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Catalytic production of biodiesel from corn oil by metal-mixed oxides

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ABSTRACT: The present study investigates the transesterification of corn oil with methanol over two oxides of MgO and ZnO at 65 °C and 1 atm. These two catalysts have been prepared via a conventional co-precipitation process. As for MgO, the corresponding mixed metal nitrate solution has been mixed and heated at the presence of urea. ZnO has also been synthesized by co-precipitation of metal acetate at the presence of oxalic acid and ethanol. The catalysts then have been characterized by means of X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). XRD results indicate high purity for both catalysts. Also, catalytic activity has been evaluated in methanol reflux temperature through corn oil transesterification, with the impacts of reaction variables, like catalyst amount, methanol/oil molar ratio, and reaction time on biodiesel yield, investigated by means of HNMR spectrum. Under appropriate transesterification conditions at 65 °C (catalyst amount= 5%, methanol/ oil ratio= 20, and reaction time= 10 hr), an ME content of 62.61% can be achieved, using MgO catalyst. Similarly, the experiments have been repeated to achieve the best yield, using ZnO catalyst, with the highest rate, equal to 53.1%, obtained in 9% of catalyst and methanol/oil ratio of 30 over 10 hr. Furthermore, reusability of ZnO and MgO has been evaluated in transesterification reaction.

Keywords: biodiesel, corn oil, MgO, transesterification, ZnO.

INTRODUCTION

Biodiesel is an alternative biomass-based fuel, synthesized through transesterification of vegetable oils/ animal fat with a short chain alcohol at the presence of catalysts (Chai et al., 2007). The physicochemical and fuel properties of this environmentally-friendly fuel are similar to those of petroleum-based diesel oil (Kim et al., 2004; Golzary et al., 2015). Moreover, biodiesel can be applied to compression-ignition diesel engines with very little or without modifications (Arzamendi et al., 2008; Saber et al., 2016). Regarding the emissions, it has been demonstrated that exhausted gas from biodiesel combustion contains no SOX and relatively small amount of CO and unburned hydrocarbons, compared to combustion products of conventional diesel fuels (Leclercq et al., 2001; Peterson & Scarrah, 1984; Watkins et al., 2004). In addition, its

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lubricating nature can prolong the engine's life (Granados et al., 2007). Other benefits of the biodiesel are high cetane number, high flash point, and acceptable cold filter plugging point (CFPP) (Dorado et al., 2004; Singh & Singla, 2015).

Conventionally, the process of biodiesel production is performed by transesterification of triglycerides in oils and fats with short chain alcohols in presence of homogeneous basic catalysts, such as sodium and potassium, hydroxides carbonates, or alkoxides (Ono, 2003; Daliry et al., 2017).

Many types of heterogeneous solid base catalysts are also studied for transesterification of vegetable oil, which includes a wide range of rare earth and alkaline oxides like MgO, CaO, SrO, alkali metal compounds supported on alumina or zeolite, alkoxides, hydroxides, and hydrotalcites (Liu et al., 2017; Demirbas, 2016; Gu et al., 2015; Sirajuddin et al., 2015), most of which show low activity, hence the reaction time would be considerably prolonged (6 to 24 h). Poor recyclability and inefficiency at the presence of free fatty acids and water are another obstacle of transesterification reaction with these catalysts. Therefore, there has been several attempts to study the optimization of reaction conditions in order to reach the highest yield in the shortest reaction time (Nakajima et al., 2007; Xie et al., 2006; Gryglewicz, 1999; Gelbard et al., 1995). In the present work, we compare catalytic activity of our self-prepared ZnO and MgO catalysts in transesterification reaction.

MATERIAL AND METHOD

Catalyst preparation and characterization

Both catalysts were prepared by conventional co-precipitation method. In a typical method of MgO preparation, the required amounts of $MgO(NO_3)_2$ and urea are properly dissolved in de-ionized water. The mixture was then stirred and heated to drain all of its water ccontents. Once precipitation was completed, the precipitant was filtered and washed with water thoroughly. The resultant catalyst mass was oven-dried at 80 °C for 24 h, followed by calcination at 450 °C for 5 h.

In case of ZnO, the required amount of $C_4H_6O_4Zn$ was perfectly dissolved in methanol. The ethanolic solution was added to oxalic acid under heating and vigorous stirring conditions. The resultant mixture was then left to age for 24 h at 80 °C. Consequently, te dried gel was calcined in a muffle furnace at 800 °C for 2 h.

Synthesized catalysts structure and cluster size were then determined by X-Ray Diffraction technique, using Philips X'Pert MPD X-Ray Diffractometer with Cu-K α radiation (λ= 1.54 °A) at a generator voltage of 40 KV and a generator current of 40 mA.

Scanning Electron Microscopy (SEM) images were recorded by Quanta 400 thermal field from Philips FEI Company.

Transesterification of corn oil

Refined edible oil was donated by Colaleh Industry Co, Ltd, while methanol, with purity of 99%, was purchased from local market. Both were used without any further purification. Acidic contents of corn oil was investigated via titration process and transesterification reactions were carried out in a 150 mL, tree neck round bottom flask, equipped with a magnetic stirrer with a stirring rate of 800 rpm, a thermometer, and a reflux condenser. All reactions were carried out in 65 °C (methanol reflux temperature) with the reaction time being 10 h. The samples were taken out from the reaction mixture every 2 h. Reaction progress was assessed with HNMR spectrum (model DPX-400; Bruker) in deuterated chloroform (CDCL3), using tetramethylsilane as internal standard. Methyl ester content in the reaction mixture was estimated with Equation (1) (Hao et al., 2008).

$$Yield=A_1*2/A_2*3 \qquad (1)$$

where A1 and A2 are the area of HNMR

peaks, corresponding to methoxy and methylenic protons, respectively.

RESULTS AND DISCUSSION

Characterization of MgO and ZnO catalysts

In order to appreciate the degree of catalytic activities of MgO and ZnO in corn oil transesterification, the catalysts were characterized by different methods such as XRD and SEM. Figure 1 (A and B) gives the information about purity and conformity of particles in XRD patterns of MgO and ZnO, respectively. XRD patterns of both precipitate calcined catalysts revealed strong and clear peaks, corresponding to only MgO and ZnO, without any characteristic peaks for other impurities to be observed. The photographs in Figure 2 (A and B) show particle size and morphological studies of the catalysts, taken by scanning electron microscope SEM. Elemental composition and physicochemical properties of synthesized oxide catalysts also are summarized in Table 1.

Table 1. Physicochemical properties of calcined MgO and ZnO

Catalyst	Particle Size (nm)^a	Cluster Size(nm)^b	Average size(nm)^c	Morphology^d
MgO	150-750	47.21	387	Cubic
ZnO	300-1500	36	641	Round

a) Drived from SEM images
b) Measured by Scherrer formula
c) Measured by Paint Software
d) Driven from SEM images

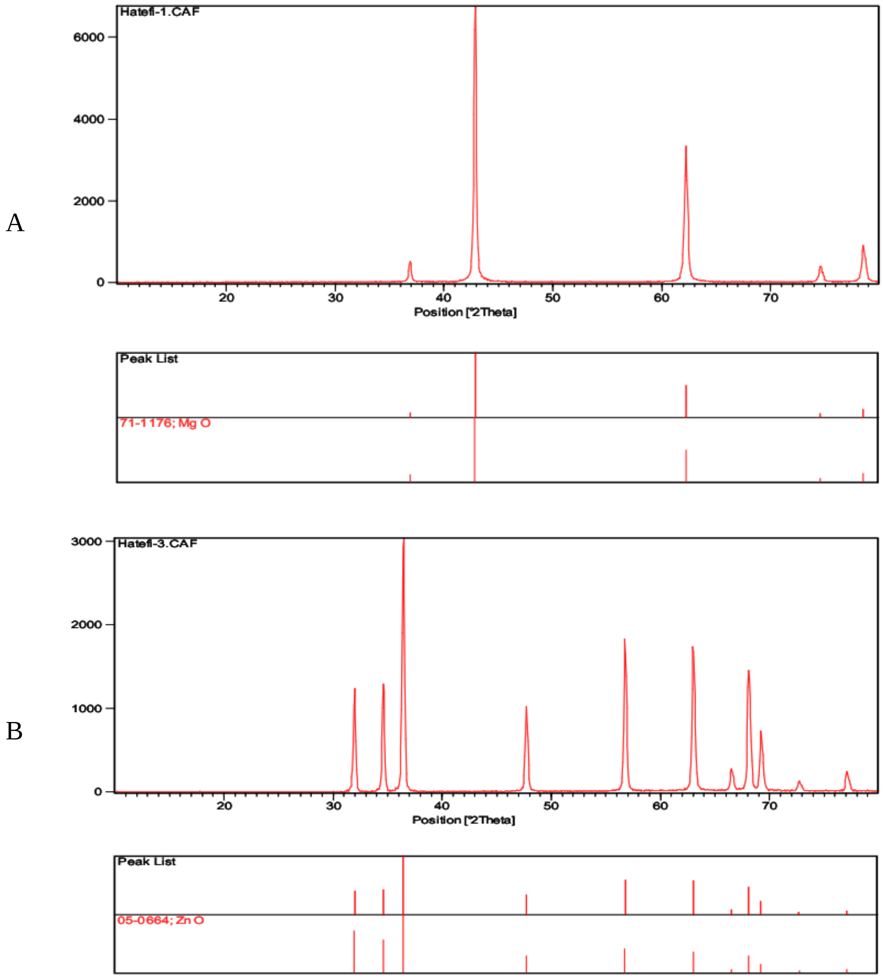

Fig. 1. XRD pattern of (a) MgO, (b) ZnO catalyst

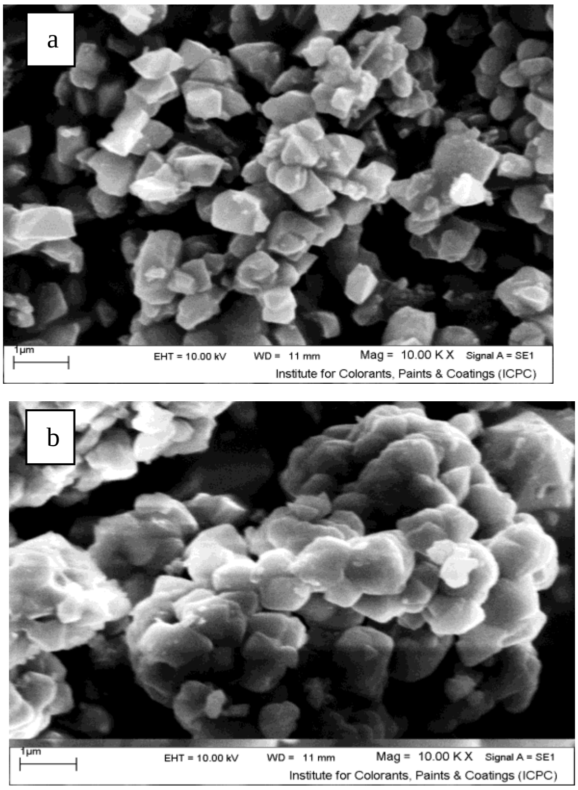

Fig. 2. SEM image of (a) MgO, (b) ZnO

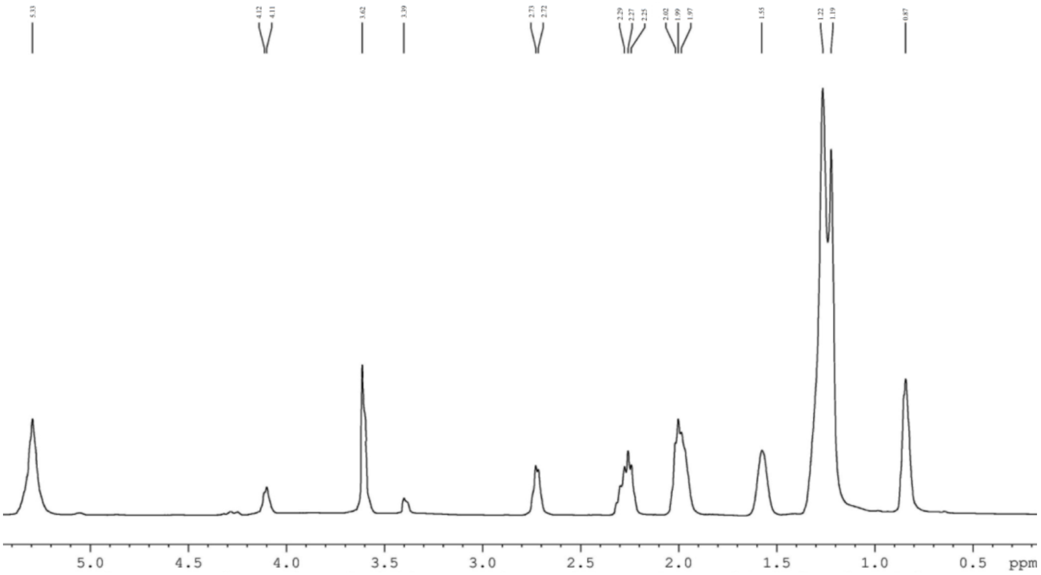

Fig. 3. HNMR spectra and peak assignment for transesterification reaction of corn oil in 36.66% yield

Evaluation of reaction progress

The trend of transesterification progress was evaluated by H-NMR spectrum. To illustrate this with an example, Figure 3 shows an H-NMR image, demonstrating oil conversion to methyl ester in the yields of 36.66%.

The relevant peak to methyl ester is a triple one, appearing in 3.7 ppm, representative of methoxy groups. Methoxy groups' peak was considered A_1 in the formula. Methylenic protons appear in 2.3-2.5 ppm, showing multiple peaks and the methylenic group was considered A_2 in Equation (1).

Impacts of catalyst loading on transesterification yield

In order to investigate the impact of catalyst loading on transesterification reaction yield, some experiments were conducted, which used various amounts of catalysts (both MgO and ZnO) in constant methanol/ oil molar ratio, all conducted at a temperature of 65 °C and for a reaction time of 10 h.

It can be seen from Figure 4 that the conversion of corn oil to bio diesel was 31.8% when 2% of MgO was applied as catalyst in transesterification reaction over 10 h. Further increasing the catalyst load caused methyl ester yield to grow. Transesterification yield ascended from 31.8% to 56.1% when the catalyst load was increased from 2% to 5%; however, the yields slightly declined, being 53.4% and 51.9% in catalyst loads of 7% and 9%, respectively.

Similar experiments were carried out, using ZnO as the catalyst. According to Figure 5, oil to methyl ester conversion soared from 27.64% to 40.07% as the amount of ZnO rose from 2% to 5%. It can be seen that a further increase in catalyst weight resulted in better methyl ester conversion as the reaction yield increased to 44%, using 7% wt of catalyst, followed by a yield of 51.3% with 9 wt% of catalyst. Similar to MgO, by increasing the catalyst amount beyond a certain percentage, the yield descended. This catalyst percentage was 11% for ZnO as the relevant yield was reportedly 43.46%.

Results illustrate that the biodiesel yield improved significantly as the catalyst amount increased, which can be explained thus: the solubility of alcohol in oil is limited so transesterification reaction can be carried out in the interface of two phases when catalyst loading is scarce. Reaction will be promoted by increasing the catalyst load to increase the proton concentration in the interface; consequently, more methyl ester will be formed (Vicente et al., 2004; KoohiKamali et al., 2012; Uprety et al., 2016).

As for decreasing oil conversion yield by increasing catalyst load beyond 5% and 9% in case of MgO and ZnO, respectively, the extra amounts of the catalyst will expedite the rate of soap formation, apparently reducing the yield of biodiesel.

As a result, recommended amount of catalyst load was reportedly 5% for MgO and 9% for ZnO.

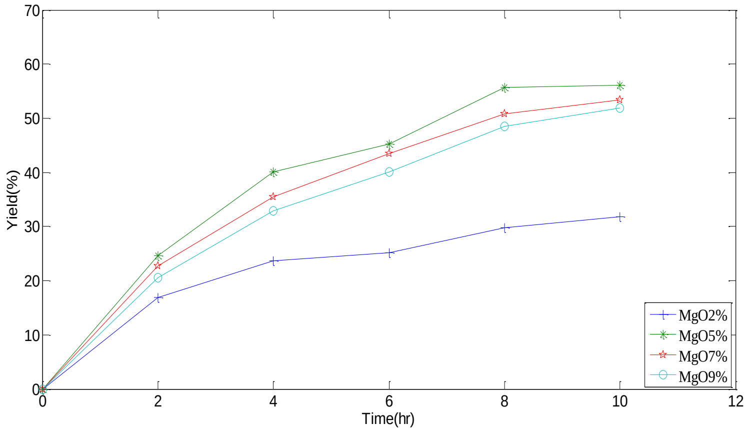

Fig. 4. Effect of MgO catalyst loading on transesterification of corn oil, Methanol/ oil ratio= 15, Temperature= 65 ºC

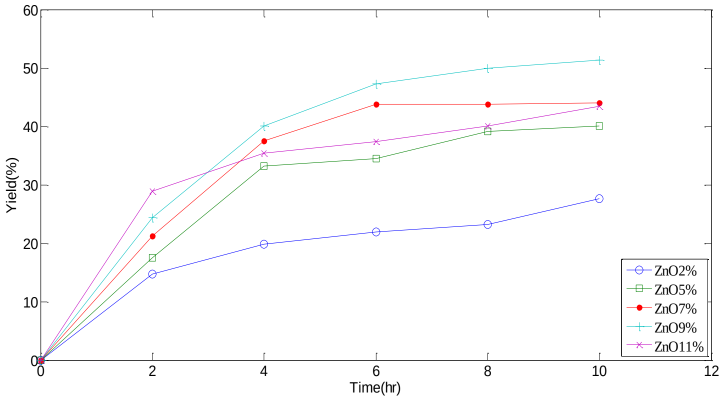

Fig. 5. Effect of ZnO catalyst loading on transesterification of corn oil, Methanol/ oil ratio= 15, Temperature= 65 ºC

Effects of alcohol ratio on transesterification yield

Transestrification is a reversible reaction; therefore, alcohol needs to be in excess in order to force the reaction towards the formation of methyl ester. The experiments were conducted, using different molar ratios of alcohol/oil (from 10 to 30) in constant amounts of catalyst load. The amount of catalyst was 5% and 9% for MgO and ZnO, respectively, which was the best amounts of catalyst load for transesterification reaction to reach its best yields. Reaction time was 10 h and the temperature, 65 °C for all experiments. Based on Figure 6, it can be seen that the conversion of corn oil gradually increased when the alcohol ratio rose from 10 to 20. The highest yield was 62.61%, which occurred in alcohol ratio of 20, after which the it descended to 60.7%, when the ratio reached 30.

Similarly, the same experiments were repeated, using ZnO as catalyst. According to Figure 7, the highest yield was 51.3% for alcohol ratio of 20; thereafter, it declined to 50.11% and 50.04% when alcohol ratio increased to 20 and 30.

The drop in conversion can be explained as follows:

1. Excessive amount of methanol triggers the conversion of triglycerides into monoglycerides, which improve the solubility of glycerol in methyl ester, so the phenomenon called “glycerolysis” happens for methyl ester, in turn decreasing triglycerides conversion.

2. Normally, transesterification begins when triglycerides are chemisorbed on the active sites. These are then protonated at the carbonyl group to give a carbocation ion that can undergo attacks by methanol to form esters.

When methanol is in excess, the approach of its molecules to the carbocation is enhanced, resulting in increased conversion. However, when the ratio of methanol/cottonseed oil is too high, the large excess of methanol will cause active sites to flood. As a result, in these experiments increased molar ratio hindered the complexation of triglycerides, protonated in the active sites (Tiwari et al., 2007; Mardhiah et al., 2017; Zhang et al., 2017).

From the analysis above, a molar ratio of methanol to oil equal to 20 was recommended when MgO was the catalyst and the optimum alcohol to oil ratio was 15, when ZnO acted as the catalyst.

Comparison between catalysts

Catalytic properties of each catalyst was evaluated and compared. From Figure 8, it can be seen that MgO had relatively better catalytic activity than ZnO.

In order to investigate the reasons, corn oil was titrated under heating condition, its fatty acid being 1.3%. According to this number, it is plainly visible that corn oil transesterification will be effectively expedited, using base catalysts than acid catalysts, which is why MgO was more effective than ZnO in transesterification reaction.

Reusability and regeneration of the catalysts

Reusability is one of the most important features of heterogeneous catalyst for its commercialization. The current study applied one method of regeneration. First, the catalysts were separated by centrifuging the reaction mixture. They were then washed, and dried in an oven at 100 °C. Figure 9 and Figure 10 compare catalytic activities of the catalysts in transesterification reaction. It can be observed that when MgO and ZnO catalysts were used in succession, ME content was remarkably reduced to 24.4% and 8.3%, respectively. Catalyst deactivation was due to the fact that alkali metal compounds were dissolvable in methanol, which corroded the active ingredients, leading to a decrease in the biodiesel yields in the reiterated experiments (Alcantara et al., 2000; Rade et al., 2015; Negm et al., 2017).

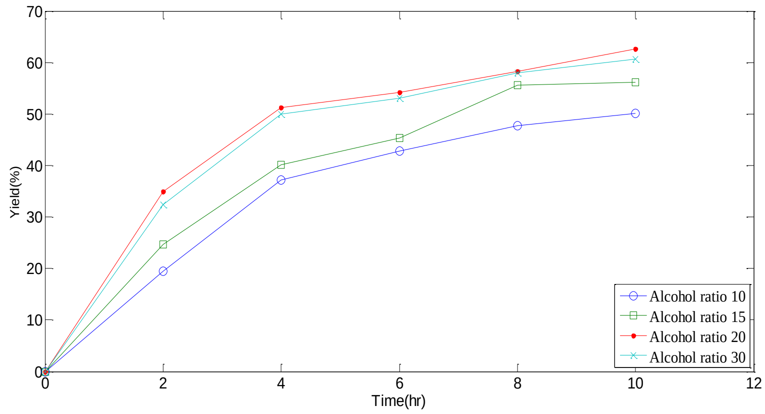

Fig. 6. Dependence of methyl ester content on methanol/oil molar ratio over MgO catalyst. catalyst amount= 5 wt%, Temperature= 65 °C

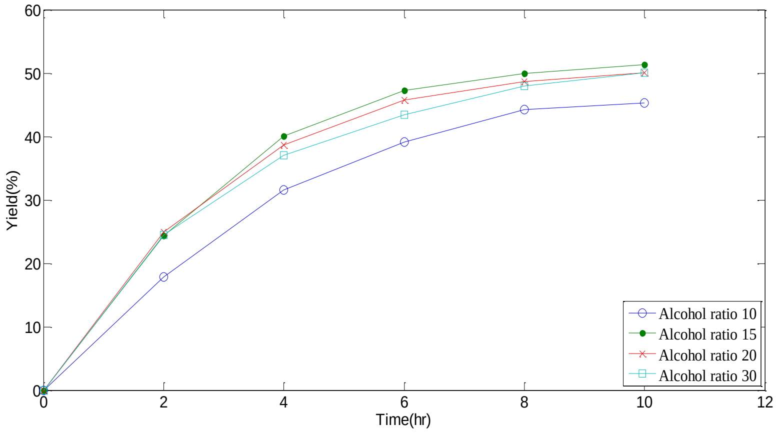

Fig. 7. Dependence of methyl ester content on methanol/oil molar ratio over ZnO catalyst. catalyst amount= 9 wt%, Temperature= 65 °C

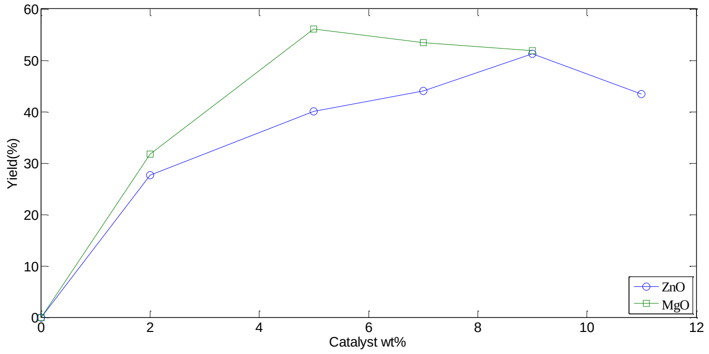

Fig. 8. Comparison between MgO and ZnO in different catalyst loads and methanol/ oil ratio of 15, in 65 ºC

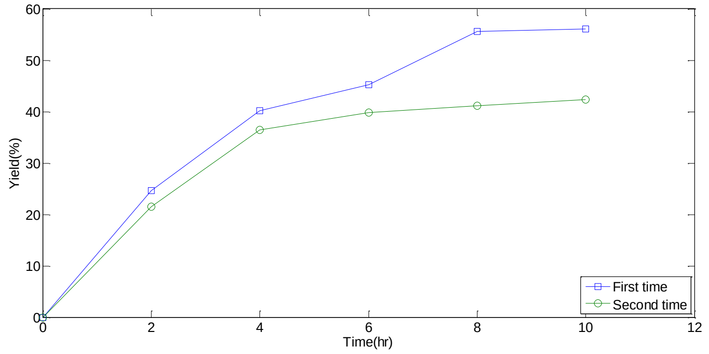

Fig. 9. Biodiesel yield, using recycled MgO as catalyst, Catalyst loading = 5 wt%, Methanol/oil ratio= 15, Temperature= 65 ºC

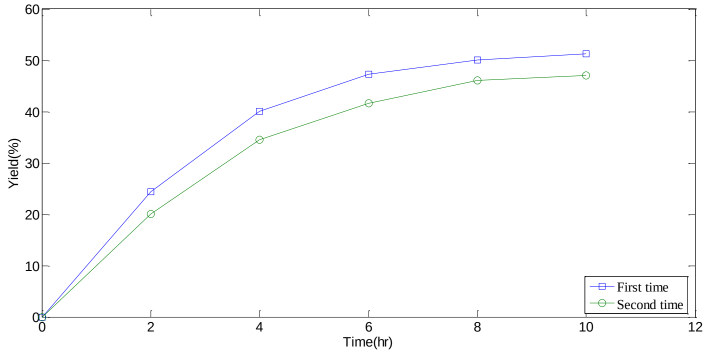

Fig. 10. Biodiesel yield, using recycled ZnO as catalyst of, Catalyst loading= 9wt%, Methanol/oil ratio= 15, Temperature= 65ºC

CONCLUSION

The present study synthesized MgO and ZnO, investigating their performance in corn oil transesterification. Particles were prepared through co-precipitation process and catalysts' characteristics were assessed by means of XRD and SEM methods. During transesterification reaction, MgO displayed a more satisfying performance, due to its alkaline properties. This can be related to the size and surface area of MgO catalyst. As SEM images illustrate, MgO particles were smaller, fully-separated, and more uniform; hence effective reaction surface would be greater in comparison with ZnO catalyst. Results show that biodiesel yield was significantly improved by increasing the catalyst amount. For Alcohol Ratio on Transesterification Yield, a molar ratio of methanol to oil of 20 is recommended when MgO was catalyst and the optimum alcohol to oil ratio was 15 when ZnO acted as the catalyst. Catalytic properties of each catalyst was evaluated and compared, making it plainly visible that corn oil transesterification will be effectively expedited, using base catalysts than acid ones. That is why MgO was more effective than ZnO in transesterification reaction. By comparing catalytic activities of the catalysts in transesterification reaction, it could be seen that ME content was remarkably reduced to 24.4% and 8.3% in successive uses of MgO and ZnO catalysts, respectively.

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