Effect of Rhombohedral and Spherical BiFeO₃ Catalyst on Biodiesel Production from Waste Cooking Oil

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ABSTRACT: The present investigation deals with the transesterification of waste cooking oil (WCO) in the presence of bismuth ferrite (BiFeO₃) with different morphologies (rhombohedral and spherical) as catalysts for biodiesel production. The rhombohedral BFO was synthesised via biotemplated sol-gel technique in the presence of carrageenan, whereas the spherical was synthesised using the hydrothermal method. The average particle sizes of the rhombohedral and spherical BiFeO₃ were found to be 88 nm and 15 μ m, respectively. In addition, the crystallite sizes of the rhombohedral (19.39 nm) were smaller than the spherical (71.83 nm) catalyst. The WCO applied in this study contained a high amount of palmitoleic acid, palmitic acid and stearic acid to be converted into their methyl esters in the presence of both catalysts. The best condition for a maximum yield of fatty acid methyl esters (FAME) using the rhombohedral BiFeO₃ as catalyst was 1:6 oil to methanol molar ratio, 0.02 g mass of catalyst, 80°C reaction temperature and one hour of reaction time while for spherical sample, it required a 0.03 g catalyst mass, reaction temperature of 110°C within 3 h with 1:12 oil to methanol molar ratio. The rhombohedral

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catalyst showed better performance than the spherical catalyst in producing maximum methyl esters with low temperatures and a short time.

Keywords: waste cooking oil, biodiesel, bismuth ferrite, methyl esters, heterogeneous catalyst, transesterification

1. INTRODUCTION

The rise in oil demand due to the severe fuel shortage in the world increases fuel prices.¹ Such a phenomenon leads to the development of alternative energy or the substitute for petroleum-based diesel fuels. Chemically known as fatty acid methyl esters (FAME), biodiesel is a non-petroleum biodegradable fuel free from sulphur and other aromatic compounds.² It is eco-friendly and sustainable with low exhaust emission, low toxicity, high flash point, better lubricity, is more renewable and can be utilised with no engine modification; enabling it to serve as an alternative for diesel fuel in the automotive.^{3–6} Biodiesel can be produced from vegetable oils, such as soybeans, sunflower, palm oil, castor oil and rapeseed. However, for some reasons, including unnecessary clearing of forests and food versus fuel competition, it is challenging to commercialise biodiesel from these sources.⁷

Waste cooking oil (WCO), called gutter oil, is the oil residue obtained after cooking, with an annual production of about 16.5 million tons.⁸⁻¹⁰ It is one of the most cost-effective selections to yield biodiesel, yet it's illegally dumped into rivers and landfills, leading to environmental pollution.^{11,12} Biodiesel can be produced through the chemical reactions of alcohols and long-chain fatty acids.¹³ However, uncatalysed biodiesel production is expensive, require more energy, reaction time and under other extreme conditions.¹⁴ In view of that, homogeneous and heterogeneous catalysts are employed for biodiesel production.^{15,16}Among these methods, heterogeneous catalysts are eco-friendly, easy to separate and reusable.¹⁷

Nowadays, various natural and synthetic materials have been used as heterogeneous catalysts for biodiesel production.¹⁸ Among the heterogeneous catalysts, calcium oxide (CaO) is frequently reported for transesterification reactions due to its low production cost, high basicity, low solubility and non-corrosive nature.^{19,20} Unfortunately, CaO causes upper respiratory tract, eyes and skin irritation, ulceration, pneumonia, vomiting and diarrhoea, necessitating the exploration of other metal oxides for transesterification.^{21,22}

Bismuth ferrite (BiFeO₃) is one of the heterogeneous catalysts that received significant attention in catalysis.²³ It is chemically stable, has excellent magnetic

property and exhibits room-temperature multiferroic behaviour.^{24–26} In our present study, the effect of BiFeO₃ morphology in catalysing a transesterification process would be studied for the first time. Because of that, we target synthesising rhombohedral and spherical BiFeO₃ for use as catalysts to produce biodiesel from WCO. Apart from characterisations of the catalysts, different parameters for the best transesterification process, including the oil to methanol molar ratio, reaction temperature, catalyst loading and reaction time, would also be investigated.

2. MATERIALS AND METHODS

2.1 Materials

Bismuth nitrate pentahydrate (Bi(NO₃)₃.5H₂O), iron nitrate nanohydrate (Fe(NO₃)₃.9H₂O) and carrageenan were obtained from Sigma-Aldrich. Hydrochloric acid (HCl) (37%), potassium hydroxide (KOH) and sodium hydroxide (NaOH) pellets were provided by R&M Chemicals. Other chemicals used were anhydrous methanol (QReC, 99.7%), hexane (QReC, 99.7%), ethanol (QReC, 99.7%), diethyl ether (QReC, 99.7%) and external standard FAME Mix C4-C24 (Supelco). All WCO was collected from student cafeteria, Universiti Sains Malaysia (USM), Penang. All these chemicals were used without additional purification unless otherwise stated.

2.2 Synthesis of BiFeO₃ with Rhombohedral Morphology

The rhombohedral BiFeO₃ nanoparticles were synthesised using carrageenan as the biotemplate.²⁷ Bi(NO₃)₃.5H₂O (1.4201 g, 3 mmol) and Fe(NO₃)₃.9H₂O (2.0202 g, 5 mmol) were dissolved in distilled water and transferred to 25 ml volumetric flask. A total of 10 ml of the mixture solution was added to 1 wt% (1 g in 100 ml distilled water) carrageenan solution. The pH of the solution was adjusted to pH 10 with 1.0 M NaOH solution and stirred for 2 h. The solution was dried overnight at 80°C in an oven to form a gel-like mixture. The mixture was calcined at 550°C for 2 h. The powder formed was washed with distilled water and ethanol to remove impurities and leftover precursors.

2.3 Synthesis of BiFeO₃ with Spherical Morphology

The spherical morphology of BiFeO₃ nanoparticles was synthesised using the hydrothermal method.²⁸ Bi(NO₃)₃.5H₂O (1.4553 g, 3 mmol) and Fe(NO₃)₃.9H₂O (1.2120 g, 3 mmol) were dissolved in 10 ml dilute nitric acid solution. 6 M of KOH solution was added to the solution dropwise under magnetic stirring, and a dark brown suspension solution was formed. The solution was ultrasonicated for

8 min, followed by vigorous stirring for 30 min. The mixture was then sealed in a Teflon-lined stainless-steel autoclave and heated at 200°C for 6 h. The mixture was cooled to room temperature, and the resultant dark brown precipitate was washed with distilled water and ethanol to remove the salt impurities. The precipitate was dried in an oven at 80°C for another 12 h.

2.4 Catalysts Characterisation

The morphology of the catalysts was determined using field emission scanning electron microscopy (FESEM FEI-QUANTA FEG 650, Oregon, USA) model equipped with energy dispersive X-ray (EDX) system Oxford instrument X-MAX. The samples' phase structure and purity were determined using X-ray diffraction (XRD Bruker D8 Advance, Bruker Instrument, Germany) with Ni-filtered Cu-K α radiation ($\lambda = 0.1541800$), operating at 40 kV and 40 mA. The chemical composition of the samples was determined using Fourier transform infrared spectroscopy (FT-IR) Perkin Elmer 2000 (Perkin Elmer Instrument, USA).

2.5 Determination of Waste Cooking Oil Properties

2.5.1 Density

An empty 10 ml volumetric flask was weighed, and 10 ml of WCO was poured into the volumetric flask. The increased in mass was determined. The density of WCO was calculated using the formula:

2.5.2 Acid Value

The acid value of the waste cooking oil was determined by the American Oil Chemists' Society (AOCS) official method.²⁹ A total of 5 g of fatty acids was weighed into a 500 ml Erlenmeyer flask and 75 ml of hot neutral ethanol was added to the fatty acids. Agitation and heating were required to dissolve the fatty acid into the solution completely. About 0.5 ml of phenolphthalein indicator solution was added, and titration of the solution was carried out immediately with 0.5 M NaOH to the first pink colour for 30 s.

Acid value = (volume of titrant, $ml \times M \times 56.10$)/(mass of test portion, (g)) (2)

Where M = molarity of accurately standardised sodium hydroxide

2.5.3 Saponification Value

The saponification of the WCO was determined using the official analysis methods of Association of Official Analytical Chemists (AOAC).³⁰ About 1.0 g of WCO was dropped into the conical flask, and 15 ml of 1 N potassium hydroxide solution and 10 ml of distilled water were added to the flask. The mixture was heated under a reserved condenser for 30 min to ensure the oil sample completely dissolved into the solution. The sample was cooled down and two drops of phenolphthalein was added into the solution. It was then titrated with 0.5 M HCl until a pink endpoint was reached. A blank was determined with the same condition.

The saponification value of the WCO was determined using the formulae:

Saponification value of $= \operatorname{mg}$ of KOH consumed by 1 g (3) the number of fat of fat (3) Weight of KOH $= \operatorname{normality}$ of KOH \times equivalent weight \times volume of KOH in L

Volume of KOH consumed by 1 g of fat
$$=$$
 [Blank – test] ml (5)

2.5.4 Average Molecular Weight

The average molecular weight of the WCO was determined using the formula:³¹

$$M = 56.1 \times 1000 \times 3 / (SV - AV)$$
(6)

Where AV is the acid value (mKOH/ moil, mg/g) and SV is the saponification value (mKOH/ moil, mg/g).

2.6 Transesterification of WCO

The transesterification of the WCO with methanol was carried out based on the research reported by Madhuvilakku and co-workers with some modifications.³² The reaction was carried out using a 250 ml 3-necked round bottom flask immersed in paraffin oil. A total of 10 ml WCO was poured into the flask, and 0.0200 g of catalyst was added. Magnetic was stirrer placed in the flask. The flask was immersed in the paraffin oil equipped with a reflux condenser. The mixture was heated to 100°C for 10 min before adding 2.64 ml of methanol into the flask to

remove the moisture content in the mixture. The oil to methanol molar ratio used was 1:6. The mixture was vigorously stirred and refluxed for 1 h at the reaction temperature. After the reaction, the product was cooled down to room temperature before centrifuging and extracting the FAME with hexane for gas chromatography-flame ionisation detector GC-FID analysis, (Agilent Technologies 7890A, Agilent, Wilmington, DE, USA).

2.7 Analysis of the Conversion of FAME

2.7.1 Gas Chromatography-Flame Ionisation Detector (GC-FID)

The FAME was analysed using gas chromatography equipped with FID (Agilent Technologies 7890A, Agilent, Wilmington, DE, USA). The capillary column Elite 5 (30 m \times 0.25 mm, 0.25 μ m) and nitrogen carrier gas were used. The injector volume was 1 μ l, the injector temperature and oven temperature were both 275°C. Oven temperature programming was used for the analysis with the initial temperature of 140°C, initial holding time of 0 min, ramping rate of 10°C/min, final temperature of 275°C and final holding time of 1.5 min. The flow rate of the carrier gas was 1.5 ml/min and the 10:1 split ratio was used. The FAME percentage was calculated using the following equation.

%FAME =
$$(Total area of FAME peaks)/(Total area of all peaks-Area of solvent peak) \times 100\%$$
 (7)

2.7.2 Gas Chromatography-Mass Spectrometry (GC-MS)

The FAME, WCO and standard were analysed using Shimadzu GC-2010 Plus gas chromatography (Shimadzu, Japan) equipped with a mass spectrometer (MS). The capillary column BPX5 (30 m \times 0.25 mm, 0.25 µm) was used. The carrier gas used was helium. The injector volume was 1 µl, the injector temperature and oven temperature were both 275°C. Oven temperature programming was used for the analysis with the initial temperature of 140°C, initial holding time of 0 min, ramping rate of 10°C/min, final temperature of 275°C and final holding time of 1.5 min. The flow rate of the carrier gas was 1.5 ml/min and the 10:1 split ratio was used. The mass spectrometer ion source temperature was set to 200°C, interface temperature 300°C, tuning mode standard, measurement mode scan from m/z 40 to 900, the event time 0.3 s and ionisation voltage 70 V.

3. RESULTS AND DISCUSSION

3.1 Morphology and Elemental Analysis of Catalyst

Figures 1(a) and (b) shows rhombohedral shape BiFeO₃, while Figures 1(d) and (e) shows the spherical BiFeO₃. The average particle sizes of the rhombohedral and spherical BiFeO₃ are 88 nm and 15 μ m, respectively. Figures 1(c) and (f) show the EDX spectrum of rhombohedral and spherical BiFeO₃. The weight percentage of rhombohedral BiFeO₃ consisted of Bi (53.46%), Fe (25.34%), O (19.87%) and Na (1.34 %). The weight percentage of the spherical BiFeO₃ consisted of Bi (68.36%), Fe (16.30%), O (15.18%), and K (0.17%). Low amounts of sodium and potassium are present in the sample due to the incomplete washing of the catalysts.



Figure 1: (a,b) FESEM images of rhombohedral, (c) EDX spectrum of rhombohedral, (d,e) spherical and (f) spherical BiFeO₃ with a magnification of 4,000× and 60,000×.

3.2 X-ray Diffraction (XRD) Analysis

The powder XRD analysis of both the crystal planes morphologies of BiFeO₃ were presented in Figures 2(a) and (b). Figure 2(a) showed the reflection from (0 1 2), (1 0 4), (1 1 0), (0 0 6), (2 0 2), (0 2 4), (1 1 6), (1 2 2), (2 1 4), (3 0 0), (2 0 8) and (2 2 0) planes at 2θ values 22.41°, 31.75°, 32.06°, 38.94°, 39.47°, 45.76°, 51.27°, 51.70°, 56.97°, 57.14°, 66.34° and 67.06° that matched the JCPDS file 01-086-1518 which corresponded to the bismuth iron oxide of rhombohedral structure R-3c. The highest intensity peak appeared at the (1 1 0) plane which corresponded to the $2\theta = 32.06^{\circ}$. The crystallite size calculated using the Scherrer's equation was 71.83 nm. The diffraction pattern for spherical $BiFeO_3$ as presented in Figure 2(b) showed the reflection from (0 0 6), (1 1 0), (1 1 6), (0 2 0), (0 2 6), (2 2 0), (1 1 12), (1 3 0), (0 2 12), (1 3 6), (2 2 12) and (0 4 0) planes at 2θ values 22.52°, 22.66°, 32.18°, 32.28°, 39.73°, 46.31°, 51.88°, 52.15°, 57.32°, 57.50°, 67.33° and 67.57° that matched the JCPDS files 01-073-3907 which corresponded to orthorhombic structure Ibam. The spherical BiFeO₃ also matched the JCPDS file 01-072-2112 peaks at 22.48°, 31.91°, 32.20°, 39.51°, 45.90°, 51.52°, 51.80°, 56.76°, 57.11°, 57.26°, 66.65° and 67.16° which indexed to the diffraction plane $(1 \ 0 \ 1)$, $(0 \ 1 \ 2)$, $(1 \ 1 \ 0)$, $(0 \ 2 \ 1)$, $(2 \ 0 \ 2)$, $(1 \ 1 \ 3)$, $(1 \ 0 \ 4)$, (2 1 1), (1 2 2), (3 0 0), (0 2 4) and (2 2 0), respectively. The structure is in agreement with JCPDS file 01-072-2112 that of corresponded to rhombohedral structure R-3m. It is interesting to note the spherical BiFeO₃ showed the combination of rhombohedral and orthogonal phase of bismuth iron oxide. The combination phases may lead to the formation of spherical structure of the sample. The average crystallite size of the sample calculated using Scherrer's equation was found to be 19.39 nm which was calculated using the highest intensity peak appeared at the (1 1 0) plane at $2\theta = 32.20^{\circ}$. The difference of the relative intensity for each diffraction planes between the rhombohedral and spherical BiFeO₃ were due to the difference in their crystal morphology.³³



Figure 2: The XRD spectra of the rhombohedral and spherical BiFeO₃.

3.3 Fourier transform infrared (FTIR) Spectroscopy

Figure 3 shows the FTIR spectrum of both catalysts. Weak absorption band at 3,453 cm⁻¹ was assigned to the terminal hydroxyl group in both samples, and the peak at 1,618 cm⁻¹ indicated the H-O-H bending vibration of water.³⁴ The characteristic peak at 1,384 cm⁻¹ corresponded to the N-O stretching modes of the NO₃⁻ ions.³⁵ The spherical BiFeO₃ has strong peaks at 445 cm⁻¹ and 559 cm⁻¹ corresponds to the Fe-O stretching and bending vibrations, respectively.³⁶ The presence of these peaks indicated the formation of perovskite structure in BiFeO₃. For the rhombohedral BiFeO₃, significant peaks at 447 cm⁻¹ and 568 cm⁻¹ resemble the Fe-O stretching and bending vibrations, respectively. The peak at 1630 cm⁻¹ indicated the H-O-H bending vibration of water, and the broad bands at 3,200 cm⁻¹ to 3,400 cm⁻¹ were assigned to the O-H stretching, confirming the existence of water molecules in the sample.



Figure 3: FTIR spectrum of spherical and rhombohedral BiFeO₃.

3.4 N₂ Adsorption – Desorption

 N_2 adsorption – desorption isotherm method was used in studying the specific surface area of rhombohedral and spherical BiFeO₃ (Figure 4). The specific surface area of rhombohedral BiFeO₃ is 5.98 m²/g and that of spherical BiFeO₃ was found to be 1.44 m²/g. From the values, rhombohedral BiFeO₃ is found to have large surface area, an indication that it can offer a greater number of active sites for catalytic reaction.³⁷



Figure 4: N₂ adsorption – desorption isotherm for (a) spherical and (b) rhombohedral BiFeO₃.

3.5 **Properties of WCO**

The density of the WCO determined at 20°C was 0.91135 g/ml. The acid and saponification values determined were 10.54 mg KOH per gram and 211.36 mg KOH per gram. The resulted molecular weight of the WCO was 838.21 g/mol. The higher the saponification value, the lower the biodiesel yield.³⁸ The molecular weight of the WCO was determined to be close to the palm oil's average molecular weight 847.3 g/mol.³⁹

3.6 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The analysis revealed that the WCO obtained contained 46.98% of palmitoleic acid $(C_{16}H_{30}O_2)$. The second highest percentage compound was palmitic acid $(C_{16}H_{32}O_2)$ of 29.47% which can be obtainable naturally in palm oil and palm kernel oil. Next, stearic acid was 12.48% and diglyceride such as glycerol 1,3-dihexadecanoate was obtained to be 0.20% while squalene was 4.88% from WCO. Other compounds such as myristic acid, margaric acid, vitamin E acetate and vitamin E were also detected in the WCO. Only 0.23% oleic acid and 0.40% of linoleic acid were presence in the WCO which might be due to the cooking process of the palm oil. The retention time for WCO is shown in Figure S1. Similarly, the retention time for FAMA is shown in Figure S2.

3.7 Transesterification of WCO Using Rhombohedral and Spherical BiFeO₃

Transesterification analysis has been carried out to determine the calculation of reaction parameter to produce FAME content of the WCO. The most significant evaluation is the effect of different morphologies of BiFeO₃ towards the yield of product obtained. A rhombohedral and spherical BiFeO₃ have been used in the reaction of 10 ml of WCO with methanol under different parameters such as oil to methanol molar ratio, reaction temperature, mass of catalyst and the reaction time. The analysis of the percentage FAME content was determined by GC-FID (Figure S3).

3.7.1 Effect of oil to methanol molar ratio and catalyst dosage

Figure 5(a) shows the effect of oil to methanol molar ratio. As the ratio increased from 1:3 to 1:6, the percentage yield of FAME was not increased significantly for the rhombohedral BiFeO₃. Nevertheless, the percentage yield of FAME in the presence of spherical BiFeO₃ slightly increased from 49.82% to 51.03%. Further increase in the molar ratio of oil to methanol resulted in a reduction in FAME production for the rhombohedral catalyst. Meanwhile, the percentage of biodiesel production using the spherical BiFeO₃ did not improve further. The increased amount of methanol promoted the methoxy species formation on the catalyst surface, which shifts the chemical equilibrium toward forming the FAME.⁴⁰ A huge amount of methanol in the system decreases the conversion rate because glycerol dissolves in the excessive methanol and thus prevents the reaction of the methanol and the triglycerides. The maximum FAME production for rhombohedral BiFeO₃ appeared at 1:12 oil to methanol molar ratio with the 53.45% rate of conversion.



Figure 5: The graph of FAME yield at different (a) molar ratio of oil to methanol and (b) mass of catalyst.

Figure 5(b) shows the effect of catalyst dosage on the conversion rate. The FAME conversion in the presence of spherical BiFeO₃ increased up to 55.72%. The optimum yield of the spherical BiFeO₃ occurred at 0.0300 g. A higher amount of catalyst is required for biodiesel conversion using the spherical BiFeO₃. Rhombohedral BiFeO₃ required a maximum amount of 0.0200 g of catalyst to increase the conversion to 57.24% yield in the transesterification process. The increased amount of rhombohedral BiFeO₃ from 0.0100 g to 0.0200 g significantly increased the yield, to approximately 6.5%. However, a further increase in the catalyst amount decreased the biodiesel production yield due to the increased viscosity of the reaction mixture.⁴¹

3.7.2 Effect of reaction temperature and time

The percentage conversion of FAME in the presence of spherical BiFeO₃ increased from 42.90% to 54.01% with increase in temperature, as depicted in Figure 6(a). Pukale and co-workers reported that the increment of the reaction temperature increased the solubility of the methanol in oil, thus resulting in a higher yield of product.⁴² In the presence of spherical BiFeO₃, the highest conversion of 54.01% was observed at the reaction temperature of 110°C. In contrast, the rhombohedral BiFeO₃ achieved a maximum conversion rate at 80°C, giving a yield of 60.06%. Further increase in the temperature resulted in a slight decrease in FAME production, as methanol exists in a vapour state and the phase difference cause higher mass transfer resistance.⁴³ The analysis revealed that the rhombohedral BiFeO₃ required only 1 h to reach the maximum yield of FAME production. Further increase in the reaction time decreased the FAME yield. In the presence of spherical BiFeO₃, a different trend was observed whereby the percentage of

biodiesel produced slowly increased over time. In general, the highest percentage of FAME was 67.38% in 3 h in the presence of the spherical $BiFeO_{3}$, while the rhombohedral shapes produced 60% yield within 1 h.



Figure 6: The graph of FAME yield against the (a) reaction temperature and (b) reaction time.

4. CONCLUSION

BiFeO₃ with different morphologies have been successfully synthesised. The rhombohedral and spherical BiFeO₃ have average particle sizes of 88 nm and 15 µm, respectively. The XRD confirmed the rhombohedral R-3c structure obtained for BiFeO₃ and the spherical BiFeO₃ has both the orthorhombic structure Ibam and rhombohedral structure R-3m. The average crystallite sizes for rhombohedral and spherical BiFeO₃ calculated from the Scherrer's equation were 71.83 nm and 19.39 nm, respectively. The optimised condition to yield 60.06% biodiesel in the presence of rhombohedral BiFeO₃ was 1:6 oil to methanol molar ratio, 0.0200 g mass of catalyst, reaction temperature at 80°C and 1 h reaction time. The optimised condition for spherical BiFeO₃ occurred at 1:12 oil to methanol molar ratio, the mass of catalyst required 0.0300 g, the reaction temperature higher than 110°C and the reaction time for the process greater than 3 h. The findings from this study revealed that all the structures of BiFeO₃ do not share the same condition for maximum production of fatty acid methyl ester using methanol and WCO as the reactants. Nevertheless, the rhombohedral BiFeO₃ significantly appeared to be more porous with larger surface area resulting in a better performance than $BiFeO_3$ in a spherical shape.

5. ACKNOWLEDGEMENTS

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Supplementary Material



Figure S1: Chromatogram of the GCMS analysis of the waste cooking oil.

The retention time of the major compounds presence in the waste cooking oil

Retention time (min)	Compounds
8.797	Palmitic acid
10.543	Palmitoleic acid
10.676	Stearic acid
16.599	Squalene



Figure S2: Chromatogram of the GCMS analysis of the product (FAME).

The retention time of the	FAME present in the product

Retention time (min)	Compounds
4.310	Methyl laurate
6.237	Methyl tetradecanoate
8.262	Methyl palmitate
9.992	Methyl oleate
10.203	Methyl stearate



Figure S3: Chromatogram of the GC-FID analysis of the product (FAME).