Synthesis of Waste Cooking Oil Based Biodiesel via Ferric-Manganese Promoted Molybdenum Oxide / Zirconia Nanoparticle Solid acid Catalyst: Influence of Ferric and Manganese Dopants

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Abstract: The utilization of ferric-manganese promoted molybdenum oxide/zirconia (Fe-Mn- MoO₃/ZrO₂) (FMMZ) solid acid catalyst for production of biodiesel was demonstrated. FMMZ is produced through impregnation reaction followed by calcination at 600°C for 3 h. The characterization of FMMZ had been done using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), temperature programmed desorption of NH₃ (TPD-NH₃), transmission electron microscopy (TEM) and Brunner-Emmett-Teller (BET) surface area measurement. The effect of waste cooking oil methyl esters (WCOME's) yield on the reactions variables such as reaction temperature, catalyst loading, molar ratio of methanol/oil and reusability were also assessed. The catalyst was used to convert the waste cooking oil into corresponding methyl esters (95.6%±0.15) within 5 h at 200°C reaction temperature, 600 rpm stirring speed, 1:25 molar ratio of oil to alcohol and 4% w/w catalyst loading. The reported catalyst was successfully recycled in six consecutive experiments without loss in activity. Moreover, the fuel properties of WCOME's were also reported using ASTM D 6751 methods.

Key words: ferric-manganese promoted molybdenum oxide/zirconia (FMMZ), waste cooking oil methyl esters (WCOMES), crystallite size, Debye-Scherrer's relationship

1 INTRODUCTION

With decreasing fossil based-oil supply and outrageous increase in the cost of petroleum fuels, joined to the raise in green anxiety and recent financial decline, thus it would be vital to expand environmentally uncontaminated and power-competent skills for synthesizing maintainable outcomes¹⁾. Waste cooking oil methyl ester, a biofuel that can directly substitute for petroleum diesel fuels has gained much attention due to its renewable nature, green properties, calorific value, low toxic emission, carbon neutral, environmental benefits and their low cost²⁻⁴⁾. The costs of biofuel production would be more enhanced upon utilization of inexpensive raw materials e.g. spent cooking vegetable oil. Yet, the cheapest acidic oil incompatible for the preparation of biodiesel via liquid basic catalysts since this process is associated with a very complicated product purification protocol and serious impact to the environment⁵⁾.

Planning to reduce problems related to the liquid catalysis system a number of solid catalysis systems had been recommended^{6, 7)}. These systems are able to minimize the need for separation and washing protocol assist regeneration and reusability of the catalyst⁸⁾. Moreover, this group suggests efficient, environmental, industrial and financial gains which are significant factors towards enhanced and efficient procedure for preparation of biodiesel⁹⁾.

The growth of heterogeneous catalyst has been quite recent area of research in production of biodiesel. Generally, the heterogeneous catalysts have highest density of both basic and acidic Brönsted-Lowry and Lewis active centres further, this feature is recognized like enter parameter to their activity in the preparation of biodiesel^{10, 11)}. Additionally, catalysts incorporated tungsten-molybdenum metal had been comprehensively assessed in many operations such as isomerisation, cyclic alkenes, oxidation,

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alcohol dehydration and biodiesel synthesis¹²⁾. Moreover, the biodiesel production via various kinds of acidic heterogeneous systems such as molybdated supported on silica and molybdenum oxide doped zirconia has been reported by K. Jacobson *et.al.*¹¹⁾. It was found that, the biodiesel yield achieved was 60 and 71%, respectively. In our previous study¹³⁾, we developed Fe-Mn-W-Zr catalyst which showed high density of active sites, whereas in the current study, the incorporation of Fe-Mn dopant may increase the surface area and amount of active sites of Fe-Mn- MoO₃/ZrO₂ catalyst.

As far as our knowledge, no effort was made till now on biodiesel synthesis utilizing ferric-manganese promoted molybdenum oxide/zirconia (FMMZ) catalyst. In this study the catalytic activity of FMMZ was assessed in a simultaneous synthesis of biodiesel employing spent acidic triglyceride. The characterization has been done using XRD, TPD-NH₃, TGA, BET, EDS, TEM and XPS. Moreover, the influence of reaction factors including temperature of the process, loading of catalyst, time, spent oil/methyl alcohol ratio and recycling have also discussed. Efforts were also made to characterize the produced biodiesel and some of important fuel properties according to ASTM methods.

2 EXPERIMENTAL

2.1 Chemicals and Materials

Sample of waste cooking oil was obtained from local market - Serdang Malaysia. A total of 7.5 kg of oil was used for the optimization of biodiesel production process. The materials ferric nitrate nonahydrate, manganese nitrate tetra hydrate and ammonium molybdate tetra hydrate (99.0%), zirconium oxy chloride and ammonium hydroxide (28 – 30%) were obtained from (Sigma- Aldrich-Malaysia) and employed in the preparation of the catalyst^{13, 14)}.

2.2 Pre-treatment of Feedstock

For a completion of the simultaneous reaction and high yield of biodiesel from acidic oil the oil must be free of water and other impurities. Initially, the received feedstock was heated for 6 h at 105°C to remove water and debris of food. The free fatty acid (FFA) content was determined by a standard titration method¹⁴⁾.

2.3 Characterization of Waste Cooking Oil

Determinations of acid and saponification value of the waste cooking oil were carried out according to the standard AOCS methods¹⁵⁾.

2.4 Catalyst Preparation

7.5 g of hydrate zirconyl oxychloride ZrOCl₂ were dissolved in about 150 ml of deionised water, drop wise addition of 3.95 gm of a 30% aqueous solution of ammonia led

to precipitation; as much of the ammonia solution was added as was necessary to reach a pH in range of (9-10). The precipitate was aging for 12 h filtered by vacuum, washed several times until a negative test of chloride ion and dried for about 24 h at 120°C.

Fe(NO₃)₃·9H₂O (1.728 g), Mn(NO₃)₂·4H₂O (0.3645 g) and ammonium molybdate tetra hydrate (5.481 g) were dissolved in about 150 ml of deionised water in amounts corresponding to the desired stoichiometry and the solution was added drop wise under vigorous stirring to zirconium oxyhydroxide solution and the mixture was left under vigorous stirring at room temperature for 4 h. The mixture is then dried at 120°C for 12 h then calcined at 600°C for 3 h¹³⁾.

2.5 Catalyst Characterization

The powder X-ray diffraction analysis was carried out using a Shimadzu diffractometer model XRD 6000. The diffractometer employing Cu-K α radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The Cu-K α radiation was generated by Philips glass diffraction X-ray tube broad focus 2.7 kW type. The crystallite size D of the samples was calculated using the Debye-Scherrer's relationship^{16, 17)}.

$$D = 0.9 \lambda / (B \cos \theta)$$

Where D is the crystallite size, λ is the incident X-ray wavelength, β is the full width at half-maximum, and θ is the diffraction angle.

XPS spectra were obtained using a modified AXIS ULTRA DLD (KRATOS) photoelectron spectrometer equipped with a hemispherical analyzer. For excitation, AlK α (1486.6 eV) radiation was used. The analyzer was operated in the fixed analyzer transmission mode at 40 eV pass energy. The X-ray gun was operated at 4 mA emission current and 15 kV acceleration voltages. Samples were pretreated under vacuum (1×10^{-9} Torr) at 22 ± 2 for 2 h before measurements. The base pressure of the analyzer chamber was 1×10^{-9} Torr; during data collection the pressure was still always $< 1 \times 10^{-9}$ torr. Binding energy (BE) corresponding to C 1s, Mo 3d, Zr 3d, Fe 2p, Mn 2p and O 1s were measured. All binding energies are relative to C 1s peak taken as 284.5 eV.

The TGA analysis was done on a Mettler Toledo TG-SDTA apparatus (Pt crucibles, Pt/Pt-Rh thermocouple) with the purge gas (nitrogen) flow rate of 30 ml min⁻¹ and the heating rate of 10°C min⁻¹ from room temperature to 1000°C.

The acidity of the catalyst was performed by temperature programmed desorption using NH₃ as probe molecule. The TPD-NH₃ experiment was conducted using a Thermo Finnigan TPDRO 1100 apparatus equipped with a thermal conductivity detector. Approx 0.1 g of catalyst was placed in the reactor treated under 150°C for 15 min in N₂ (20 ml

min⁻¹) and NH₃ in helium gas was ramped at 1°C min⁻¹ for 60 min. the purging with N₂ was done at room temperature for 45 min to remove NH₃ in the gas phase. The analysis of NH₃ desorption was then carried out between 50°C and 900°C under helium flow (15°C min⁻¹, 20 ml min⁻¹) and detected by a thermal conductivity detector.

The elemental chemical composition of the prepared ferric-manganese promoted molybdenum oxide/zirconia acid catalyst was determined by Shimadzu X-ray fluorescence (XRF) with a Rayny EDX-720 spectrometer.

TEM (Hitachi H-7100, Japan) was also used to examine the crystal shape. For TEM analysis the powder was dispersed in deionized water dropped onto carbon-cover copper grids placed on a filter paper and dried at room temperature.

The BET surface area of the catalysts was achieved using Brunauer–Emmer–Teller (BET) method with nitrogen adsorption at -196°C. Analysis was conducted using a Thermo Fisher Scientific S.p.A (model: SURFER ANALYZER) nitrogen adsorption-desorption analyzer.

2.6 Simultaneous Reaction of Waste Cooking Oil

The simultaneous esterification and transesterification reaction of waste cooking oil containing 17.5% free fatty

acids was done using prepared ferric-manganese promoted molybdenum oxide/zirconia acid catalyst in BERGHOF (250 mL) high pressure laboratory reactor (Fig. 1). A different amount of catalyst, methanol and 25 g oil in each were added to the reactor. The reaction was started by stirring at 600 rpm and heated to specified temperature and time. Then, the reaction mixture was cooled to room temperature and the catalyst has been separated by centrifuge (Kubota 4200) at rpm 350 for 20 min¹³. Furthermore, the excess methanol is removed via rotary evaporator.

2.7 Product Analysis

The biodiesel produced was determined by gas chromatography a Shimadzu (GC-14B) with Flame Ionization Detector (FID) detector equipped with Rtx-65 capillary column (30 m × diameter 0.25 mm × 0.25 μm). Helium was used as carrier gas with the initial oven temperature at 100°C held for 0.5 min and subsequently increased to 260°C (hold 10 min) at 20°C/min. Temperatures of the injector and detector were set at 250°C and 280°C, respectively. In each run, 1 μL of the sample was injected into the column. Methyl heptadecanoate was used as the internal standard to calculate the yield of WCOME's. The yield of ester was determined by the following Eq.^{18, 19}.

Fig. 1 The reactor assembly for transesterification reaction.

1-Heater, 2-Safety temperature controller, 3-Reactor vessel, 4-PTFE insert, 5-PTFE O-ring, 6-PTFE lid lining, 7-K-type thermocouple, 8-TPFE covered stirrer, 9-Temperature regulation, 10-Standard fittings (N₂), 11-Pressure measurement, 12-special fittings, 13-Reactor lid, 14-Stirring, 15-Closure, 16-Thermocouple connector line, 17-Stainless steel line (input), 18-Stainless steel line (output), 19, Stirring connector line, 20, Temperature controller line, 21-Controller, 22-Centrifuge, 23- Rotary evaporator, 24- Gas chromatography.

$$\text{Yield of WCOMes (\%)} = (\text{Total weight of methyl esters} \times 100) \div \text{Total weight of oil sample}$$

2.8 Catalyst Reusability and Leaching Tests

The catalyst separated from the reaction mixture through centrifuge at 350 rpm for 20 min. and then filtration was initially washed with hexane to remove non-polar compounds such as methyl esters on the surface. Moreover, the catalyst was washed with methanol to remove polar compounds such as glycerol and finally dried at 120°C for six h. The leaching of the catalyst into the reaction mixture was evaluated with a Rayny EDX-720 spectrometer.

2.9 Fuel Properties

The fuel properties of the WCOME's were analysed subsequently by ASTM methods: cloud point (ASTM D2500), pour point (ASTM D97), kinematic viscosity (ASTM D445), flash point (ASTM D93) and density (ASTM D5002). Triplicate determinations were carried out for every experiment and the data are presented as mean $\pm$ standard deviation.

3 RESULTS AND DISCUSSION

3.1 Characterization of Fe-Mn- MoO₃/ZrO₂ Catalyst

The powder X-ray pattern of the Fe-Mn- MoO₃/ZrO₂ (FMMZ) catalyst calcined at 600°C for 3 h is presented in Fig. 2. The XRD pattern of Fe-Mn- MoO₃/ZrO₂ shows a mixture of both tetragonal and monoclinic crystal system.

Nevertheless, sharp diffraction lines at $2\theta = 30.1^\circ$, 34.8° , 50.1° and 60.0° are due to the tetragonal form of zirconia (JSPDS file No: 00-050-1089 ZrO₂). While the diffraction peaks at $2\theta = 23.4^\circ$, 32.5° , 43.1° and 57.1° are attributed to the monoclinic phase of zirconia (JSPDS file No: 01-079-0764 ZrO₂). Reflections lines appeared at $2\theta = 25.7^\circ$ and 27.3° are due to the molybdenum oxide^{20, 21}. In addition, the strength of the peak matching the monoclinic phase is lower in the ferric-manganese promoted molybdenum oxide/zirconia suggesting the stabilization of the tetragonal phase. The absence of characteristic peaks matching to Fe₂O₃ and MnO imply that the metal oxides were found in the composition of hard solution or it is well distributed in surface of zirconia. The dispersion of Fe₂O₃, MnO particles and MoO₃ assisted stabilization of zirconia tetragonal crystal system²¹. Clearly, Molybdenum resists transformation of zirconia tetragonal crystal system to the monoclinic ones. Yet, there was a research study regarding yttrium and lanthanum oxide as stabilizer for zirconia tetragonal phase via improvement of the particle-border and consequently enhances the surface area of the catalyst²⁰⁻²².

To identify the influence of Molybdenum oxide amount on the FMMZ crystal system the size of zirconia and FMMZ were obtained via Debye-Scherrer's equation. The addition of Molybdenum oxide has been related to the size reduction which changes from 25.5 to 10.0 nm for zirconia (Z) and Fe-Mn- MoO₃/ZrO₂ (FMMZ), respectively. This may be coupled with the Molybdenum oxide which stays bounded to the catalyst surface thus reduce the enlargement of zirconia particles in agreement therefore with the oxides of transition metals, such as titania and stannia²³. Reduction in the size of crystallite could be illustrated with concept

Fig. 2 XRD patterns of Fe-Mn-MoO₃/ZrO₂ (FMMZ) catalyst calcined at 600°C for 3 h. (O) monoclinic phase; (◆) tetragonal phase of zirconia and (♥) MoO₃ Phase.

Table 1 The influence of Ferric and Mn-dopants on the catalytic activity of Fe-Mn-MoO₃/ZrO₂.

Catalyst	Ester yield (%)	BET (m ² /g)	Density of active sites (μmol/g)
ZrO ₂	48.6 ± 1.14	34.5	630.4
MoO ₃ /ZrO ₂	73.0 ± 0.25	37.0	1144.0
Fe-Mn- MoO ₃ /ZrO ₂	95.6 ± 0.15	49.5	2411.0

Fig. 3 TGA of uncalcined FMMZ catalyst.

which points out that, " the dispersed Fe₂O₃ and MnO particles along with MoO₃ species lying on zirconia surface avoiding throughout the calcination process the generation of agglomerated form of them"²⁴⁾.

Generally, the strength and the density of energetic centres have been determined via temperature programmed desorption (TPD) technique. In addition, ammonia and pyridine have been employed as probe indicators for the evaluation of the acid strength and density of energetic centres for acidic heterogeneous catalysis systems.

According to the data obtained from ammonia TPD profile of the Fe-Mn- MoO₃/ZrO₂ catalyst, the total acidic sites density on surface of catalyst has been found to be around 2411.0 μmol/g as shown in Table 1.

TGA analysis of uncalcined FMMZ catalyst is depicted in Fig. 3. The loss of the mass obtained with thermogravimetric study profile consent comparatively with the resultant decomposition to the constituents of catalyst. The TGA profile of the FMMZ consists of two mass losses steps in temperature ranged mainly between 30.0-314 and 315.50-463.0°C, respectively. The first decomposition point starts at about 30°C and ended at 314°C is due to the removal of physisorbed water, ammonia, nitrogen oxides, dehydroxylation process of ZrO(OH)₂ and complete decomposition of metal salts to their free oxides (Ferric oxide, Manganese oxide and MoO₃)²⁵⁻²⁷⁾. The second thermal decomposition phase begins at about 315.5°C reaching constant weight

losses at about 463.0°C. This step corresponds to solid-solid interaction between the metal oxides²⁸⁾. At the same time, the thermogram of FMMZ catalyst does not show any noticeable weight loss at a temperature more than 860°C, which might be attributed to the presence of Fe/Mn/Zr oxide suppressing the evaporation of MoO₃ at higher temperature²¹⁻²⁶⁾.

The BET surface area and average pore diameter of FMMZ catalyst obtained using BET method were 49.5 m²/g and 85.0 nm, respectively. In correspondence to 5.8 nm which ascribes to a diameter of triglyceride, the pore size of ferric-manganese promoted molybdated zirconia catalyst was 85.0 nm, therefore, triglyceride molecule could be easily inter through the pores of FMMZ and allowed the reactants to be in touch with active centres which improves catalytic activity.

In the meantime, the leaching of the prepared Ferric-manganese doped molybdated zirconia solid acid catalyst was determined by Shimadzu X-ray fluorescence (XRF) with a Raynu EDX-720 spectrometer since (EDS) the energy dispersive spectroscopy has been applied to study the elemental composition of the materials^{29, 30)}. Accordingly, the metallic constituent of Fe-Mn-MoO₃/ZrO₂ is presented in Table 2.

Figure 4 displays nanosized crystal shape in the FMMZ catalyst as characterized by TEM. It has been obvious that the FMMZ nanoparticles are in the order of tetragonal system with sizes in a limit of 5-10 nm having standard diameter of ~6.2 nm. Moreover, most of FMMZ nanoparticles have been connected to each other while the others are isolated implies the existence of electrostatic attraction and repulsion among FMMZ nanoparticles.

The Fe-Mn-MoO₃/ZrO₂ (FMMZ) sample displayed an emission peak around 530.0 electron volts assigned to O 1s while the 182.5 eV characteristic of Zr 3d5/2. Thus, the emission line depicted in Fig. 5(a) and (b) attributed to the

Table 2 Quantitative percentage of elements for the fresh and used Fe-Mn-MoO₃/ZrO₂ catalyst.

Catalyst	% Fe ₂ O ₃	% MnO	% MoO ₃
Fresh	2.354	0.558	4.161
fourth run	2.285	0.556	4.149
Seventh run	2.225	0.554	4.135

Fig. 4 TEM of Fe-Mn-promoted molybdenum oxide/zirconia nanoparticles calcined at 600°C for 3 h.

zirconia. **Figure 5(c)** confirms the molybdenum emission peaks of Fe-Mn-MoO₃/ZrO₂ (FMMZ). In addition, the emission line at 233.2 and 235.8 electron volts match to emission peaks generated by 3d5/2 and 3d3/2 electrons of molybdenum, respectively. Nonetheless, the established significances of binding energy have been attributed to Mo (+6)²². **Figure 5(d)** illustrates the photoelectron emission peaks of Fe (+3)-Mn-MoO₃/ZrO₂ (FMMZ) in ferric 2p zone. The ferric 2p3/2 and 2p1/2 photoelectron peaks were appeared at about 711.3 and 724.0 eV, respectively, which maintains the presence of ferric oxide on the Fe-Mn-MoO₃/ZrO₂ surface. This band is apparent confirmation for existence of Fe⁺³ which basically matching to the data reported for ferric oxide³¹. Manganese emission had been identified simply through relatively noisy sign. **Figure 5(e)** depicts the XPS spectrum of Fe-Mn-MoO₃/ZrO₂ catalyst in 2p zone of manganese. Furthermore, 2p3/2 and 2p1/2 photoelectron peaks which appeared around 642.5 and 653.4 eV, respectively, indicated the existence of manganese oxide at the surface of the Fe-Mn-MoO₃/ZrO₂ catalyst.

Fig. 5 XPS spectra of the Fe-Mn-MoO₃/ZrO₂ (FMMZ) (O 1s, Zr 3d) (a-b), (Mo 3d, Fe 2p and Mn 2p) (c-e).

3.2 Catalytic Activity of Fe-Mn- $\text{MoO}_3/\text{ZrO}_2$ Catalyst

3.2.1 Impact of Process Factors on the Esters Yield

The impact of different process parameters which includes temperature of the process, catalyst concentration (wt/wt%), time and molar ratio of alcohol/waste cooking oil on the process employed to synthesize the biodiesel were appraised.

3.2.1.1 The influence of temperature

The temperature of the simultaneous process was recognised to be considerably influenced on the biodiesel yield³²⁾. Thus, the experiments using the FMMZ nanoparticles solid acid catalyst were performed at 80°C up to, 220°C at interval of 20°C. The product improved by raised

the simultaneous process temperature thus attained the maxima at around 200°C with negligible increased in yield at around 220°C as presented in Fig. 6(a). Therefore, the temperature of the process was optimized at 200°C, for the additional study.

3.2.1.2 The Influence of Reaction Time

Figure 6(b) shows the difference of produced biodiesel with duration of the process. At an optimized condition of the process, it has been seen that the biodiesel yield was low at first h. However, while the duration of the process rises the product has been improved gradually until the fourth h and subsequently kept almost persistent. The approximately process equilibrium had been attained about

Fig. 6 Optimization of reaction parameters: (a) Impact of temperature of simultaneous process at 5 h, loading of catalyst 4%, molar ratio of spent cooking feedstock oil /methyl alcohol 1/25 and speed of mechanical mixer 600 rpm. (b) Impact of duration of the simultaneous process using 4% amount of enhancer, ratio of methyl alcohol/ spent cooking feedstock 25/1, temperature of the process 200°C and speed of mechanical mixer 600 rpm. (c) Impact of Fe(+3)-Mn- $\text{MoO}_3/\text{ZrO}_2$ loading throughout 5 h, ratio of methyl alcohol/ spent cooking feedstock 25/1, temperature of the process 200°C and speed of mechanical mixer 600 rpm. (d) Impact of the ratio of methyl alcohol/ spent cooking oil, during 5 h, temperature of the methanolysis process 200°C, speed of mechanical mixer 600 rpm and catalyst dosage 4%wt/w.

95.6% at 5 h of reaction time. Hence, 5 h were considered as an optimum reaction time for preparation of biodiesel employing spent cooking oil via nanoparticles ferric-manganese doped molybdated zirconia solid acid catalyst.

3.2.1.3 The influence of Catalyst Quantity

The catalyst quantity is key parameter that required optimization in order to enhance biodiesel quantity. Thus, higher amount of enhancer has been necessary in improving accessibility of energetic centres. Nevertheless, impact of $\text{Fe} (+3)\text{-Mn- MoO}_3/\text{ZrO}_2$ loading (1-6 % w/w) on WCOME's yield was evaluated utilizing the optimum condition of the process. As shown in Fig. 6(c) rising loading of $\text{Fe} (+3)\text{-Mn- MoO}_3/\text{ZrO}_2$ which begins with 1% (wt/wt) till 6% (wt/wt) result in a clear enhance in the yield from 70 to 96%. However, when the amount of the catalyst rose to 6% wt. the amount of WCOME's insignificantly improved. Therefore, the quantity of $\text{Fe} (+3)\text{-Mn- MoO}_3/\text{ZrO}_2$ catalyst have considerable impact on the quantity of WCOME's. Thus the optimum quantity of $\text{Fe} (+3)\text{-Mn- MoO}_3/\text{ZrO}_2$ is found to be 4% wt/wt.

3.2.1.4 Influence of Molar ratio of Waste Cooking Feedstock / Methyl Alcohol

As far as the simultaneous methanolysis reaction for the synthesis of WCOME's is reversible, excess quantity of methyl alcohol wants to make the reaction towards the formation of WCOME's³²⁾. In order to assess the impact of alcohol/waste cooking feedstock molar ratio on the quantity of WCOME's using FMMZ catalyst a series of experiments had been done employing spent cooking feedstock to methyl alcohol ratio in a range of (5–30) keeping other parameters at the optimum level. According to Fig. 6(d), it has been clearly seen that, the transformation of spent cooking feedstock using FMMZ catalyst revealed a durable need on the spent cooking oil/ methyl alcohol molar ratio. However, once the dosage of methyl alcohol improved, consequently the product enhanced significantly thus the maximum yield found at dosage of 1/25, further than this quantity has no noteworthy development in WCOME's yield so the extra methyl alcohol would be collected, hence reprocessed.

3.3 The Effect of Ferric and Manganese-dopants on the Performance of $\text{Fe-Mn-MoO}_3/\text{ZrO}_2$

The consequence of ferric and manganese dopants on the surface of $\text{Fe-Mn-MoO}_3/\text{ZrO}_2$ were examined via the performance of the prepared solid acid catalysts (Zirconia, molybdated zirconia and ferric-manganese doped molybdated zirconia (FMMZ) for the preparation of biodiesel simultaneously. The comparative process was carried out at 5 h, stoichiometric ratio of waste oil to methyl alcohol 1:25 with 4% wt/wt. catalyst amount, temperature at 200°C and the 600 rpm stirrer. As a result the experimental yield of methyl esters obtained from zirconia, molybdated zirconia and ferric-manganese doped molybdated zirconia was

found to be 48.6 ± 1.14 , 73.0 ± 0.25 and $95.6\% \pm 0.15$, respectively. However, previously it had been reported that the methyl esters yield obtained via zirconia and molybdated zirconia only was found to be 49.3 and 65.0%, respectively^{11–19)}. In addition, Table 1 shows that ferric-manganese doped molybdated zirconia gives highest ester yield as well as specific surface area and density of active centres which indicates that the ferric and manganese dopants increase the surface area, acidity and thus the catalytic activity of ferric-manganese doped molybdated zirconia relative to that of zirconia and molybdated zirconia catalysts.

3.4 Assessment of Reusability

Reusability established as the major phase in manufacturing feasibility as it decreases the cost of biodiesel synthesis³³⁾. Thus, the recycling of the FMMZ catalyst for biodiesel synthesis has been considered for several runs after the purification step has been carried out using hexane and then alcohol to eliminate the unreacted triglyceride and the product stacked on the pores of FMMZ. Hence, FMMZ catalyst was finally dried at 120°C for six h. For the assessment of reusability, the reaction was performed under the optimized parameters of the methanolysis process. The consequences of a series of the methanolysis experiments have been displayed in Fig. 7. Accordingly, the product remains almost the same up to the sixth cycle and then drop to around 93.7% in the seventh run suggesting the successful reusability of the catalyst for six cycles. The decrease of WCOME's yield may be attributed to the slight leaching of iron and molybdenum and/or partial blockage of pores with oil. Therefore, it can be concluded that, the $\text{Fe-Mn-MoO}_3\text{-ZrO}_2$ catalyst is simply reused without any leaching of manganese and insignificant leaching of iron and molybdenum even after the seventh run as shown in Table 2.

Fig. 7 Reusability of FMMZ nanoparticle catalyst calcined at 600°C for 3h.

3.5 The Determination of FAME's through GC Analysis

The GC results showed that, waste cooking oil methyl esters has the lowest measurement of saturated lipid acids (43.4%) compared to unsaturated fatty acids (52.2%).

3.6 Fuel Quality of Biodiesel Derived from Spent Cooking Oil

The fuel characteristics (flash point, pour point (PP), pour point (CP), kinematic viscosity (40°C), and density) of produced WCOME's were determined, as depicted in Table 3 according to biodiesel ASTM¹⁶⁻³⁴⁾ standard methods. In appraisal to palm oil methyl esters (POME)³⁴⁾ from Malaysia and also diesel fuel, WCOME's demonstrated high gumminess value on 40°C (4.4 mm²/s Table 5.3); but WCOME's was surrounded by agreed American Society for Testing and Materials Standard No. 6751 (1.9–6.0 mm²/s) kinematic viscosity conditions. However, the flash point of WCOME's and palm oil methyl esters was in the range of (162°C and 165°C) which was greater than diesel fuel. On the other hand, WCOME's and POME³⁴⁾ revealed improved cloud point and power point compared to conventional diesel, whereas WCOME's executing better than POME³⁴⁾. However, the density of WCOME's (0.87 kg/L) was also found to be fit contained by the standards of American Society for Testing and Materials (0.82–0.9 g/cm³) biodiesel standards Table 3.

4 CONCLUSIONS

Ferric-manganese promoted molybdenum oxide/zirconia (FMMZ) nanoparticles catalyst exhibited high porosity, specific surface area, thermal stability, good reusability and excellent catalytic performance via methanolysis transformation of used frying vegetable oil. WCOME's yield reached 95.6% at 5 h reaction, catalyst loading 4% w/w, molar ratio of methanol to WCO 1:25 as molar ratio of methyl alcohol to used frying vegetable oil and 200°C and reduction of FFAs level closely to around 0.590% proof that the FMMZ is greatly operative to methanolysis conversion of waste cooking oil. Moreover, No considerable decrease in methyl esters yield had been detected subsequently six successive methanolysis process sets. In conclusion, FMMZ has potential for widespread applica-

tions especially for industrial scale preparation of renewable fuel employing any acidic oil.

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Table 3 Quality of biodiesel derived from used cooking vegetable oil.

Features	WCOMES	Conventional fuel	ASTM D 6751	EN 14214
Cloud point (°C)	-5 ± 1.25	—	—	—
Density (g/cm ³)	0.8780 ± 0.005	0.85	0.82-0.9	0.86-0.90
Flash point (°C)	162 ± 12.3	68	130 minimum	120 minimum
Kinematic viscosity (mm ² /s) at 40°C	4.4 ± 1.5	2.6	1.9-6.0	3.5-5.0
Pour point (°C)	-10 ± 1.9	—	—	—

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