Efficient W-Mo mixed oxide supported CaO catalyst for the production of biodiesel from high FFA waste cooking oil: Stoichiometric effect

N Mansir1,2, Y H Taufiq-Yap2
1Department of Chemistry, Faculty of Science, Federal University Dutse, 7156 Dutse, Jigawa, Nigeria
2Catalysis Science and Technology Research Centre, Faculty of Science, University Putra Malaysia, 43400, Serdang, Selangor, Malaysia

Email: nmansir09@yahoo.com

Abstract. Biodiesel is considered as one of the most promising biofuels produced from the vegetable oils. This is due to its environmental benign and availability of variety of feedstock. It is generally produced by either esterification reaction of free fatty acid (FFA) or transesterification reaction of triglycerides, using acid or base catalysts, respectively. In this work, the solid tungsten molybdenum supported by calcium oxide catalyst (Wx-Moy/CaO 0.3≤x, 0.7≤y) was developed and used to produce biodiesel from high FFA waste cooking oil. The catalyst was synthesized using simple wet impregnation method. The stoichiometric effects of transition metal oxides loading on acid-base properties, surface area and porosity of the catalyst were studied. The catalytic activity of the catalyst for transesterification reaction increases with the increase in the tungsten molar weight ratio over Molybdenum from 0.3 to 0.7. The W0.6-Mo0.4/CaO catalyst recorded the highest biodiesel yield of 96.2% under mild reaction conditions of 15:1 methanol to oil molar ratio, 70°C reaction temperature, 2 wt.% catalyst loading and 2 h reaction time. The newly synthesized catalysts were characterised using X-Ray Diffraction (XRD), Temperature Programmed Desorption(TPD) and Vapour Pressure Scanning Electron Microscope (VPSEM).

1. Introduction
Increase in global population in developing countries and latest advancement in technology lead to the high energy demand for transportation services as well as production of goods necessary for life [1–3]. Global warming due to the release of toxic gases into the atmosphere is one of the major reason behind the search of renewable source of energy that is alternative to fossil fuel. Biofuels have recently been recognized as possible replacement option to conventional fossil fuel [4]. Biofuel is referred as fuel produced from biomass and used in internal combustion engines. It could be in liquid or gaseous form.

Biodiesel or fatty acid methyl ester (FAME) is one of the most promising alternative biofuel that is considered to replace the popular fossil fuel [5]. Biodiesel has excellent characteristic properties such as availability of feedstock, renewability, environmental benign, less toxicity and similar physico chemical properties.
properties to that of conventional fossil fuel [6,7]. Biodiesel have been produced at laboratory scale for decades and therefore not produced at industrial scale as a result of some bottlenecks faced such as utilization of food grade vegetable oil as feedstock (soybean oil, palm oil etc) and the conventional catalyst system (homogeneous catalyst) [8].

Utilization of food grade vegetable oil as biodiesel feedstock would make biodiesel production process very expensive, beside other disadvantages such as food versus fuel competition, which may result to possible shortage of food stuff in the near future. Conventionally, the production of biodiesel using vegetable oil utilizes the homogeneous catalyst system such as potassium hydroxide (KOH), Hydrochloric acid (HCl) [9].

The homogeneous catalyst system is associated to separation problems after the reaction, possible reactor corrosion and water pollution due to disposal of the liquid catalyst after use [10]. Heterogeneous catalytic system is now adopted for the production of biodiesel considering its ability to convert low grade feedstock such as palm fatty acid distillate (PFAD), high FFA waste cooking oil and jatropha curas oil [11]. Moreover, this catalyst system is less corrosive, easy separation after the reaction, reusability and less disposal problem [12].

The aforementioned advantages of solid heterogeneous catalyst system reaffirmed its economic viability and sustainability for the commercialization of biodiesel. Heterogeneous catalyst could either be acid or base. Different heterogeneous catalyst system has been utilized for the production biodiesel from vegetable based oil as reported by Lokman et al., 2014 and Mansir et al., 2018 [13,14], recording excellent conversion of vegetable oil to biodiesel at mild reaction conditions.

In this work, efficient Tungsten Molybdenum supported Calcium oxide catalyst was synthesized, and the stoichiometric effect of the compositional metals on the production of biodiesel from high FFA waste cooking oil was investigated. The synthesized catalyst samples were characterized using X-ray diffraction machine (XRD), Temperature programmed desorption of CO₂ and NH₃, and Variable Pressure Scanning electron microscope (VPSEM).

2. Experimental
2.1 Materials
The Phosphotungstic acid hydrate (H₃PO₄.12WO₃.xH₂O) (Sigma Aldrich), and Ammonium heptamolybdat-tetrahydrate [(NH₄)₆Mo₇O₂₄.4H₂O] (Merck) salts were purchased from Fisher Scientific (M) Sdn Bhd. The anhydrous methanol for analysis (Merck 99.7%), potassium hydroxide pellets for analysis (Merck) and ethyl alcohol (System 95%) were purchased in Malaysia. The waste egg shell and waste cooking oil (WCO) were obtained from the restaurant in the Universiti Putra Malaysia. The used oil was filtered using Buchner Funnel and filter paper grade 1 with a pore size of 11μm to remove the food debris before used for the reaction. All solvents and reagents used were of analytical grade. The physico-chemical properties investigation of the feedstock (waste cooking oil) was performed based on American Society for Testing and Material (ASTM) standard, European Standard (EN) and Malaysian palm oil board (MPOB) official method and the values for the feedstock characterization results are summarized in Table 1.

2.2 Catalyst preparation
2.2.1 Calcium oxide catalyst
The calcium oxide (CaO) was synthesized from the waste raw egg shell. The waste egg shell was washed with hot water to remove all the dirt attached to it and dried overnight in an oven at the temperature of 100°C. The dried raw waste egg shell was crushed into fine powder using milling machine. The obtained eggshell powder was calcined in a furnace at the temperature of 900°C for 4 h. The obtained CaO catalyst support was kept in the air tired container for subsequent use.
2.2.2 Tungsten-Molybdenum based catalyst

Wet impregnation technique was employed to prepare the tungsten–molybdenum catalyst, which follows calcination in an open air furnace at a temperature of 650°C. Typically, the total of 0.7 g in the form of $W_{x}$-$Mo_{y}$ ($x\geq 0.3, y\leq 0.7$) from $H_3PO_4.12WO_3.XH_2O$ and $(NH_4)_6Mo_7O_24.4H_2O$ were dissolved in a 50 mL beaker containing distilled water and stirred vigorously for 1 h, after which the resultant solution was impregnated onto the powdered CaO (4.93 g) to make the total of 5 g. The mixture was stirred at 450 rpm for 4 h at room temperature to ensure total homogeneity. The resultant slurry was dried in an oven at 110°C for 24 h. The catalyst was then calcined at 650°C in a furnace for 4 h. The same procedure was repeated to prepare $W_{0.3}$-$Mo_{0.7}$/CaO, $W_{0.4}$-$Mo_{0.6}$/CaO, $W_{0.5}$-$Mo_{0.5}$/CaO, $W_{0.6}$-$Mo_{0.4}$/CaO and $W_{0.7}$-$Mo_{0.3}$/CaO catalyst samples, respectively [15].

2.3 Catalyst characterization

The structure and crystal size analysis of the synthesized heterogeneous solid catalyst samples were determined by X-ray diffraction (XRD) technique. The analysis was performed on a Shimadzu model XRD6000 power X-ray diffractometer, using Cu, Kα radiation (27.7 kW and 30mA) with wavelength ($\lambda$) of 1.54 A, over the $2\theta$ range of 10° to 80° with a step of 0.04° at screening speed of 2° min$^{-1}$. The crystallite sizes of the catalyst samples were determined by the Debye-Scherer’s equation

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where $D$ = Crystallite size for phase (nm)

$\lambda$ = X-ray wavelength of radiation for Cu, Kα

$\beta$ = Full width at half maximum of the peak (FWHM)

$\theta$ = Diffraction angle for phase.

Temperature programmed desorption of carbon dioxide and ammonia (TPD-CO$_2$ & TPD-NH$_3$) technique were used to evaluate the basic and acidic sites strength, density and distribution of the synthesized solid catalysts, respectively, using a Thermo Finnigan TPD/R/O 1100 series apparatus equipped with thermal conductivity detector (TCD). The detail procedure of the analysis was adopted from (reference) without any modification [16].

Variable pressure Scanning electron microscope (VPSEM LEO 1455 model) was employed to investigate the surface morphology of the catalyst. The catalyst samples were coated in gold using a Sputter Coater before been analysed using scanner.

2.4 Catalytic activity evaluation for biodiesel production reaction

The catalytic activity of the synthesized catalyst was evaluated using the transesterification process of waste cooking oil to biodiesel using methanol. Waste cooking oil contains both saturated and unsaturated fatty acids (monocarboxylic acids with trihydric alcohol glycerides). During the reaction process, the catalyst assists in the conversion of triglycerides to diglycerides and diglycerides to monoglycerides and then finally monoglycerides to glycerol and biodiesel [17].

3. Results and Discussion

3.1 Preliminary investigation of feedstock and Catalyst characterization

3.1.1 Feedstock characterization

The feedstock (waste cooking oil) was characterized to investigate it’s physical and chemical properties before the biodiesel production reaction and the results obtained are presented in Table 1.
Table 1. Physico-chemical properties of waste cooking oil (WCO)

| Description                        | Analysis | Standard method |
|------------------------------------|----------|-----------------|
| Moisture content (wt.%)            | 0.6      | MPOB<sup>a</sup> |
| Saponification value (mg KOH g<sup>-1</sup>) | 187.2    | ASTM (D464)<sup>b</sup> |
| Molecular weight (g mol<sup>-1</sup>) | 898.9    | ASTM (D464)<sup>b</sup> |
| Acid value (%)                     | 11.0     | ASTM [D974(00)]<sup>b</sup> |
| FFA content (%)                    | 5.5      | ASTM [D974(00)]<sup>b</sup> |
| Fatty acid composition (wt.%)      |          |                 |
| Myristic acid (C14:0)              |          | 0.7             |
| Palmitic acid (C16:1)              |          | 60.1            |
| Stearic acid (C18:0)               |          | 10.8            |
| Oleic acid (C18:1)                 |          | 27.2            |
| Linoleic (C18:2)                   |          | 1.14            |

MPOB<sup>a</sup> = Malaysian palm oil board official method
ASTM<sup>b</sup> = American society for testing and material

3.1.2 Structure & Crystallography

The structure of the synthesized catalyst samples was determined by X-ray diffraction machine (Model 6000, Shimadzu, Japan). The crystal size was computed using Derby Scherer equation. The XRD patterns of synthesized W-Mo/CaO supported catalyst containing various stoichiometric compositions of W<sub>x</sub>-Mo<sub>y</sub> where x ≤ 0.3, y ≤ 0.7 wt % are depicted in Figure 1. The diffraction patterns showed sharp peaks at various 2θ positions, which are attributed to high crystallinity of the material. There was formation of W and Mo oxide when the tungsten and molybdenum were impregnated on CaO composite.

The characteristic diffraction patterns of cubic calcium oxide (JCPDS 82-1691) is the major phase while hexagonal Ca(OH)<sub>2</sub> (JCPDS 84-1275), tetragonal WO<sub>3</sub> (JCPDS 00-001-0806) and MoO<sub>3</sub> (JCPDS files 47-1320) are the minor phases present in the catalyst as supported by XRD spectra. Hexagonal Ca(OH)<sub>2</sub> was formed as a result of reaction between CaO and H<sub>2</sub>O during catalyst preparation. The crystallite size of the different stoichiometric ratio of W and Mo are within the same range with slight differences. This is attributed to the variability in the stoichiometric composition of W and Mo over CaO as shown in Table 2.
3.1.3 Temperature programmed desorption of carbon dioxide and ammonia

Temperature programmed desorption of ammonia and carbon dioxide (TPD-NH$_3$ and TPD-CO$_2$) were employed as probe gases to determine the level of acidity and basicity of the prepared catalyst, respectively. In each case, the peaks desorbed at high temperature indicate the high strength bond of the supported active sites and those desorbed at lower temperature region indicate low strength bond at the supported active site. Therefore, high temperature region indicates high acidity or basicity while lower temperature region indicates lower acidity or basicity of the catalyst sample.

Typically, any peak desorbed below the temperature region of 300°C is regarded as weak (acid or base) strength and those desorbed between the temperature region of 300 to 500°C is considered of moderate (acid or base) strength while peaks desorbed at the temperature region of above 500°C are considered as strongly acidic or basic [18].

The basic and acid characteristics of the synthesized catalyst samples (W$_{0.3}$-Mo$_{0.7}$/CaO, W$_{0.4}$-Mo$_{0.6}$/CaO, W$_{0.5}$-Mo$_{0.5}$/CaO, W$_{0.6}$-Mo$_{0.4}$/CaO and W$_{0.7}$-Mo$_{0.3}$/CaO) determined by TPD-CO$_2$ and TPD-NH$_3$ are presented in Fig. 2 and 3, respectively. The TPD-CO$_2$ profile of the synthesized samples W$_x$-Mo$_y$/CaO ($x\geq0.3$ and $y\leq0.7$) desorbed their CO$_2$ peaks at various temperature region, ranging from 600 to 750°C. This shows that all the five samples desorbed their CO$_2$ peaks within the strong basicity zone. While the TPD-NH$_3$ profile presented the NH$_3$ desorbed peaks at their respective temperature region. The desorption temperature range from 400 to 700°C, which indicate the medium acid strength and strong acid strength possessed by the catalyst samples [19]. The excellent basicity of these catalysts was due to high basic contribution from natural CaO oxide (egg shell powder) and the major contributors in the formation of acid site in the synthesized catalyst are tungsten oxide (WO$_3$) and molybdenum oxide (MoO$_3$). The variation in basic and acid density sites among the catalyst samples is attributed to different stoichiometric composition of W-Mo bimetallic oxides as presented in Table 2.
3.1.4 Surface morphology characteristic
The micrographs of synthesized Wₓ-Moy/CaO (x≥0.3 and y≤0.7) catalyst samples with variable W to Mo mass ratio are presented in Fig. 4. Variable pressure Scanning electron microscope (VPSEM) images presented the agglomerated particles typical to cubic CaO structure and the irregular shapes of WO₃ and MoO₃ (Fig. 4). The subsequent images undergo slight change in their morphology from large agglomerated spheres to a bit homogeneous spherical structures when the mass ratio of W-Mo over CaO surface increases from W₀.₅–Mo₀.₅/CaO to W₀.₆–Mo₀.₄ and W₀.₇–Mo₀.₃ (Fig.4d-e). The non-uniform structure (spherical and cubic) of the particle size distribution might formed either as a result of high dispersion of WO₃ and MoO₃ particle size over the CaO surface or merging the particle size structures of WO₃, MoO₃ and CaO together during the catalyst synthesis [15]
Table 2. Acid and basic site densities, crystal size of the synthesized catalyst samples and FAME yield

| Catalyst sample | Basic site density (µmol/g) | Acid site density (µmol/g) | Crystal size (nm) | FAME Yield (%) |
|-----------------|-----------------------------|-----------------------------|-------------------|----------------|
| W0.3-Mo0.7/CaO  | 1334                        | 3085                        | 46.421            | 91.0           |
| W0.4-Mo0.6/CaO  | 1336                        | 2989                        | 52.236            | 92.4           |
| W0.5-Mo0.5/CaO  | 1361                        | 3731                        | 52.234            | 94.0           |
| W0.6-Mo0.4/CaO  | 1365                        | 3738                        | 52.225            | 96.2           |
| W0.7-Mo0.3/CaO  | 1322                        | 3901                        | 52.234            | 95.0           |

Figure 4., VPSEM images of (a) W0.3-Mo0.7/CaO (b) W0.4-Mo0.6/CaO (c) W0.5-Mo0.5/CaO (d) W0.6-Mo0.4/CaO (e) W0.7-Mo0.3/CaO

3.2 Catalytic activity in biodiesel production from waste cooking oil
3.2.1 Effect of stoichiometric composition of W and Mo

The catalytic activity of the synthesized catalyst samples with various W to Mo stoichiometric ratio compositions were tested on transesterification reaction of waste cooking oil to produce biodiesel. The stoichiometric composition of W and Mo ratios over CaO are prepared in the form of W0.3-Mo0.7/CaO,
W_{0.4}-\text{Mo}_{0.6}/\text{CaO}, W_{0.5}-\text{Mo}_{0.5}/\text{CaO}, W_{0.6}-\text{Mo}_{0.4}/\text{CaO} and W_{0.7}-\text{Mo}_{0.3}/\text{CaO}. The catalytic activity of these catalyst samples was tested and the result obtained is presented in Table 2. Although a good conversion yield of at least 91% was recorded by all the synthesized catalyst samples moreover, W_{0.6}-\text{Mo}_{0.4}/\text{CaO} sample achieved the best biodiesel yield of 96.2% under mild reaction conditions. This might be attributed to the possession of the best base and acid site densities that are appropriate for the transesterification of the utilized waste cooking oil to FAME. Moreover, possession of the most appropriate dispersion of stoichiometric ratio composition of W and Mo over the surface of CaO is another probable factor for the remarkable biodiesel yield recorded by this sample.

Although there was no exact W-Mo/CaO catalyst reported for transesterification of waste cooking oil to biodiesel before this studies, however, the catalytic activity of W_{0.6}-\text{Mo}_{0.4}/\text{CaO} catalyst was compared with similar studies from related catalysts for the transesterification of waste cooking oil. The synthesized catalysts of this study displayed better biodiesel yield under the most economical reaction conditions Table 3.

| Catalyst sample          | Synthesis method of catalyst | Feedstock and FFA level (%) | Reaction conditions | FAME yield | Ref.          |
|-------------------------|------------------------------|-----------------------------|---------------------|-----------|---------------|
| CaO                     | Calcination                  | Waste cooking oil (FFA <1)  | 65°C, 5 wt.%, 2h    | 86.0%     | [20]          |
| CaO-ZrO$_2$             | Co-precipitation             | Waste cooking oil (FFA <3)  | 65°C, 10 wt.%, 30:1, 2h | 92.1%     | [21]          |
| Mo-Mn$_{15}$/%-Al$_2$O$_3$ | Impregnation                | Waste cooking oil (FFA 1.64)| 100°C, 27:1, 4h    | 91.4%     | [22]          |
| W$_{0.6}$-Mo$_{0.4}$/CaO | Impregnation                | Waste cooking oil (FFA 5.5) | 70°C, 2 wt.% 2h, 15:1 | 96.2%     | This study    |

4. Conclusion
The CaO supported W-Mo catalyst sample with variable stoichiometric compositions were synthesized (W$_x$-Mo$_y$/CaO, $x$≤3, $y$≤7) and utilized for the production of biodiesel from waste cooking oil. The catalyst demonstrated excellent catalytic performance recording excellent biodiesel yield of 96.2% by W$_{0.6}$-Mo$_{0.4}$/CaO catalyst sample under the reaction conditions of 15:1 methanol to oil molar ratio, 2 wt.% catalyst loading, 70°C reaction temperature and 2 h reaction temperature. The excellent basic and acid site densities appropriate for the simultaneous transesterification and esterification of the waste cooking oil sample used in this study, are behind the outstanding catalytic activity among these stoichiometric ratios.

References
[1] Mansir N, Taufiq-Yap Y H, Rashid U, Lokman I M 2017 Energy Convers Manag. 141 171–82.
[2] Lokman I M, Rashid U, Yunus R, Taufiq- Y H. 2014 Catal Rev Sci Eng. 56 187–219.
[3] Alhassan F H, Yunus R, Rashid U, Sirat K, Islam A, Lee H V 2013 Appl Catal A Gen 456 182–187.
[4] Lam M K, Lee K T, Mohamed A R 2009 Appl Catal B Environ. 93 134–9.
[5] Taufiq-yap YH, Hwa S, Rashid U, Islam A, Zobir M 2014 Energy Convers Manag. 88 1290–6.
[6] Peng B-X, Shu Q, Wang J-F, Wang G-R, Wang D-Z, Han M-H 2008 Process Saf Environ Prot. 86 441–7.
[7] Banković-Ilić IB, Stamenković OS, Veljković VB 2012 Renew Sustained Energy Rev. 16 3621–47.
[8] Furuta S, Matsuhashi H, Arata K 2005 Biomass and Bioenergy. 30 870–3.
[9] Malins K, Kampars V, Brinks J, Neibolte I, Murnieks R 2015 Applied Catal B Environ 176–177 553–8.
[10] Galadima A, Muraza O 2014 Energy 78 0–11.
[11] Kaur N, Ali A 2015 RSC Adv 5 13285–95.
[12] Koberg M, Abu-much R, Gedanken A 2011 Bioresour Technol. 102 1073–8.
[13] Lokman IM, Rashid U, Zainal Z, Yunus R, Taufiq-yap Y H 2014 J Oleo Sci. 855 849–55.
[14] Mansir N, Hwa ST, Rubi I, Taufiq-Yap Y H 2018 Chem Eng J. 347 137–44.
[15] Amani H, Ahmad Z, Hameed BH 2014 Applied Catal A, Gen. 487 16–25.
[16] Shajaratun Nur ZA, Taufiq-Yap YH, Rabiah Nizah MF, Teo SH, Syazwani ON, Islam A 2013 Energy Convers Manag. 78 738–44.
[17] Hua Y, Omar M, Nolasco-hipolito C, Taufiq-yap YH 2015 Appl Energy. 160 58–70.
[18] Rabiah Nizah MF, Taufiq-Yap YH, Rashid U, Teo SH, Shajaratun Nur ZA, Islam A 2014 Energy Convers Manag. 88 1257–62.
[19] Liu L, Wang B, Du Y, Zhong Z, Borgna A 2015 Applied Catal B Environ. 174–175 1–12.
[20] Sirisomboonchai S, Abuduwayiti M, Guan G, Samart C, Abliz S, Hao X 2015 Energy Convers Manag. 95 242–7.
[21] Dehkordi AM, Ghasemi M 2012 Fuel Process Technol. 97 45–51.
[22] Farooq M, Ramli A, Subbarao D 2013 J Clean Prod. 59 131–40.