed with vigorous stirring for 2 hours in a silicone oil bath to minimise the mass transfer limitation. After completion of the reaction, the heating was stopped, and the used catalyst was separated from the reaction medium by filtration. Then, the mixture was moved to the separating funnel and left for 24 hours to allow the liquid containing biodiesel and glycerol to separate. Lastly, the biodiesel yield was calculated as the following [8]-[9]:

$$Biodiesel\ yield\ (\%) = \frac{Amount\ of\ biodiesel\ (g)}{Mass\ of\ UFO\ (g)} \times 100\ \% \quad (1)$$

EXPERIMENTAL RESULTS

Characterisation of Catalyst

The FTIR spectra for both BPW and Modified-BPW catalysts are presented in Figure 1. As observed, both spectra have shown similar band patterns. However, there were some differences in the intensity, as the spectrum of the Modified-BPW catalyst was higher than

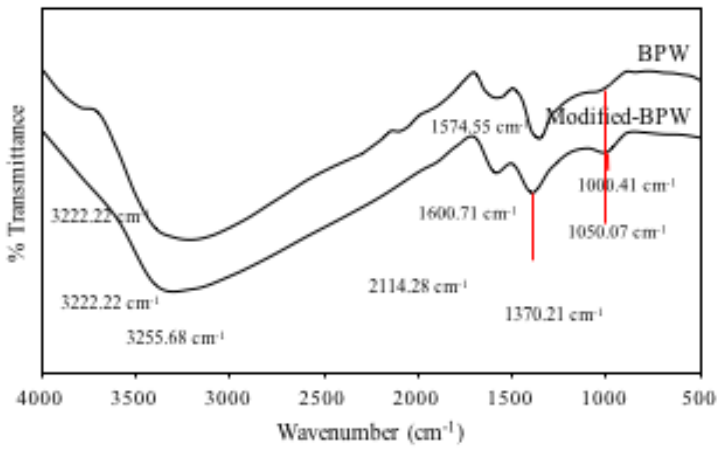

Figure 1 FTIR spectra of both banana peel waste and modified banana peel waste catalyst

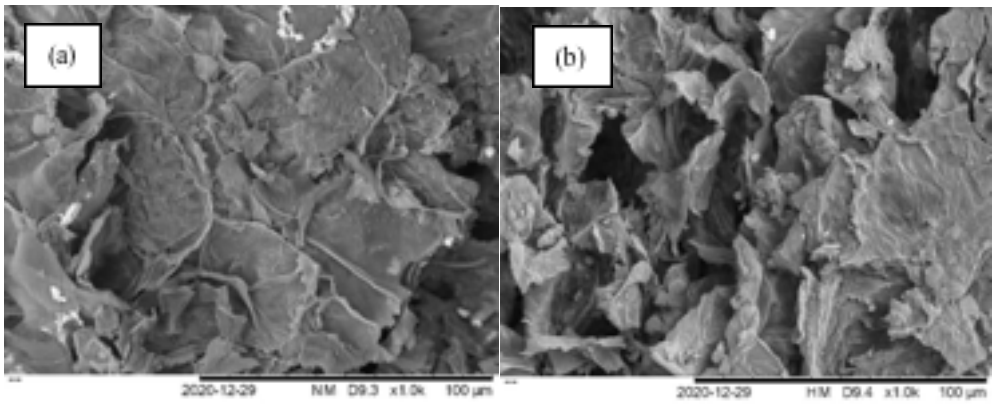

Figure 2 SEM images of (a) the banana peel waste and (b) the modified banana peel waste

BPW. The spectra of BPW and Modified-BPW catalysts were displayed at bands between 4000 and 500 cm^{-1}, respectively, which can be assigned to the presence of cellulose-hemicellulose-lignin matrix.

Specifically, the BPW characteristic band at 3222 cm^{-1} can be assigned to O-H stretching, and the band at 2114 cm^{-1} corresponded to the C-C asymmetric stretching, indicating the alkyne group. Then, bands at 1574 cm^{-1} and 1370 cm^{-1} related to the C-O bond were found, which could be derived from CO_2 released during calcination and may be chemisorbed on the alkali compounds [10]. The peak at 1050 cm^{-1} can be associated with the presence of cellulose.

Conversely, for the Modified-BPW catalyst, the characteristic band at 3255 cm^{-1} may be attributed to the O-H vibrations [6] and the band at 1600 cm^{-1}, corresponding to the C-C asymmetric stretching of alkyne. Then, the band at 1400 cm^{-1} was the stretching vibration of O-H of the metal oxide surface [11]-[12] attributed to KOH. The vibrational band of the frequency region at 1000 cm^{-1} was attributed to the stretching vibrations of K-O.

The surface morphology of BPW and Modified-BPW catalysts were examined from the SEM images shown in Figures 2a and 2b. Based on the observed SEM-magnified image, the BPW had a rough and less-porous surface than the Modified-BPW. However, after the BPW modification with KOH, the surface appeared to have more pores in flake structures, making catalytic activity possible in the pore site [13]. The pores can be due to the KOH activation on BPW during the catalyst preparation. This justifies that the dispersion of KOH has occurred all over the surface of BPW, which then causes structural deformation [14].

Performance of the Catalytic Activity

The results for the effect of methanol to oil molar ratio were summarised in Figure 3. The figure proved that the biodiesel yield increases gradually when the molar ratio increases for every transesterification process from 3:1 to 12:1 of molar ratio.

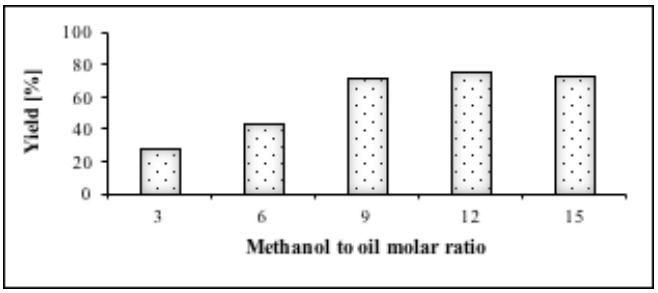

Figure 3 Effect of methanol to oil molar ratio on the biodiesel yield of UFO by using modified banana peel waste

With the rise in the molar ratio, the probability of full interaction between the reactants increases [15]-[16]. This was attributed to the transesterification reaction's reversible behaviours. The biodiesel yield started to decrease after it reached 12:1 of the molar ratio. Therefore, it can be stated that the 12:1 methanol to oil molar ratio was the optimum ratio to achieve an equilibrium state of the reaction. An optimum ratio of 12:1 was claimed by Yusuff et al. [16], who synthesised biodiesel from used cooking oil using coal fly ash-supported zinc oxide as a catalyst.

From the results, it can be explained that increasing the methanol to oil molar ratio increased the process efficiency initially. Still, then the efficiency decreased with increasing methanol content to a certain extent. This can be due to the increasing amount of excess

methanol in the process, which may lead to incomplete transesterification reactions [5]. It happened because increasing the concentration of methanol can diminish the catalyst and oil concentration, which may delay the transesterification reaction and decrease the efficiency of biodiesel yield. Besides that, the phenomena can be attributed to the limited contact between the reactant's stoichiometric ratio. Moreover, it can also interfere with the separation of alkyl ester and glycerol by increasing the solubility of glycerol [17].

Different catalyst loading amounts were tested to determine the optimum value for the percentage of biodiesel yield. It can be seen from Figure 4 that the maximum biodiesel yield was obtained at 1 wt.% of catalyst loading. As the amount of the catalyst loading increased beyond 1 wt.%, the biodiesel yield began to decrease. As more catalyst loading was added, it created diffusion problems because an excess catalyst could disrupt the reaction mixture. According to Al-Muhtaseb et al. [18], increasing the amount of the catalyst when it has achieved the optimal value can trigger problems with reactant interaction with active sites. It was worth noting that, in some cases, increasing the catalyst amount leads to increased viscosity of the reaction medium. As a consequence, the mass transfer rate of the reactants to the catalyst surface decreases, resulting in lower conversions [10]. Product desorption may decrease, although more reactants were adsorbed on the catalyst in an excess catalyst quantity, which results in a decrease in biodiesel yield.

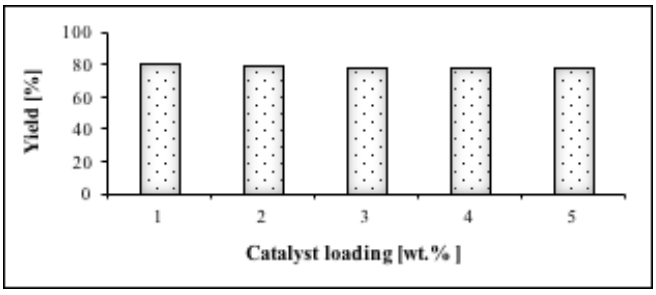

Figure 4 Effect of amount of catalyst loading on the biodiesel yield of UFO by using modified banana peel waste

In order to determine the maximum water resistance of the catalyst, the transesterification reactions of UFO were performed against different amounts of water in the reaction mixture. The result of biodiesel yield produced for the different amounts of water content is shown in Figure 5. When a small amount of water was added to the mixture, the biodiesel yield gradually

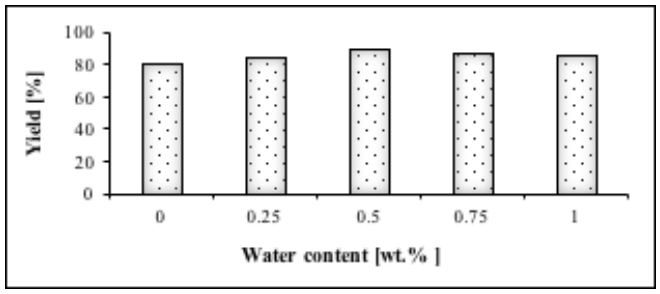

Figure 5 Effect of amount of water content on the biodiesel yield of UFO by using modified banana peel waste

increased until it reached equilibrium. Afterwards, the biodiesel yield reduced as the water content increased from 0.75 to 1 wt.%. The presence of water was proposed by Karmakar and Halder [19] to benefit the reaction mixture as it facilitates the hydrolysis of the triglycerides found in the liquid, producing FFAs. The formation of FFAs raises the reaction rate, so it was possible to esterify the FFAs, thereby raising the biodiesel yield. Extending the amount of water present in the reaction mixture beyond the limitation has led to a decrease in the biodiesel yield. The reason was the presence of moisture and FFA in the feedstock resulted in a side reaction, which paved the way for emulsion and soap formation. Therefore, the reaction mixtures become more viscous, making biodiesel separation from the product stream difficult and, consequently, leading to a reduction in biodiesel yield [20].

CONCLUSION

As a result, a highly potential and renewable heterogeneous catalyst derived from BPW for biodiesel production from UFO has been reported. Based on the transesterification reaction conducted in this study, there was approximately 88.7% of biodiesel produced when 12:1 of methanol to oil molar ratio with 1 gwt.% of catalyst loading was used at 2 hours of reaction time at 65°C and the present 0.5 wt.% of water content in the reaction mixture. The results of this work portrayed that the Modified-BPW catalyst confirms the suitability of the catalyst for the transesterification reaction of UFO to produce biodiesel.

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