PRELIMINARY STUDY ON THE USE OF MAGNETIZE Fe_3O_4-ZrO_2 CATALYST FOR BIODIESEL PRODUCTION

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Abstract

Plant oil as second generation biofuel especially waste cooking oil has been found to simplify the shortcomings experienced by its predecessors. However, high free fatty acid content represents the major limitation which requires the waste cooking oil to undergo a two-step process to produce biodiesel. As an alternative, in this study, Fe_3O_4-ZrO_2 catalysts were developed for simultaneous esterification–transesterification of waste cooking oil to biodiesel. The magnetic function of Fe_3O_4 has the advantage in the separation process, avoid the loss of catalyst and increase its reusability. First, Fe_3O_4 was synthesized using co-precipitation method where $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ were combined in deionized water to form black precipitate. Then, the precipitate was dried at 40°C for 24 hours. The Fe_3O_4-ZrO_2 catalysts were further synthesized using various Fe_3O_4 loadings (10-30 wt.%) via incipient wetness impregnation method, dried at 120 °C followed by calcination at 700 °C for 5 hours. All catalysts were characterized using Thermogravimetric Analysis (TGA) for degradation behaviour and Fourier Transform Infrared Spectroscopy (FTIR) to detect the functional groups presence. It was found that the highest biodiesel yield was achieved by 20Fe-Zr catalyst using 12:1 methanol to oil ratio and 10wt% catalyst loading at 60°C for 7 hours.

Keywords: *Biodiesel, waste cooking oil, magnetize catalyst, transesterfication.*

INTRODUCTION

Concerns over finite supply of fossil fuel and rapid fossil fuel price in 2007-2008 has stimulated interests in biodiesel. Doherty (2012) predicted the fossil fuel that generate into oil will run out by 2052, gas by 2060 and coal will last till 2090. Research on the use of alternative energy has escalated tremendously and shows a bright future for the replacement of conventional fossil fuel. This makes biodiesel an interesting renewable energy resource as compared to petroleum diesel which takes millions of years to regenerate from the decay of animals and plants.

High consumption of petroleum diesel can generate high production of carbon monoxide emissions into environment as compared to biodiesel (Shahir et al., 2015). High carbon monoxide emissions can lead to air pollution, greenhouse effects and global warming (Levy, 2015). Therefore, the use of biodiesel should be highlighted to reduce the pollution to nature. Biodiesel or fatty acid methyl ester (FAME) is a promising alternative energy as it has similar properties to petroleum diesel. Also, it is non-toxic, biodegradable and has a low concentration of sulphur, carbon monoxide and carbon dioxide (Huang et al., 2012).

In the production of biodiesel, the selection of feedstock is vital as it determines the final biodiesel processing cost. Interestingly, biodiesel can be produced from waste cooking oil (WCO) using suitable catalyst and reaction conditions. Using WCO for biodiesel production has a dual advantage which is an effective way to reduce the production cost of biodiesel and reduce environmental pollution problems due to the disposal of the WCO. Transferring the WCO into processing equipment that can change it into a new valuable product is far better than channelized it into the sewage system in which can cause water pollution (Mandolesi de Araújo et al., 2013).

Generally, homogeneous catalysts are used in the production of biodiesel via transesterification process. However, the use of homogeneous catalysts leads to several problems such as soap production, reactor corrosion, difficult to recover and produce large amounts of wastewater. All of these drawbacks can increase the overall cost of biodiesel production. Therefore, the use of heterogeneous catalyst is promising to overcome the drawbacks associated with the homogeneous catalysis process.

Other challenges of using heterogeneous catalyst is the catalyst recovery after the transesterification for reuse potential. Successful of the catalyst recovery is important from both the economic and the environmental point of view. Fe_3O_4-ZrO_2 was selected as the potential heterogeneous catalyst in this study due to its amphoteric character to simplify the reaction process as well the magnetize properties of the catalysts which enable them to be recovered easily after completion of the process by using a magnet.

METHODOLOGY

1. Characterization of Feedstock

The WCO was collected from café around Universiti Sains Islam Malaysia where it was used for frying purpose. WCO was washed with hot water and filtered to remove salt and undissolved materials. The oil was further dried in oven at 110˚C for 24 hours. The properties of WCO such as acid value (Santos et al., 2018) and saponification value (Tan et al., 2013) were determined experimentally following the standard test methods. The average molecular weight of WCO was calculated using the following formula:

$$Average\ molecular\ weight = 56.1 \times 1000 \frac{3}{SV - AV}$$

Where,

SV = Saponification value (AOCS method Cd 3a-94)
AV = Acid value (European Standard EN 14104)

2. Synthesis of Fe_3O_4-ZrO_2 Based Heterogeneous Catalyst

Ferric oxide nanoparticles were developed using co-precipitation method. 0.02M $FeSO_4.7H_2O$ and 0.01M $FeCl_3.6H_2O$ were mixed in 60 ml of deionized water to preserve the 2:1 ratio. The solution was sonicated for 30 min at 65˚C. In 100 ml of deionized water, 4M NaOH was prepared and put into the ferum solution drop by drop until the pH achieved 13, resulting in black precipitate. The flask was then sealed, and the reaction was allowed to run for an hour in the sonicator at 65˚C. After the reaction was finished, the mixture was allowed to cool at room temperature before being centrifuged for 8 minutes at 10000 rpm. The supernatant was removed, but the black precipitate was retained. The resulting precipitate was washed several times with deionized water and ethanol. Finally, the precipitate was dried in a 40˚C oven for 24 hours (Yadav et al., 2020). The Fe_3O_4-ZrO_2 catalyst was then produced using incipient wetness impregnation process. The estimated quantity of ferric oxide, corresponding to 10, 20, and 30 wt.% Fe_3O_4, was dissolved in deionized water, and the needed amount of ZrO_2 was slowly added into the solution, which was agitated at 100 rpm for 5 hours. Water was then removed from the catalyst by drying it in an oven at 110˚C for 5 hours before it was calcined at 700˚C in a furnace for 5 hours.

3. Characterization of Catalyst

The heat stability and degradation behaviour of the catalysts were determined using thermogravimetry analysis (TGA). TGA was done on a Mettler Toledo from room temperature to 700˚C at a heating rate of 10˚C min^{-1} using N_2 gas flow of 20 mL min^{-1}. Fourier Transform Infrared Spectroscopy (FTIR) was used to capture the functional group and chemical bonds in a molecule by creating an infrared absorption spectrum using the Nicolet -iS50 model.

4. Screening of Catalyst Performance

Transesterification was carried out in a 100 mL three-neck glass flask provided with a water-cooling condenser and thermometer. Initially, the transesterification was tested using all of the synthesized catalysts in order to discover the most active catalyst for this procedure. The reaction parameters were 12:1 methanol to WCO ratio, 10 wt.% catalyst loading, and 3 hours at 60°C with continual stirring at 350 rpm.

The transesterfication was further optimized using the most active catalyst via standard one-factor-at-a-time (OFAT) method with various catalyst loading (10, 20, 30 wt.%) and reaction periods (3, 5, 7 h) with continual stirring. The methanol to WCO ratio and reaction temperature were set at 12:1 and 60°C, respective. The agitation speed was kept constant at 350 rpm.

After the reaction has been completed, the top layer containing FAME will be collected and washed with warm water and ethanol to eliminate saponified by-products. This equation was used to determine the percentage yield of biodiesel:

$$biodiesel\ yield\ (\%) = \frac{weight\ of\ biodiesel}{weight\ of\ oil} \times 100$$

RESULTS AND DISCUSSION

1. Characterization of Feedstock

WCO is regarded as one of the best feedstocks for the synthesis of biodiesel since its cetane number, diesel index, viscosity, specific gravity, pour point, cloud point, and other fuel properties studied were equal to those of virgin oil (R U et al., 2011). The qualities of WCO as a feedstock for biodiesel synthesis were assessed in this study based on acid value and saponification value, as well as its average molecular weight, as indicated in Table 1.

Table 1: The properties of selected waste cooking oil.

Property	Unit	Value
Acid value	mg KOH/g	1.6238
Saponification value	mg KOH/g	221.0184
Average molecular weight	g/mol	767.1109

The acid value of the WCO was 1.6238 mg KOH/g, confirming the existence of free fatty acid content (0.81%) in the oil. Free fatty acid is a chemical compound generated from waste cooking oil. A high content of free fatty acid promotes saponification and a poor percentage yield of biodiesel. Furthermore, a large concentration of free fatty acid will enhance viscosity. The maximum FFA value needed in biodiesel is only 0.05 mgKOH/g (Yaakob et al., 2013). The saponification value was discovered to be 221.0184 mg KOH/g. The obtained saponification value is more than the 198 mg KOH/g given by Alias et al (2018). In biodiesel, the maximum saponification value necessary is 312 mgKOH/g. The lower the saponification value, the less suitable the oil is for creating soap, which is beneficial for biodiesel processing. The WCO has an average molecular weight of 767.1109 g/mol that had been calculated by using SV and AV.

2. Characterization of Catalyst

TGA is critical technique for determining the decomposition temperature and thermal stability of the catalysts. Figure 1 shows the TGA curves of ZrO_2, 10Fe-Zr, 20Fe-Zr and 30Fe-Zr catalysts. TGA data show that all of the catalysts are thermally stable up to 700°C. Sulaiman (2020) reported similar results, reporting that the thermogravimetric curve showed practically constant sample weight after 700°C, suggesting that $Fe/Ba/Al_2O_3$ catalysts had completely dissolved, giving pure metal oxide. As a result, a calcination temperature of 700°C was discovered to be sufficient for employing Fe_3O_4-ZrO_2 catalyst, which may improve the transesterification process.

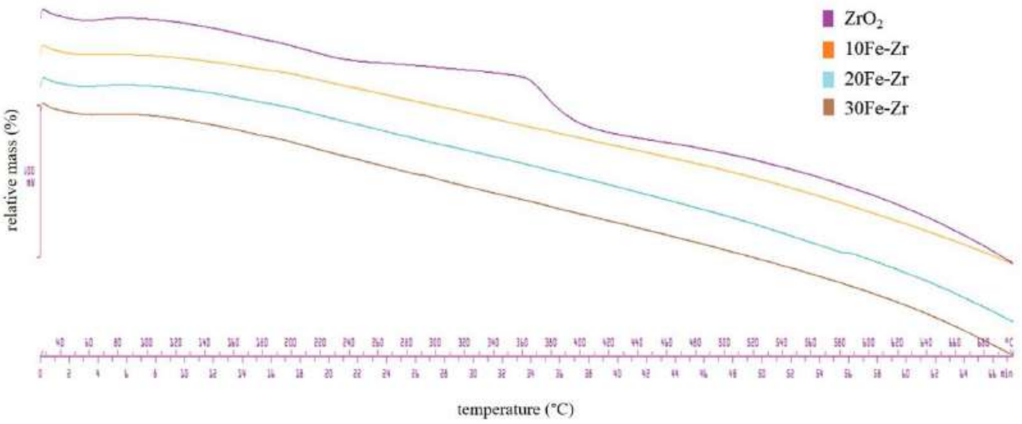

Figure 1: TGA curves of synthesized catalysts.

FTIR is used to detect the functional groups presence in the compound. Figure 2 shows the FTIR curves of 10Fe-Zr, 20Fe-Zr, 30Fe-Zr, $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$. Corresponding to FTIR results two broad peaks at 3682.12 cm^{-1} and 988.88 cm^{-1} which attributed to the sulphate ($FeSO_4.H_2O$) group and three broad peaks at 3249 cm^{-1}, 1633 cm^{-1} and 739 cm^{-1} which attributed to the chloride ($FeCl_3.6H_2O$) group, respectively, were lost after calcination. The FTIR spectra of Fe_3O_4 exhibited intense peaks between 580 and 630 cm^{-1}, which attributed to the stretching vibration mode associated with the bonds of Fe-O in the Fe_3O_4 crystal lattice. Further the absorbance peak present at 628 cm^{-1} could be attributed to the Zr–O bond (metal and oxygen bond) which generally represented the presence of ZrO_2 particles. From the result we can see that there are no sulphate and chloride peaks observed in the catalyst samples after calcination at 700°C. This shows that Fe-Zr was produced as a metal and oxygen bond without other materials. The Fe-Zr catalysts used is also safe from the occurrence of unwanted reactions that will hinder the esterification and transesterification process in the production of biodiesel.

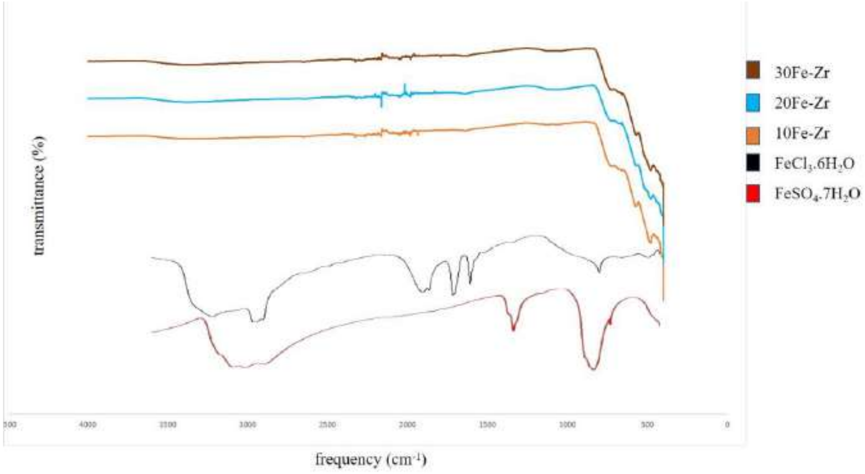

Figure 2: FTIR spectra of the synthesized catalysts.

3. Screening of Catalyst Performance

The synthesized catalysts were then employed in the transesterification of WCO to make biodiesel. Figure 3 compares the catalytic performance of Fe-Zr catalysts and single ZrO_2 under fixed reaction conditions, 12:1 methanol to oil ratio and 10% catalyst loading at 60°C for 3 hours with continual stirring at 350 rpm. As can be seen, the percentages yield of biodiesel are 2.66, 2.53, 4.04, 1.87 for ZrO_2, 10Fe-Zr, 20Fe-Zr and 30Fe-Zr catalysts, respectively. The results show that the mixed oxide catalyst of 20Fe-Zr possess higher biodiesel yield than single ZrO_2. Sun et al. (2010) found that the strong catalytic performance of the catalysts is due to sites situated between the various oxides. Umdu et al. (2009) discovered that CaO and MgO were not active for transesterification when using similar biodiesel feedstock. However, when a mixed oxide catalyst of 80 wt.% CaO/Al2O3 was used with a methanol to WCO molar ratio of 30, 97.5% biodiesel production was obtained. The researchers noted that using a mixed oxide catalyst enhanced not only the basic site density but also the basic strength of the catalyst for high biodiesel conversion. Thus, in the subsequent experiment 20Fe-Zr catalyst was selected in the synthesis of biodiesel.

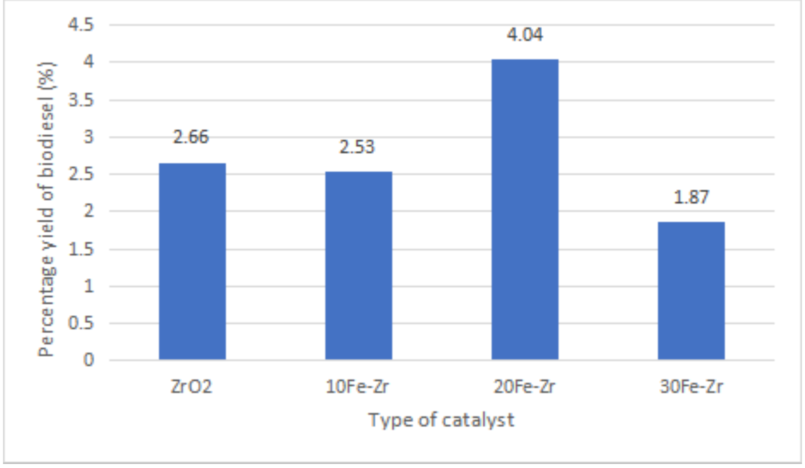

Figure 3: Biodiesel yield using different synthesized catalysts.

Understanding the individual influence of process factors is critical for optimising reaction conditions and achieving the intended outcome in both qualitative and quantitative terms. Based on the outstanding performance of the 20Fe-Zr catalyst, it was chosen for additional optimization studies in order to create a high percentage yield of biodiesel utilising the classic one-factor-at-a-time (OFAT) technique with varying catalyst loading and reaction periods. The methanol to WCO ratio was specified at 12:1 and the reaction temperature was set to 60 °C.

The effect of varying catalyst loadings on the percentage yield of biodiesel employing 20Fe-Zr as the catalyst is shown in Figure 4. The results indicate that increasing the amount of catalyst from 10 to 30 wt.% produces a drop in biodiesel yield. A significant quantity of catalyst is required to produce enough active sites for full transesterification. A high concentration of catalyst, on the other hand, may produce agglomeration of the catalyst particles. This issue may lead to a stagnant mass transfer rate, hindering biodiesel production and produce lower percentage yield of biodiesel. Similar study was found by Agarwal et al. (2012) using KOH-alumina catalyst. The higher the amount of catalyst in the same amount of oil and methanol, the more concentrated the solution in terms of catalyst, resulting in poor mixing at the same agitation speed, which may cause some amount of catalyst to remain unused due to increased mass transfer resistance which lead to low conversion.

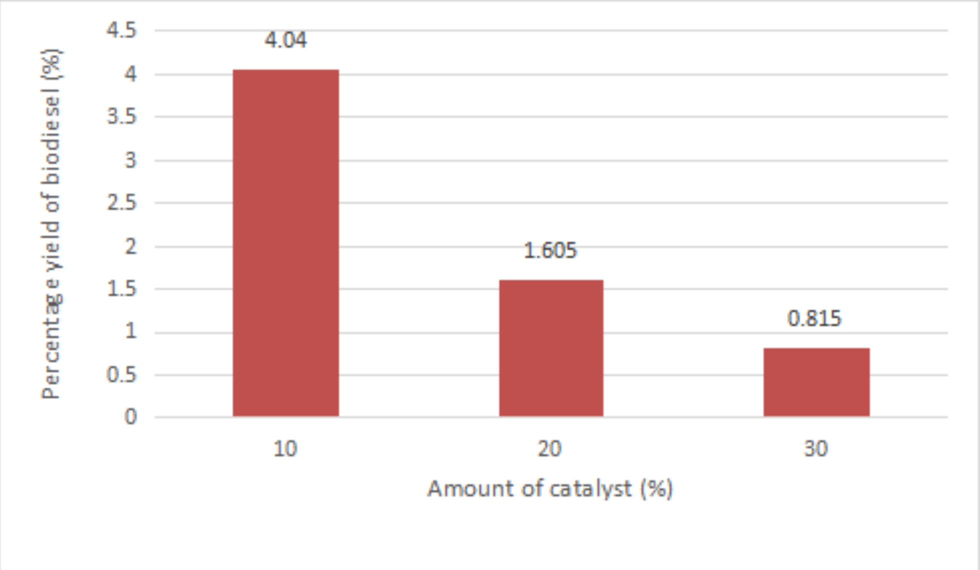

Figure 4: Effect of catalyst loading on percentage yield of biodiesel. The reaction was carried out using 12:1 methanol to WCO ratio at 60 °C reaction temperature for 3 hours.

Reaction time is an important characteristic to produce high percentage yield of biodiesel in a short amount of time and, as a result, decrease process cost, especially in large-scale production. Figure 5 shows the influence of reaction time on percentage yield of biodiesel. As can we see from the results obtained, increasing the duration causes an increase the percentage yield of biodiesel. Basically, increasing the reaction times will increase the frequency of collision between catalyst and substrate molecules in the mixture which lead to high formation of interest products. This is obvious from the data, as the percentage yield of biodiesel was increased slightly from period of 3 to 7 hours to give an optimal point of 4.855%. A prolonged reaction time at high temperatures may cause methanol evaporation and diminish the mass transfer rate, lowering the percentage yield of biodiesel. Nizah et al. (2014) discovered a poor biodiesel yield at 3 hours reaction time while producing biodiesel from Jatropha curcas using a Bi_2O_3-La_2O_3 catalyst. It was due to the lack of period for the methanol to mix and disseminate into the oil. Similarly, a maximum percentage yield of biodiesel was produced after 4 hours of reaction time, despite the higher reaction temperature of 150 °C compared to this investigation. In this study, the maximum biodiesel yield of 4.855% was achieved using 12:1 methanol to WCO ratio and 10 wt% 20Fe-Zr catalyst at 60 °C reaction temperature for 7 hours.

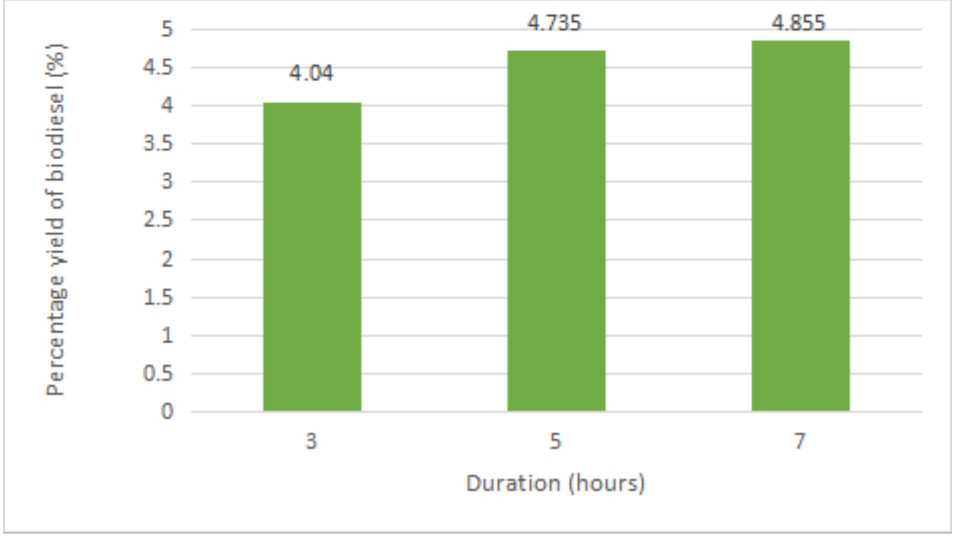

Figure 5: Effect of reaction time on percentage yield of biodiesel. The reaction was carried out using 12:1 methanol to WCO ratio and 10 wt% 20Fe-Zr at 60 °C reaction temperature.

In the current study, even though the biodiesel did not achieve a high percentage yield (>90%) of biodiesel, the synthesized catalyst has magnetic properties which enable them to be recovered easily after completion of the process by using a magnet. Figure 6 shows the magnetize properties of synthesized 20Fe-Zr.

Figure 6: The magnetize properties of synthesized 20Fe-Zr catalyst.

CONCLUSION

Biodiesel was succesfully synthesized from WCO using Fe_3O_4-ZrO_2 as heterogeneous catalysts. It was found that the mixed oxide catalysts exhibited better catalytic activity compared to the single ZrO_2, where 20Fe-Zr presented the superior catalytic activity (4.04%) for the synthesis of biodiesel. The maximum biodiesel yield achieved was 4.855% using 12:1 methanol to WCO ratio and 10wt% catalyst loading at 60°C for 7 hours.

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