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Transesterification of cooking palm oil via Mn-Al mixed oxides catalysts: effects of metal ratio

Siti Athirah Ramli[1], Wan Zuraida Wan Kamis[1,*], Nur Alwani Ali Bashah[1], Vicinisvarri Inderan[1], Norain Isa[1 *]

[1]*Chemical Engineering Studies, Universiti Teknologi MARA, Cawangan Pulau Pinang, Permatang Pauh Campus, 13500 Pulau Pinang, Malaysia*

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ABSTRACT

The abstract Biodiesel or fatty acid methyl ester (FAME) is an environmentally friendly fuel that is an alternative to diesel fuel. In this study, mixed oxides catalysts of Mn-Al were synthesised via the sol-gel method at various metal ratios and used in the transesterification of cooking palm oil (CPO) to produce FAME. The reactions were conducted in a batch reactor at a temperature of 55 °C, with a reaction time of 3 h and a catalyst loading of 2.5 wt%. The effects of Mn:Al metal weight ratios of 1:1, 1:2, 2:1, 0:1, and 1:0 were investigated based on the FAME density obtained from the reaction. The thermal stability and the presence of surface functional groups were investigated using thermal gravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR), respectively. The results show that the Mn-Al catalyst prepared at 1:2 metal weight ratio and calcined at 500 °C for 2 h obtained a FAME density of 862 kg/m3, which is the closest to standard palm oil biodiesel density. The catalysts with different metal ratios contained similar active surface functional groups. The TGA analysis of the Mn-Al metal ratio 1:2 showed no significant weight loss observed after 300 °C, indicating good thermal stability. The findings indicate that Mn-Al mixed oxides have the potential as heterogeneous catalyst in the transesterification of CPO to produce FAME.

1. INTRODUCTION

Biodiesel, also known as fatty acid methyl ester (FAME), is an alternative fuel that plays a crucial role in reducing the amount of hazardous pollutants emitted by fossil fuels [1]. Biodiesel has physicochemical properties similar to petroleum fuel, with advantages such as lower SO_2 and NO_2 emissions and being

[1*] Corresponding author. *E-mail address*: zuraida326@uitm.edu.my
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environmentally friendly. Biodiesel is commonly produced through the transesterification of plant oils and alcohols with the aid of a catalyst [2]. Plant oil is considered the best raw material for biodiesel production due to its sustainability, renewability, energy security, and high energy content [3].

The benefits of palm oil as a biodiesel feedstock lie in its high oil content and high yield per hectare, compared to other oil crops such as soybean, rapeseed, and sunflower. Moreover, palm oil is cheaper than other plant oils and has lower sulphur content, which reduces the SO_2 emissions when fuel is burned [4]. Using homogeneous catalysts in FAME production resulted in wastewater pollution from the extensive use of water during the downstream process of washing and purification steps [5]. Alternatively, the heterogeneous catalyst has many benefits such as a simplified separation and purification process, less wastewater and non-corrosiveness to the reactor. There are different catalysts used to produce FAME such as metal oxides, sulphate metal oxides and also non-metal catalysts [6].

Metal oxides catalysts, such as manganese oxide, are particularly active in FAME synthesis due to their acidity [7]. The transesterification of mahua oil using manganese doped zinc oxide catalyst achieved high biodiesel yield [8]. Aluminium oxide is used as a metal oxide catalyst due to its high chemical inertness, strength, and high surface area [9]. Chromium-aluminium mixed oxides catalyst effectively produced FAME from microalgae [10]. Mixed metal oxides $CrWMnO_2$ were effective in the esterification of palm fatty acid distillate to produce FAME mainly due to its acidity property [11]. Some of the independent properties and catalyst activity of Mn and Al metal oxides have been reported in the literature [7,8,9,11,12]. However, limited studies are available on the Mn-Al mixed oxides characteristics in terms of thermal stability, surface functional groups and effects on FAME density. FAME density is an important biodiesel property related to fuel efficiency [13].

In our previous work, the transesterification of cooking palm oil (CPO) utilised chromium-titanium (Cr-Ti) mixed metal oxides has shown good potential as a heterogeneous catalyst in producing FAME [13]. In the present work, CPO was also used as feedstock in the reaction utilising mixed oxides manganese-aluminium (Mn-Al) that were synthesised via the sol-gel method. The effects of catalyst synthesis conditions in terms of metal ratio were investigated based on the FAME density obtained from the reaction. In addition, the analysis of catalyst thermal stability and functional group characteristics was also conducted.

2. METHODOLOGY

2.1 Materials and chemicals

The chemicals that were used in the catalyst preparation are aluminium nitrate nonahydrate with 99 wt% purity (Qrec), manganese nitrate tetrahydrate with 99 wt% purity (Merck), nitric acid with 65 wt% purity (Qrec), ethanol with 99.8 wt% purity (Qrec) and methanol with 99 wt% purity (Qrec). Cooking Palm Oil (CPO) was purchased from Vesawit Malaysia.

2.2 Preparation of Mn-Al mixed oxides catalysts

The Mn-Al mixed oxides catalysts were prepared via the sol-gel method [1]. In a typical catalyst preparation, aluminium nitrate nonahydrate and manganese nitrate tetrahydrate with a weight ratio of 1:1 were weighed and mixed with 10 mL of deionised water in separate beakers. Each solution was then slowly added to a beaker containing 40 mL of ethanol and 2 mL of nitric acid. The solution was allowed to stir for 4 h at 40 °C on a magnetic stirring hot plate and then left for 24 h aging process until gel was formed. The sample was dried in an oven for 12 h at 120 °C followed by calcinations in air using a muffle furnace at a temperature of 500 °C and time of 2 h. The catalyst obtained is designated as 1:1 metal ratio, which contains Mn:Al weight ratio of 1:1. The steps were repeated for all remaining Mn:Al ratios of 0:1, 1:0, 2:1 and 1:2.

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The calcination conditions and metal ratios were selected based on reported works in the synthesis of metal oxides catalysts [14,15].

2.3 Transesterification of CPO and catalyst characterisations

The transesterification of CPO was carried out using the prepared catalysts. Under typical conditions, the reactants mixture, consisting of a 15:1 methanol to oil molar ratio was filled into a 250 mL beaker with catalyst loading of 2.5 wt.% of oil. The system and its content were continuously stirred at a maximum of 500 rpm with an overhead stirrer throughout the reaction to keep the system in uniform suspension and maintain a temperature of 55 °C with a reaction time of 3 h [1]. Upon completion of the reaction, the hot plate and overhead stirrer were switched off, and the system was left to cool to room temperature. The product mixture was separated from the catalyst via centrifugation at 3000 rpm for 15 min. It was then left to settle for 12 h to separate into 2 layers. FAME was observed at the top layer, while glycerol was at the bottom layer. The FAME density of the sample obtained was analysed by the Micromeritics pycnometer model AccuPyc II 1340 [13]. The characterisations of catalysts were done using Fourier Transform Infrared (FTIR) analysis to determine the active surface functional groups using a Nicolet, Thermo Scientific instrument with 4000-400 cm^{-1} spectra range. The thermal gravimetric analysis via Q600, Research Instruments was used to measure the weight changes in the sample as a function of temperature in a controlled atmosphere. The sample purge was set at 10 mL/min, and the temperature range was from 0 °C to 600 °C.

3. RESULT AND DISCUSSION

3.1 Transesterification of CPO at various Mn:Al metal ratio

Fig. 1. shows the FAME density obtained from the transesterification of CPO with the mixed oxide catalysts prepared at various Mn:Al metal ratios. The FAME density is higher at 875 kg/m^3 and 871 kg/m^3 for catalyst prepared at Mn:Al metal ratios of 1:1 and 0:1, respectively. However, the FAME density is lower at below 865 kg/m^3 for Mn:Al metal ratio of 2:1, 1:2 and 1:0. The catalyst prepared at Mn:Al metal ratio of 1:2 obtained a FAME density of 862 kg/m^3 which is closest to the standard palm oil biodiesel density of 864 kg/m^3 [16]. The FAME density obtained is similar to that of the reaction using palm fatty acid distillate (PFAD) via Cr-Ti catalyst [5]. FAME density is an important property of biodiesel because it influences the efficiency of fuel atomisation [17]. High fuel density may affect exhaust emissions, resulting in increased emissions of particulate matter and undesirable NOx gaseous pollutants.

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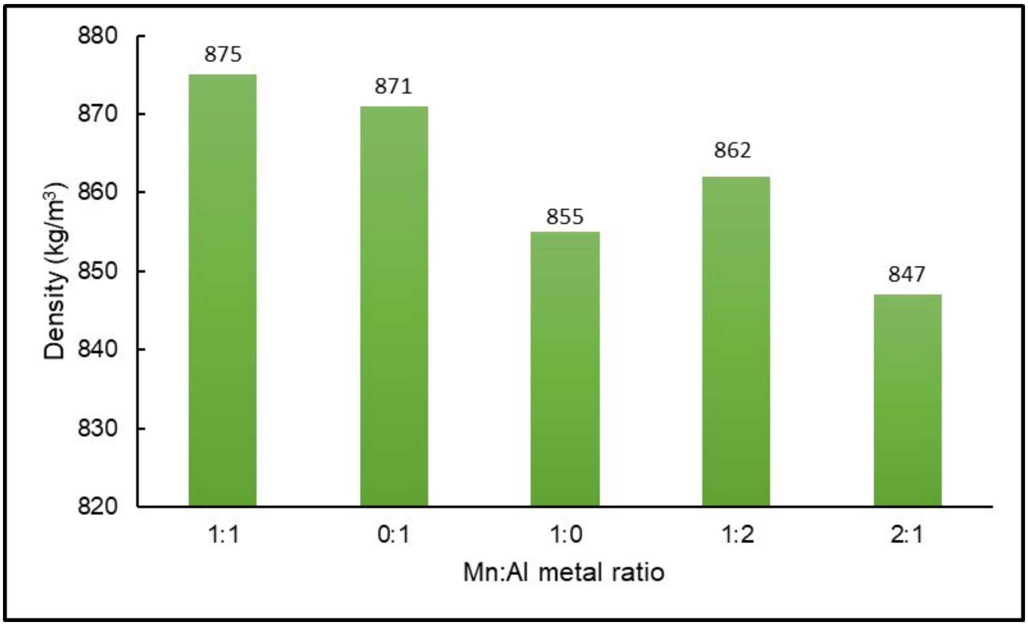

Fig. 1. Effects of different metal ratios of Mn-Al mixed oxides catalyst on FAME density

3.2 Surface functional characteristics of Mn-Al mixed oxides catalysts

Fig. 2. shows the FTIR spectrums of Mn-Al mixed oxides catalysts at various metal ratios. In general, the spectrums for the metal oxides are broad and appear at lower wavenumbers within 400 to 1200 cm^{-1}. The spectrums show the characteristic bands of inorganic compounds as opposed to organic compounds, which have sharper and more distinct bands arising from the C-H and C-C bond stretching and bending vibrations, giving valuable information about the metal oxides. The bands characteristic of metal oxides containing metal (M) and oxygen (O) include the M-O bending or stretching vibrations that appear in the fingerprint region of 400-1100 cm^{-1}. The appearance of small bands at approximately 1600 cm^{-1} corresponds to the M-O-H bending vibrations of the surface hydrated layer [11]. The findings indicate the presence of trace amounts of water vapour that are physisorbed on the surface of the metal oxides. The small bands that appeared at the high wavenumber region of 3600-3800 cm^{-1} represent the O-H stretching vibrations [18]. Fig. 2. also suggests that a variation in the metal ratio formulations affects the peak intensities possible due to the differences in the net dipole moment of the bi-metal oxides during vibration resulting in the less intense peak for Mn:Al metal ratio of 2:1 compared to 1:1 and 1:2 [11]. The FTIR spectrums indicate Mn-Al mixed oxides catalysts mainly consist of metal oxide and metal hydroxide surface functional groups.

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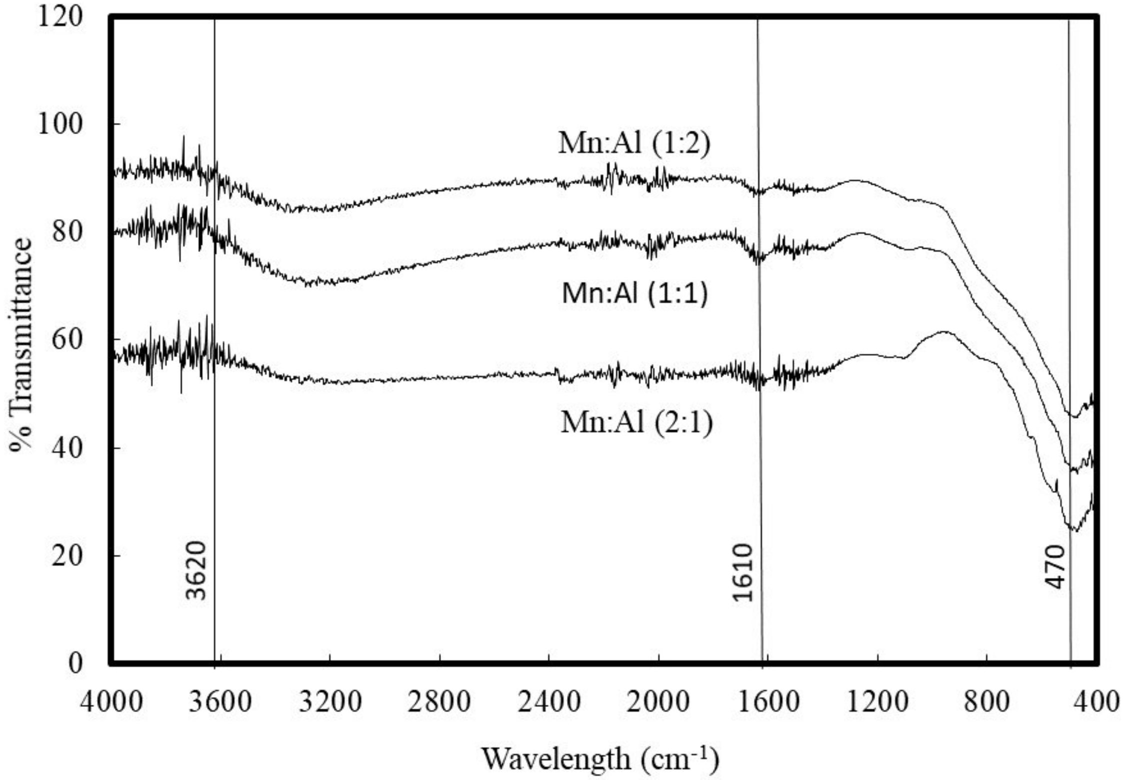

Fig. 2. FTIR spectrums of Mn-Al mixed oxides at different metal ratios

3.3 Thermal gravimetric analysis of Mn-Al mixed oxides

Fig. 3. shows the TGA profile for the catalysts Mn:Al metal ratio of 1:2 and 0:1 that were calcined at 500 °C for 2 h. The profiles show significant weight loss from room temperature of 25 °C to 120 °C due to the evaporation of moisture from the catalyst surface. The findings indicate that the metal oxides catalyst has a hygroscopic nature. The subsequent weight loss between 110 – 200 °C is mostly associated with the desorption of the interlayer physisorbed water molecules and decomposition of precursor substances such as nitrate compounds [19]. The percent weight loss appears less significant from 300 °C onwards for the Mn:Al metal ratio of 1:2, indicating the formation of thermally stable mixed metal oxides. However, for the Mn:Al metal ratio of 0:1, which is a single metal oxide, there is slight downward trend in weight loss from 300 °C onwards, indicating less stable compound. The findings indicate that suitable calcination treatment at 500 °C contributes to the formation of a thermally stable mixed oxides catalyst [20]. As indicated in Fig. 1., the catalyst with Mn:Al metal ratio of 1:2 achieved the FAME density closest to the standard palm oil biodiesel density. Thus, the catalyst thermal stability could be among the reasons for good activity in producing FAME.

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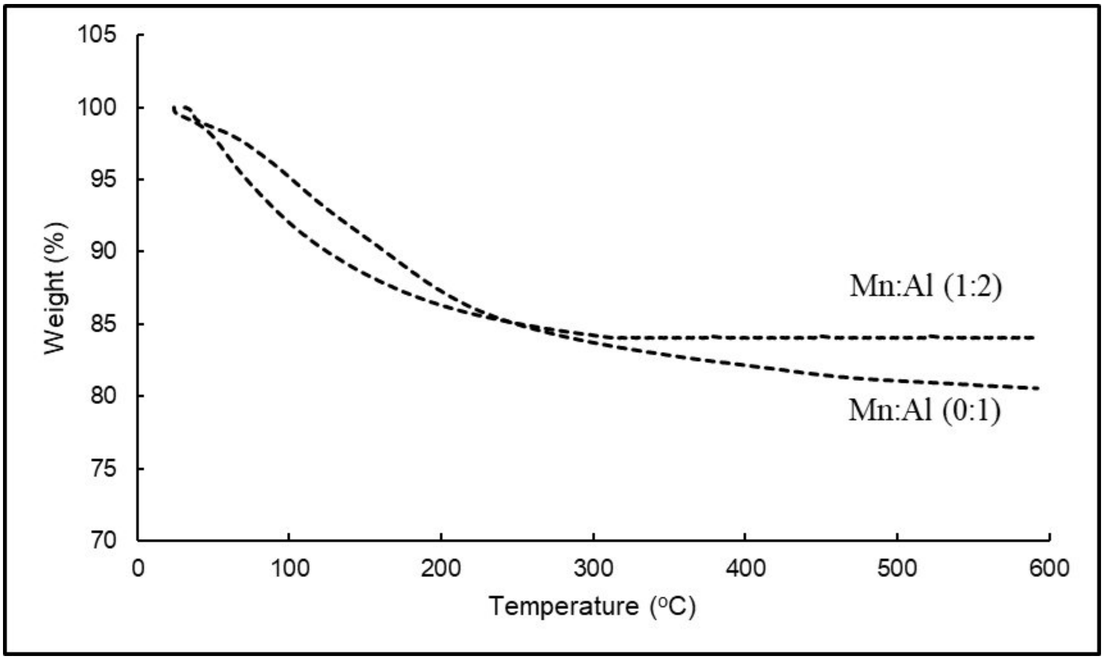

Fig. 3. TGA profiles of Mn-Al mixed oxides catalysts at different metal ratios

4. CONCLUSION

This study on Mn-Al mixed oxides catalysts in the production of FAME from CPO has shown that the catalyst used in the transesterification of CPO at 2.5 wt.% catalyst dosage and 3 h reaction time obtained the FAME density of 862 kg/m^3. The value is closest to the standard palm oil biodiesel density of 864 kg/m^3, which indicates good catalytic activity. The surface functional groups indicate the presence of OH stretching vibration and M-O bending vibrations, which are typical of inorganic metal oxides FTIR spectrums. The catalyst also has good thermal stability, which is an important characteristic for heterogeneous catalysts in reaction to produce FAME. The results indicate that the Mn-Al mixed oxides catalyst has promising application in FAME production from CPO.

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6. CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare the absence of conflicting interests with the funders.

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7. AUTHORS' CONTRIBUTIONS

Wan Zuraida Wan Kamis: Conceptualisation, supervision, writing- review and editing; Siti Athirah Ramli: Conceptualisation, methodology, formal analysis, investigation and writing-original draft; Nur Alwani Ali Bashah: Writing- review and editing; Vicinisvarri Inderan: Review, and validation; Norain Isa: Review, and validation.

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