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# Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts



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## ABSTRACT

In the present work, bifunctional heterogeneous catalysts were studied to develop an effective catalyst for biodiesel production from waste cooking oil with improved catalytic activity and stability. The catalysts were characterized by various analytical techniques to explore their physicochemical properties. The catalytic activity was evaluated in the transesterification of waste cooking oil for low cost biodiesel production. The bifunctional heterogeneous catalysts show improved transesterification activities. Among the different catalysts tested, the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst provides the maximum biodiesel yield of 91.4% in reaction time of 4 h at reaction temperature of 100 °C, methanol to oil molar ratio of 27:1 and an agitation speed of 500 rpm. Moreover, the bifunctional heterogeneous catalyst shows substantial chemical stability and could be reused for at least eight times without major loss in its catalytic activity. The physicochemical properties of the biodiesel produced from waste cooking oil were further studied and compared with the ASTM and the EN biodiesel specifications. The results show that the properties of the biodiesel produced comply with the international standard specifications.

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## 1. Introduction

The increasing energy demand, together with the depletion of fossil fuels and environmental issues are posing great challenges for researchers and the scientific community worldwide today. The present energy scenario has stimulated very active research interest in the production of renewable biofuels. Biodiesel is considered as a viable alternative to petroleum-derived diesel in the near future due to its interesting characteristics. Chemically, biodiesel is composed of monoalkyl esters of long chain fatty acids derived from renewable lipid feedstocks such as vegetable oils or animal fats (Leung et al., 2010). Biodiesel offers several advantages, including renewability, biodegradability, negligible toxicity, environmentally friendly emission profile, higher combustion efficiency, higher cetane number, higher flash point, contains 10-11% oxygen by weight and better lubrication (Pereira et al., 2012; Nair et al., 2012). The energy content and the physicochemical properties of biodiesel are almost similar to conventional diesel fuel; therefore, it can be used on its own or mixed with conventional diesel in the existing conventional compression-ignition engines without any major modifications (Robles-Medina et al., 2009).

However, the high cost of biodiesel production is the major obstacle for its commercialization. It has been reported that approximately 70–95% of the total biodiesel production cost is related to the cost of the raw materials (Zhang et al., 2003; Azócar et al., 2010). In this context, waste cooking oil (WCO) is considered to be a promising feedstock where the biodiesel production cost could be effectively reduced to 60–70% by using this low cost raw material (Math et al., 2010). Moreover, the production of biodiesel from WCO will not only avoid the competition of the same oil resources for food and fuel but will also solve the problems associated with WCO disposal.

In order to obtain reasonable conversion to biodiesel, the transesterification reaction is carried out in the presence of a suitable catalyst. Generally, homogeneous acid or base catalysts are used in biodiesel production from different feedstocks. Traditional homogeneous catalysts (acid or base) possess several advantages such as high catalytic activity (reaction complete within 1 h) and mild reaction conditions (from 40 to 65 °C and atmospheric pressure). However, the use of homogeneous catalysts leads to several problems including soap production, reactor corrosion, difficult to recover the catalyst and the production of large amounts of waste water, thus increasing the overall biodiesel production cost.

Heterogeneous catalysis is a promising technology for biodiesel production to overcome the problems associated with the use of

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homogeneous acid-base catalysts. Heterogeneous catalysts are non-corrosive and environmentally friendly, can be easily separated from the products via filtration and present fewer disposal problems than those encountered by the homogeneous catalysts (Yoosuk et al., 2010). In addition, due to better separation of the catalyst from the final products, heterogeneous catalysts can be recycled and used several times, thus offering a more economical pathway for biodiesel production. However, the major challenges associated with heterogeneous base catalysts development are their ability to tolerate the high free fatty acids (FFAs) contents of feedstocks at a mild reaction conditions and their reusability. Heterogeneous acid-catalyzed process is an efficient technology to produce biodiesel directly from low cost feedstocks, but the water present or generated during the FFAs conversion into biodiesel results in leaching and deactivation, causing contamination of the product.

Currently, new trends are oriented toward the search for bifunctional heterogeneous catalysts that can simultaneously carry out the esterification of FFAs and transesterification of triglycerides for a sustainable biodiesel production technology. Heterogeneous catalysts having both acidic and basic sites can be promising alternative catalysts to overcome the problems encountered with other catalysts. The bifunctional catalyst can act as an acid and base at the same time; therefore, it can carry out the esterification and transesterification reaction simultaneously. More importantly, a bifunctional heterogeneous catalyst can easily be modified to introduce the desired physicochemical properties so that the presence of FFAs or water does not adversely affect the reaction steps during the transesterification process (Endalew et al., 2011).

In this study, bifunctional heterogeneous catalysts were prepared by a modified impregnation method and characterized by various analytical techniques to explore their physicochemical properties. The synthesized bifunctional heterogeneous catalysts were further tested in the transesterification reaction of WCO for low cost biodiesel production. Moreover, the biodiesel production process was optimized in terms of reaction temperature, reaction time, methanol to oil molar ratio, catalyst loading and agitation speed to achieve the maximum biodiesel yield.

## 2. Experimental

#### 2.1. Catalyst preparation

The bifunctional heterogeneous catalysts were prepared by using the modified wet impregnation method. First, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–MgO mixed oxide supports with different MgO loadings (5, 10, 15 and 20 wt% with respect to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) were prepared by using the impregnation method (Farooq et al., 2011). The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–MgO supports were then impregnated with an aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O with constant stirring to achieve 5 wt% Mo loading. During impregnation, a few drops of 0.01 M HNO<sub>3</sub> aqueous solution were added to attain the maximum adsorption of ions on the support. As reported in our previous work (Farooq et al., 2011), at a pH below the point zero charge (PZC), the protonated hydroxyl groups of the metal oxide surface increase, i.e., the concentration of adsorption sites for negative species increases. This can be explained by Eq. (1) (Delmon, 1987).

$$6AlOH + 6H^{+} \rightarrow 6Al(OH)_{2}^{+} \stackrel{Mo_{7}O_{24}^{6-}}{\rightarrow} \left[ \left( Al(OH)_{2} \right)_{6}^{+} Mo_{7}O_{24}^{6-} \right]$$
(1)

The mixture was stirred for 3 h at room temperature followed by slow evaporation of water by heating at 70 °C. The catalysts were then dried at 110 °C for 12 h and finally calcined at 500 °C in the presence of air in a muffle furnace for 5 h. The Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-MgO

bifunctional heterogeneous catalysts were further modified with 5 wt% Mn metal oxide using the wet impregnation method. The catalysts were impregnated with an aqueous solution of  $Mn(NO_3)_2 \cdot 6H_2O$  at room temperature. However, during the preparation of the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–MgO bimetallic catalyst, the impregnation was carried out slightly in a basic medium using a 0.01 M KOH aqueous solution to achieve the maximum adsorption of Mn on the support surface. At a pH above the PZC, the surface hydroxyl groups are ionized hence, the adsorption of positive species (Mn<sup>2+</sup>) is favoured. This can easily be explained by Eq. (2) (Delmon, 1987).

$$2AIOH + 2OH^{-M^{2+}} (AIO)_2^{-}M^{2+} + 2H_2O$$
(2)

The mixture was stirred for 3 h at room temperature then the water was removed slowly from the mixture by heating at 70 °C and later dried at 110 °C for 12 h. Subsequently, the catalysts were calcined at 500 °C in the presence of air in the muffle furnace for 5 h and the catalysts were then stored in a desiccator prior to activity testing.

## 2.2. Catalyst characterization

The physicochemical properties of the synthesized catalysts were studied by various characterization techniques such as  $N_2$  adsorption-desorption, X-ray diffraction (XRD), temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS).

#### 2.3. Feedstock characterization

The WCO was collected from the Universiti Teknologi PETRONAS cafeteria. Prior to use, the WCO was filtered using a fine cloth to remove all the insoluble impurities and washed several times with hot distilled water to remove salt and other soluble materials. Then 10 wt% silica gel was added to the washed WCO and the mixture was stirred for 3 h to remove the water used during washing, followed by vacuum filtration using Whatman filter paper (No. 40 Quantitative) for the removal of the silica gel (Issariyakul et al., 2007). The oil was then dried at 110 °C for 24 h in an oven and stored in an air tight bottle for further studies.

The key physical and chemical characteristics of WCO, such as acid value, saponification value, flash point, specific gravity, viscosity and calorific value were determined experimentally following standard test methods (Table 1).

## 2.4. Catalyst screening and catalytic activity testing

The transesterification reaction of the WCO was performed in a three-necked 250 mL round bottom glass reactor fitted with a water-cooled condenser and thermometer. The transesterification reaction was performed using methanol and different bifunctional heterogeneous catalysts under different reaction conditions, such as reaction time, reaction temperature, catalyst amount, methanol

Table 1	
Physicochemical properties of the s	selected WCO.

Property	Unit	Value	Test method
Acid value	mg KOH/g	3.27	EN 1404
Calorific value	J/g	38462	ASTM D240
Kinematic viscosity at 40 °C	cSt	41.17	ASTM D-445
Specific gravity at 30 °C		0.903	ASTM D-7042
Saponification value	mg KOH/g	186.12	AOCS Cd 3a-94
Flash point	°C	274	ASTM D93
Moisture content	%	0.102	ASTM D6304
Mean molecular mass	g/mol	920.42	GB 5530-85

to oil molar ratio and an agitation speed to obtain optimum reaction conditions for biodiesel production. The catalyst was first dried in an oven at 80 °C for 1 h and then activated by dispersing it in methanol at 50 °C with constant stirring for 30 min. After the catalyst activation, the required amount of WCO (heated at 100 °C for 12 h prior to reaction) was added to the reactor and the reaction was carried out under the identified reaction conditions. After reaction completion, the reaction mixture was filtered through a Whatman 42 filter paper (125 mm diameter and a pore size of  $2.5 \mu m$ ) and centrifuged to separate the catalyst. The mixture was then transferred to a separating funnel and allowed to stand for approximately 24 h. The bottom layer (glycerol) was drained out and the upper layer consisting of biodiesel (methyl esters) was collected carefully. Finally, the biodiesel was dried at 80 °C in a vacuum oven for 24 h and stored in an air tight bottle for further investigations. The biodiesel yield was calculated by using Eq. (3) (Tarig et al., 2011; Birla et al., 2012).

Biodiesel yield(%) = 
$$\frac{\text{Weight of biodiesel}}{\text{Weight of oil}} \times 10$$
 (3)

## 2.5. Physicochemical properties of synthesized biodiesel

Important physicochemical properties of the biodiesel produced from WCO, such as viscosity, density, acid value, flash point, moisture content, calorific value etc were determined following the well established methods. Moreover, the biodiesel was further characterized by various analytical techniques such as Fouriertransform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy and Gas chromatography (GC) equipped with a flame ionization detector.

## 3. Results and discussion

## 3.1. Catalyst characterization

## 3.1.1. N<sub>2</sub> adsorption-desorption

The surface area, pore volume and mean pore diameter of different bifunctional catalysts are reported in Table 2. It can be observed that the surface area, pore volume and mean pore diameter decrease slightly when Mo and Mn metals were loaded on the supports. The decrease in the surface area, pore volume and mean pore diameter is due to the fact that the addition of the metal oxide species blocks some of the pores of the support during preparation. However, the decrease in the surface area is very small, suggesting that the active metal species are highly dispersed on the surface of the support.

#### 3.1.2. X-ray diffraction

The XRD patterns of different catalysts are presented in Fig. 1. The results indicate that the samples with a lower loading of MgO

## Table 2

Textural properties; specific surface area ( $S_A$ ), pore volume ( $V_P$ ), and mean pore diameter ( $D_P$ ) of different heterogeneous catalysts.

Catalyst	$S_A (m^2/g)$	$V_P(\mathrm{cm}^3/\mathrm{g})$	$D_P(Å)$
Mo/γ-Al <sub>2</sub> O <sub>3</sub>	181	0.197	77.05
Mo/y-Al <sub>2</sub> O <sub>3</sub> -5 wt% MgO	165	0.169	70.62
Mo/y-Al2O3-10 wt% MgO	149	0.160	65.87
Mo/y-Al <sub>2</sub> O <sub>3</sub> -15 wt% MgO	140	0.149	58.81
Mo/y-Al <sub>2</sub> O <sub>3</sub> -20 wt% MgO	131	0.138	48.12
Mo-Mn/y-Al <sub>2</sub> O <sub>3</sub> -15 wt% MgO	137	0.146	57.14



Fig. 1. XRD patterns of (a)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub> (b)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-5 wt% MgO (c)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-10 wt% MgO (d)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO (e)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-20 wt% MgO (f) Mo-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO heterogeneous catalysts.

display the characteristic peaks at  $2\theta = 32.62^{\circ}$ ,  $37.53^{\circ}$ ,  $45.58^{\circ}$  and  $67^{\circ}$  which are attributed to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase (Priecel et al., 2011), and no clear diffraction peaks corresponding to MgO phase are detected. This suggests that the structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> remains intact at a lower MgO loading as previously reported by Carvalho et al. (2009). However, the characteristic diffraction peaks which are attributed to the MgO phase are observed at  $2\theta = 42.75^{\circ}$  and  $62.11^{\circ}$  in the catalysts with a higher loading of MgO. In addition, no reflection of diffraction peaks attributed to MoO<sub>3</sub> and MnO are detected in any of the catalyst samples. This indicates that the MoO<sub>3</sub> and MnO metal oxides are highly dispersed on the surface of all the catalyst supports, forming very small crystallites which are below the detection limit of the XRD model used in the present work (Batista et al., 2001; Youn et al., 2007).

## 3.1.3. Temperature-programmed reduction

The TPR patterns of different catalysts are shown in Fig. 2, where the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst displays two reduction peaks with temperature maxima 529 °C and 971 °C. The first peak at 529 °C is attributed to the reduction of the Mo<sup>6+</sup> to Mo<sup>4+</sup> species in dispersed polymeric Mo structures (Lian et al., 2009). Less polarized



Fig. 2. TPR patterns of (a)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub> (b)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-5 wt% MgO (c)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-10 wt% MgO (d)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO (e)  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-20 wt% MgO (f) Mo-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO heterogeneous catalysts.

poly-molybdate species are more easily reduced, hence a lower reduction temperature is required than that of the species directly bonded to alumina (Damyanova et al., 1995). The second peak which appears at 971 °C is attributed to the further reduction of the Mo species produced during the reduction in the first stage, together with the partial reduction of the support and the strongly interacting tetrahedrally coordinated Mo species (López Cordero and López Agudo, 2000). In addition, the Mo tetrahedral species corresponding to Mo<sup>4+</sup> are also reduced to Mo metal at a high temperature (Kumar et al., 2004).

The TPR results demonstrate that the reduction temperature peak maxima increase with the increasing of MgO loading in the support. This suggests the presence of a strong metal-support interaction and a higher degree of dispersion of the Mo metal particles on the surface of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–MgO mixed oxides as compared to that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The strong metal-support interaction may be attributed to the poor electronegativity of Mg<sup>2+</sup> ions in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–MgO mixed oxides, leading to a weak Mg–O bond. As a result, the coordination ability of oxygen in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–MgO support to the Mo metal is higher, resulting in a strong metal-support interaction. However, in the case of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the electronegativity of the metal ions is greater, causing a weak metal-support interaction (Kumar et al., 2004). Among the different catalysts, the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–20 wt% MgO catalyst shows the highest reduction temperature, indicating a strong Mo-support interaction.

In the case of the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst, the peak appeared at the lower temperature of 343 °C is attributed to the reduction of manganese oxide from Mn<sup>2+</sup> to Mn<sup>0</sup> and less stable metal species which are weakly bonded to the support (Tang et al., 2009). The peak at 571 °C could be attributed to the reduction of the Mo species, whereas the shoulder peak at 703 °C could be due to the reduction of the complex oxides formed on the surface of the catalyst. Similarly, the reduction peak appeared at 1002 °C may be attributed to the reduction of the highly stable species. The TPR results further indicate that upon addition of the Mn promoter, the reduction peaks corresponding to the Mo metal shift to lower temperatures, indicating a weak metal-support interaction. This shows that Mn promoter enhances the reducibility of the bimetallic catalyst.

#### 3.1.4. X-ray photoelectron spectroscopy

The surface composition and electronic state of the elements present in the catalysts were investigated by XPS, and the results are presented in Table 3. The Mo 3d binding energy of the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is 232.41 eV, which is in close agreement with the reported value (Pereira da Silva et al., 2000). Moreover, the Mo 3d binding energy values of the synthesized catalysts show the existence of the Mo<sup>6+</sup> type species on the surface of the synthesized catalysts, which supports the presence of the MoO<sub>3</sub> phase in all of the catalyst samples (Andonova et al., 2007).

The results demonstrate that the Mo 3d binding energy increases with an increasing loading of MgO in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Among the different catalysts, the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-20 wt% MgO catalyst exhibits

Binding energies	of different	heterogeneous	catalysts
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Catalyst	Binding er	Binding energy (eV)	
	Al 2p	Mg 2p	Mo 3d
Mo/γ-Al <sub>2</sub> O <sub>3</sub>	74.58	1	232.41
Mo/y-Al <sub>2</sub> O <sub>3</sub> -5 wt% MgO	74.49	50.13	232.56
Mo/y-Al <sub>2</sub> O <sub>3</sub> -10 wt% MgO	74.41	49.82	232.67
Mo/y-Al <sub>2</sub> O <sub>3</sub> -15 wt% MgO	74.37	49.55	232.75
Mo/y-Al <sub>2</sub> O <sub>3</sub> -20 wt% MgO	74.29	49.38	232.87
Mo–Mn/γ-Al <sub>2</sub> O <sub>3</sub> -15 wt% MgO	74.45	50.04	232.58

the highest Mo 3d binding energy (232.87 eV), indicating a strong metal-support interaction as supported by the TPR results. The strong metal-support interaction is attributed to the poor electronegativity of the Mg<sup>2+</sup> ions in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–MgO mixed oxides, leading to a weak Mg–O bond. As a result, the oxygen atom in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–MgO support shows higher coordination ability to Mo metal, creating a strong Mo-support interaction which causes an increase in the Mo 3d binding energies (Kumar et al., 2004; Cai et al., 2008). However, a slight decrease in the Mo 3d binding energy was observed when a 5 wt% Mn was incorporated in the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst. The decrease in the Mo 3d binding energy of the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst is attributed to the decrease in the metal-support interaction upon introduction of the Mn metal into the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst as observed from the TPR results.

Similarly, the binding energies of Al 2p and Mg 2p of the synthesized catalysts are also listed in Table 3. The binding energies of Al 2p and Mg 2p decrease slightly with an increasing loading of MgO. The higher binding energy values for both Al 2p and Mg 2p with a lower loading of MgO are attributed to the stronger interaction between  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO in the composite oxides, where Mg<sup>2+</sup> cations occupy the surface vacant sites of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a monolayer formation, generating a new structure of Mg–O–Al. The binding energies of Mg 2p of the dispersed phases of MgO are quite different from that of their crystalline phases (Farooq et al., 2011).

## 3.2. Catalyst screening and catalytic activity tests

The catalytic activity of the synthesized catalysts was evaluated in the transesterification reaction of the WCO at the identified reaction conditions, such as the reaction temperature of 95 °C, methanol to oil molar ratio of 15:1, reaction time interval of 30-250 min, agitator speed of 450 rpm and catalyst loading of 3 wt%. Among the different catalysts tested, the Mo/y-Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst shows the best catalytic activity in the transesterification reaction and provides the maximum biodiesel yield of 74.5% in the reaction time of 4 h. The improved catalytic activity of the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst could be due to the presence of the optimum strength of the active acidic and basic sites on the surface of the catalyst to form the highly reactive methoxide species for the transesterification reaction. Moreover, no soap formation was found during the course of the reaction as the simultaneous esterification of FFAs and the transesterification of the triglycerides were carried out successfully. Generally, the strongest base is not necessarily the best catalyst for biodiesel reaction, and a solid catalyst which possesses strong basic sites may hold up the product molecules from desorbing after the reaction. On the other hand, a solid catalyst with weak basic sites may not adsorb the reactant molecules to initiate the reaction. Therefore, the optimal strength of the active basic sites is required for the transesterification reaction. This suggests that among the different catalysts, Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO may have the most optimal active site strength for the simultaneous esterification-transesterification reactions, making it an effective catalyst for biodiesel production from WCO. Based on the highest catalytic activity, the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst was selected for further studies to optimize the biodiesel production process from waste cooking oil.

#### 3.3. Optimization of transesterification reaction parameters

#### 3.3.1. Optimization of catalyst loading

Catalyst loading is one of the most important factors that affect the biodiesel yield during the transesterification reaction; therefore, it needs to be optimized to increase the biodiesel yield. Fig. 3 presents the effect of the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst loading



**Fig. 3.** Effect of catalyst loading on biodiesel yield in the transesterification reaction of WCO using Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst at reaction temperature of 95 °C, reaction time of 4 h, methanol to oil molar ratio of 15:1 and agitator speed of 450 rpm.

on the biodiesel yield at the identified reaction conditions. The catalyst loading was varied in the range of 1–8 wt%. The results demonstrate that the biodiesel yield increases with an increasing of the catalyst loading, showing that transesterification reaction strongly depends on the amount of catalyst. The maximum biodiesel yield of 78.7% is obtained at 5 wt% catalyst loading.

However, the biodiesel yield decreases as the catalyst loading is increased beyond more than the 5 wt% catalyst loading. At a higher catalyst loading the mixture becomes too viscous, causing mixing problems involving the reactants and a solid catalyst. As a result of the poor mixing, some amount of the catalyst may remain unused due to more mass transfer resistance, leading to a low biodiesel yield under the same experimental conditions (Noiroj et al., 2009; Tang et al., 2013). Moreover, at a higher catalyst loading, biodiesel products may get adsorbed on the surface of the catalyst, thus reducing the biodiesel yield during the transesterification reaction. Therefore, based on the results, the reaction is further carried out with a 5 wt% catalyst to optimize the other reaction parameters.

## 3.3.2. Optimization of methanol to oil molar ratio

The methanol to oil molar ratio is one of the major parameters that affect the biodiesel yield during the transesterification reaction. Stoichiometrically, 3 mol of alcohol are required to transesterify 1 mol of triglyceride, producing 3 mol of alkyl esters and 1 mol of glycerol. Since the transesterification of triglyceride is a reversible reaction, an excess of alcohol is required to shift the equilibrium towards the formation of alkyl esters (biodiesel) (Hoque et al., 2011). The influence of the methanol to oil molar ratio on the biodiesel yield was investigated for the selected catalyst and the results are depicted in Fig. 4. The results show that the biodiesel yield increases as the molar ratio of methanol to oil is increased. The maximum biodiesel yield of 82.6% is obtained at methanol to oil molar ratio of 27:1. However, there is no significant change in the biodiesel yield at higher methanol to oil molar ratios; thus, the 27:1 methanol to oil molar ratio is chosen for the optimization of other parameters.

## 3.3.3. Optimization of reaction temperature

The reaction rate increases exponentially with an increase in the reaction temperature, whereby the reactants are more miscible, allowing a higher reaction rate to take place (Helwani et al., 2009). The effect of the reaction temperature on the biodiesel yield was



**Fig. 4.** Effect of methanol to oil molar ratio on biodiesel yield in the transesterification reaction of WCO using  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst at reaction temperature of 95 °C, reaction time of 4 h, agitator speed of 450 rpm and catalyst loading of 5 wt%.

investigated in order to obtain the optimum temperature value for the maximum biodiesel yield from WCO.

The effect of the reaction temperature on the biodiesel yield is shown in Fig. 5. The results show that the biodiesel yield increases with an increasing the reaction temperature and the maximum biodiesel yield of 83.7% is obtained at 100 °C. Since the transesterification reaction is endothermic in nature (Yu et al., 2011), it favours a higher reaction temperature for biodiesel synthesis. However, when the reaction temperature is increased to above 100 °C, the biodiesel yield (%) decreases, indicating that 100 °C is the optimum reaction temperature for the transesterification reaction of WCO using a Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst. The highest biodiesel yield at 100 °C could be due to the accelerated chemical reaction (transesterification) by higher energy input which increases the collision among the reactant molecules thus enhancing the miscibility and mass transfer (Hoque et al., 2011). However, at temperatures above 100 °C, the biodiesel yield decreases because the vaporization of the methanol is too high and it



**Fig. 5.** Effect of temperature on biodiesel yield in the transesterification reaction of WCO using Mo/γ-Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst at reaction time of 4 h, methanol to oil molar ratio of 27:1, agitator speed of 450 rpm and catalyst loading of 5 wt%.

remains in the vapour phase in the reactor; thus, results in a decrease in the amount of methanol available for the reaction. Moreover, the polarity of methanol also decreases at high temperature, therefore decrease the concentration of reactive methoxide species in the reaction mixture (Birla et al., 2012).

#### 3.3.4. Optimization of agitation speed

The transesterification reaction of the oil in the presence of a heterogeneous solid catalyst involves multi-phases properties; therefore, the mixing speed is considered one of the most important parameters that affect the biodiesel yield (Helwani et al., 2009). The effect of the stirring speed on the biodiesel yield in the transesterification reaction of WCO was investigated at the reaction temperature of 100 °C, methanol to oil molar ratio of 27:1, reaction time of 4 h and catalyst loading of 5 wt%. The results show that the biodiesel yield increases with an increasing of the mixing speed (Fig. 6), and the maximum biodiesel yield of 85.1% is obtained at an agitation speed of 500 rpm. Further, it can be seen from the results that the biodiesel yield remains almost constant at stirring speeds greater than 500 rpm; hence, the stirring speed of 500 rpm is set as the optimum speed for the transesterification reaction of WCO. This shows that 500 rpm is sufficient to minimize the mass transfer limitations in the transesterification reaction.

The selected Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst was further modified to form a bimetallic catalyst by incorporating a 5 wt% Mn metal oxide. The catalytic activity of the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst was then evaluated in biodiesel production from WCO under optimized reaction conditions, i.e., the reaction temperature of 100 °C, reaction time of 4 h, catalyst loading of a 5 wt%, methanol to oil molar ratio of 27:1 and an agitation speed of 500 rpm. The results show that the catalytic performance of the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst is further enhanced with incorporation of a 5 wt% of Mn metal oxide and provides the maximum biodiesel yield of 91.4%. The high catalytic activity of the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst may be attributed to further improvement in the number of catalytically active sites on the surface of the catalyst which increases the biodiesel production from WCO.

## 3.4. Catalyst reusability

100

95

90

85

80

75

70

65

60

55

Biodiesel yield (%)

The catalyst reusability is an important feature for determining its commercial viability. The reusability of the  $Mo-Mn/\gamma-Al_2O_3$ -



15 wt% MgO catalyst was tested in the transesterification reaction of WCO for biodiesel production under optimized reaction conditions, i.e., reaction temperature of 100 °C, reaction time of 4 h, methanol to oil molar ratio of 27:1, catalyst loading of 5 wt% and mixing speed of 500 rpm. Ten repeated reactions were carried out to check the catalytic activity and stability of the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst where after each reaction, the recovered catalyst was first washed with methanol to remove any organic deposits (unreacted oil, biodiesel and glycerol), dried at 100 °C for 12 h, calcined at 500 °C for 2 h and then reused in the next transesterification reaction using the optimized reaction conditions with new reactants. The reusability profiles of the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst are shown in Fig. 7.

The results show that the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst possesses substantial reusability and chemical stability, and could be repeatedly used for at least eight times without any significant loss in its catalytic activity. The substantial reusability and chemical stability of the catalyst can be attributed to the existence of strong metal-support interaction as supported by the characterization techniques. However, the catalytic activity of the Mo– Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst decreases when it is successively reused for more than eight times which may be attributed to the decrease in the number of catalytically active sites present on the surface of the catalyst due to the deposition of organic materials or leaching of active metals during the transesterification reaction (Ngamcharussrivichai et al., 2008; Taufiq-Yap et al., 2011).

## 3.5. Physicochemical properties of the synthesized biodiesel

The physicochemical properties of the biodiesel obtained from WCO were analyzed and compared to those reported in literature, and are found to be within the limits set by the ASTM D-6751 and the European Standard EN 14214 (Table 4). This shows that the WCO used in this study has immense potential to be used in large scale biodiesel production with a suitable catalytic system.

#### 3.5.1. Gas chromatography analysis

GC analysis was used to identify the various compounds present in the synthesized biodiesel following the EN 14105 method (British Standard, 2003). The quantification of the glycerin, monoglycerides, diglycerides and triglycerides is essential to ensure that the quality of the synthesized biodiesel meets the international



Fig. 7. Reusability profile of the Mo–Mn/γ-Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst.

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Table 4	
Physicochemical properties of the synthesized biodiesel.	
	-

Property	Unit	ASTM D-6751	EN 14214	Synthesized biodiesel
Kinematic viscosity at 40 °C	mm <sup>2</sup> /s	1.9-6.0	3.50-5.00	4.02
Density (15 °C)	kg/m <sup>3</sup>	860-894	860-900	879
Flash point	°C	>120	>120	175
Moisture content	%	< 0.05	< 0.05	0.01
Acid value	mg KOH/g	$\leq$ 0.5	<0.5	0.17
Methyl ester content	%	>96.5	>96.5	98.34
Calorific value	J/g	_	_	40110
Monoglycerides	wt%	_	<0.8	<0.38
Diglycerides	wt%	_	<0.2	< 0.092
Triglycerides	wt%	_	<0.2	<0.068
Glycerol	wt%	0.02	0.02	0.013

#### Table 5

FAMEs composition of the synthesized biodiesel.

Peak no	Retention time (min)	Identified compounds
1	19.884	Dodecanoic acid methyl ester
2	24.724	Tetradecanoic acid methyl ester
3	26.881	Pentadecanoic acid methyl ester
4	29.817	Hexadecanoic acid methyl ester
5	29.930	9-Hexadecenoic acid methyl ester
6	31.224	Heptadecanoic acid methyl ester
7	34.124	Octadecanoic acid methyl ester
8	34.388	9-Octadecenoic acid methyl ester
9	35.083	9,12-Octadecadienoic acid methyl ester
10	35.631	9,12, 15-Octadecatrienoic acid methyl ester
11	36.033	11,14, 15-Eicosatrienoic methyl ester
12	36.891	Eicosanoic acid methyl ester
13	37.314	11-Eicosenoic acid methyl ester
14	40.110	Docosanoic acid methyl ester
15	43.225	Tetracosanoic acid methyl ester

standard specifications. The methyl ester compositions of the synthesized biodiesel are listed in Table 5 and the GC chromatogram is depicted in Fig. 8. The peaks appeared in the chromatogram, correspond to different fatty acid methyl esters present in the biodiesel sample, were identified by comparing with the profiles from the NIST107.LIB, NIST21.LIB, WILEY229.LIB GC libraries and reported data. The results show that the WCO was successfully transesterified to biodiesel using the  $Mo-Mn/\gamma-Al_2O_3-15$  wt% MgO catalyst.

#### 3.5.2. Fourier-transform infrared spectroscopy analysis

FT-IR spectra of the WCO and its biodiesel are depicted in Fig. 9 (a) and 9 (b) respectively. The WCO shows two small peaks at 3474.28 cm<sup>-1</sup> and 1635 cm<sup>-1</sup> corresponding to the stretching and bending vibration of O-H bonds of water molecule in the sample. The peaks centred at 2921 cm<sup>-1</sup> and 2852 cm<sup>-1</sup> are attributed to the antisymmetric and symmetric stretching vibrations respectively, of aliphatic C–H in CH<sub>2</sub> and terminal CH<sub>3</sub> groups. The strong single peak appeared at 1743  $\text{cm}^{-1}$  is attributed to the C= O stretching vibration of carbonyl groups of the triglycerides. The peaks in the 1400–1200 cm<sup>-1</sup> region are mainly attributed to the bending vibrations of CH<sub>2</sub> and CH<sub>3</sub> aliphatic groups like symmetric HCH bending at 1377  $\text{cm}^{-1}$  and  $\text{CH}_2$  scissoring at 1462 cm<sup>-1</sup>. The peaks in the 1125–1095 cm<sup>-1</sup> region are attributed to the stretching vibration of C–O ester groups and CH<sub>2</sub> wag. The peak at 721 cm<sup>-1</sup> is due to the overlapping of the (CH<sub>2</sub>)n rocking vibration (de la Mata et al., 2012; Shalaby and El-Gendy, 2012).

On the other hand, esters present two strong characteristic peaks at ~1742 cm<sup>-1</sup>, which is attributed to the stretching vibration of the carbonyl group (C=O), and peak at around 1300–1000 cm<sup>-1</sup> corresponding to that of the C–O stretching vibrations (antisymmetric axial stretching and asymmetric axial stretching) (Guillén and Cabo, 1997; Tariq et al., 2011). The stretching vibrations of CH<sub>3</sub>, CH<sub>2</sub>, and CH groups appeared at 2980–2950, 2950–2850 and 3050–3000 cm<sup>-1</sup>, whereas the bending vibrations of these groups appeared at 1475–1350, 1350–1150 and 722 cm<sup>-1</sup> respectively (Safar et al., 1994; Tariq et al., 2011).

The FT-IR spectra of the WCO and its biodiesel are very similar to each other due to the similarities in the chemical natures of the triglycerides and methyl esters. However, very small differences were observed where the peaks appeared at 1743, 1377, 1159, 1033 and 871 cm<sup>-1</sup> in the WCO were shifted to 1742, 1361, 1170, 1015 and 880 cm<sup>-1</sup> in the biodiesel respectively. Thus, the disappearance of the peaks at 1464, 1097 and 965 cm<sup>-1</sup> from the spectrum of the



Fig. 8. GC chromatogram of the synthesized biodiesel.

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Fig. 9. FT-IR spectrum of (a) WCO (b) synthesized biodiesel.

WCO and appearance of new peaks in the biodiesel sample at  $1435 \text{ cm}^{-1}$  and  $1195 \text{ cm}^{-1}$  clearly show the conversion of WCO into biodiesel. In addition, the absence of a broad peak in the  $3100-3500 \text{ cm}^{-1}$  region, related to the axial deformation characteristic of OH groups, suggests that synthesized biodiesel possesses low water contents as supported by the other techniques.

### 3.5.3. Thermogravimetry analysis

The volatility characteristic greatly influences the ignition quality of the fuels in the internal combustion engine (Lang et al., 2001; Sivakumar et al., 2011). TGA was performed to check the water content present in the biodiesel produced and its volatility. The TGA curves of the WCO and its biodiesel are depicted in Fig. 10. The TGA curve of the WCO shows that the WCO is thermally stable up to 210 °C and the thermal degradation of the WCO takes place in only one decomposition step between 182 and 460 °C with 99% mass loss related to the evaporation and thermal decomposition of the triglycerides (Silva et al., 2012). Similarly, the synthesized biodiesel also shows only one degradation step, where mass of the biodiesel starts to decrease at ~124 °C, and continue to decrease rapidly until all the biodiesel is completely volatilized at 250 °C.

Esters are known to be considerably less volatile than diesel fuel; however, a compression engine generates a nonfiring temperature of 800 °C where air is compressed in a cylinder (Sivakumar et al., 2011). Therefore, it can be said that the ignition of the synthesized biodiesel within the compression-ignition engine



Fig. 10. Thermogravimetric curves of the WCO and biodiesel at heating rate of 10  $^\circ C\mbox{ min}^{-1}.$ 



Fig. 11. <sup>1</sup>H NMR spectra of (a) WCO (b) synthesized biodiesel.

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as an alternative fuel would not be a problem. Moreover, the synthesized biodiesel represents a lower combustion reaction region as compared to WCO, indicating that biodiesel produced from WCO is more ignitable.

#### 3.5.4. Proton nuclear magnetic resonance analysis

The <sup>1</sup>H NMR spectra of the WCO and its biodiesel are shown in Fig. 11(a) and (b) respectively. The characteristic peak of deuteriated chloroform (CDCl<sub>3</sub>) is observed at 7.29 ppm (Kouame et al., 2012). The peak observed at 5.36 ppm is due to olefinic hydrogen (-CH=CH-) (Satyarthi et al., 2009). The peak at 3.68 ppm is assigned to methoxy group in methyl esters ( $-COOCH_3$ ), and the peak at 2.31 ppm is attributed to  $\alpha$ -methylene group of ester ( $-CH_2COOMe$ ) (Tariq et al., 2011). The peak appeared at 2.77 ppm is due to  $\alpha$ -methylene group to two double bonds ( $-C=CH-CH_2-$ CH=C-) (Satyarthi et al., 2009). These two peaks are the distinct peaks for the confirmation of methyl esters present in the biodiesel produced from WCO.

Similarly, the peak observed at 2.02 ppm is attributed to the  $\alpha$ -methylene group to one double bond (=CH–CH<sub>2</sub>–), whereas the peak appeared at 1.64 ppm is due to  $\beta$ -methylene to ester (CH<sub>2</sub>–C–CO<sub>2</sub>Me) (Deka and Basumatary, 2011). The broad peak at 1.26 ppm is due to backbone of methylenes (–(CH<sub>2</sub>)n–) (Satyarthi et al., 2009; Deka and Basumatary, 2011). The peak at 0.90 ppm is corresponding to terminal methyl protons (C–CH<sub>3</sub>). The WCO shows two addition peaks at 4.08 ppm or 4.22 ppm and 5.20 ppm which are corresponding to methylene protons at C1 and C3 of glycerides (–CH<sub>2</sub>–COOR) and methine proton at C2 of glycerides (–CH–COOR) respectively (Deka and Basumatary, 2011), where the peak at 3.68 ppm is absent. The <sup>1</sup>H NMR spectrum of biodiesel shows that WCO was successfully transferred to biodiesel using Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst.

#### 4. Conclusion

The bifunctional heterogeneous catalysts were successfully prepared by using the modified impregnation method. The results show that the physicochemical properties of the heterogeneous catalysts are affected by the metal-support interaction and chemical environment. Moreover, the bifunctional heterogeneous catalysts show improved catalytic activity in the transesterification reaction of WCO at the reaction temperature of 100 °C for 4 h with methanol to oil molar ratio of 27:1 and an agitation speed of 500 rpm. Among the different heterogeneous catalysts tested, the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst shows excellent catalytic activity and provides the maximum biodiesel yield of 91.4% at the optimized reaction conditions. The improved catalytic activity is attributed to the presence of the optimum strength of the active sites on the surface of the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst for the given biodiesel reaction. In addition, the Mo–Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15 wt% MgO catalyst shows substantial chemical stability and could be reused repeatedly for at least eight times for biodiesel production without major loss in its catalytic activity. The present study shows that the synthesized bifunctional heterogeneous catalyst has immense potential to produce low cost biodiesel from low cost feedstocks for sustainable energy production.

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