

Research Article

Comparison between Homogeneous and Heterogeneous Esterification Reactions for Biodiesel Production using Reactive Distillation

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Abstract

Biodiesel is alternative diesel that produced from oils, fatty acids and animal fats. It is produced by various processes, this research adopts a new attempt to use a system of esterification reaction of free fatty acid (lauric acid) with long chain alcohol (2-ethylhexanol) that represent an industrial wastes in the presence of many types of catalysts, homogeneous (H₂SO₄) and prepared heterogeneous catalyst (sulfated zirconia), that prepared in different methods including novel one to reach the requirements of the best operating conditions and reactive distillation technique. Many parameters were studied to indicate their influence on conversion of free fatty acid to ester (biodiesel). They have been included molar ratio of 2-ethylhexanol to free fatty acids, reaction temperature, concentration of catalyst 0.2- 1%wt for homogeneous one while for heterogeneous catalyst higher concentration was used 0.5- 3%wt, mixing speed for reaction time up 120 min in order to find the best conditions to produce biodiesel with higher conversion. Also, different preparation methods of sulfated zirconia have been studied to indicate which method give more conversion and more efficient method. The best operating conditions are, feed molar ratio 2:1 (alcohol to free fatty acid), reaction temperature 130°C, catalyst concentration 1wt % for homogeneous and 2wt % for heterogeneous, mixing speed 650 rpm, these conditions gave conversion of 97%.

Keywords: Biodiesel, Reactive distillation, Esterification, Homogeneous catalyst, sulfated zirconia, heterogeneous catalyst

1. Introduction

Nowadays we are living in a place where the world's requirement for energy persists to excess, particularly as countries develop, whilst concurrently the providing of energy seems finite and fossil fuel sources are depletion day by day (Quadrelli and Peterson, 2007). Additionally the combustion of fossil fuels has increased the atmospheric intensification of some greenhouse gases that have led to extensive warming. Other effects of combustion fossil fuels involve the production of acid rain, smog and a hike in atmospheric particles (Ogunwole, 2012).

There are several efforts worldwide to evolve replacement fuels from renewable sources. One such replacement fuel is biodiesel. Biodiesel is fuel extracted from the oils and fats of plants and animal with alcohol in the presence of a catalyst. It has several benefits over traditional petroleum diesel: it's renewable, nonpoisonous, safe and biodegradable, it includes inconsiderable quantities of sulfur that effected lubricity prolongates the diesel engine life. Additionally, it has a high flash point and high cetane number

denoted a better, safer performance and it generates less hydrocarbons, fewer carbon dioxide, and fewer particles than petroleum diesel (Kiss *et al*, 2006).

The main reversible reaction for production biodiesel was esterification of free fatty acid with alcohol to produce ester (biodiesel) and ester. The reversible reaction is hydrolysis.



The classical biodiesel production operations depended on the application of alkaline catalyst, such as NaOH or KOH. The existence of FFA and/or H₂O in the reaction medium causes saponification (Yan *et al*, 2009). A sulfuric acid or hydrochloric acid as homogeneous acid catalyst, can also be employed (Jacobson *et al*, 2008) that does not form soap and rise the fuel production. Nevertheless, corrosion and the down-effluent separation are the major issues. To avert these problems, heterogeneous acid catalysts enhance economic problems and best gain full of the biodiesel production process (Marchetti *et al*, 2008). The greatest benefits of the heterogeneous idea beyond the homogeneous method is the a long time life of heterogeneous catalyst for biodiesel production and

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can be reused. In general, heterogeneous catalysts are classified by their Bronsted or Lewis acidity, the strength and number of sites, and the structural characteristics of the support. Newly, sulfated zirconia (SO_4/ZrO_2) catalysts have many implementations in numerous acid catalyzed reactions. These catalysts are active for hydrocarbon conversion at temperatures lower than the most of the commonly used solid catalysts, usually at temperatures from 100 to 200°C or lower (Ardizzone *et al*, 1999).

As the esterification reaction is reversible, excess alcohol is consequently utilized to relay the equilibrium to the products side but this process not economic. This has accelerated the improvement of process, increase technologies such as the reactive distillation column for the production of fatty acid esters and have become more desirable in the last years (Bhatia *et al*, 2006).

Reactive distillation (RD) is a unit operation in which chemical reactions and product separations take place together in one unit and at the same time. It is an efficient substitution to the conventional integration of reactor and separation units, especially as reversible or sequential chemical reactions are included. It's beneficial for those chemical reactions in which chemical equilibrium restricts the conversion. By continuous removal of products (water) from reactants whilst the reaction proceeding, the reaction can progress to a much higher level of conversion than without removal (Tuchlenski *et al*, 2001).

The aim of the present work is to study production of biodiesel by the esterification reaction using lauric acid as free fatty acid with heavy alcohol (2-ethylhexanol) by reactive distillation technique. The investigation includes, studying different parameters that effect the process, i.e mixing speed, the molar ratio of acid to alcohol, temperature of the reaction, the concentration of the catalyst, and method of preparation catalyst.

2. Experimental Section

2.1 Materials

Lauric acid (99.4%) was supplied from China, 2-Ethylhexanol alcohol (99% from GC analysis) was maintained from Ministry of Science and Technology as industrial alcohol. Since this alcohol is typically a waste alcohol from the manufacturing of butanol, this process makes sense from an economic viewpoint. Zirconium oxychloride was used for preparing zirconium sulfate as heterogeneous catalyst, sulfuric acid as homogeneous catalyst, ethanol and phenolphthalein for titration.

2.2 Procedure for Esterification Reaction

Free fatty acid was fed into the reaction flask and heated until the reaction temperature has been reached to required temperature. The heat was supplied by oil bath, the heat controller was done by magnetic stirrer that used to change the power

of the heating in order to obtain the reaction temperature. After reaching the desired temperature, alcohol and catalyst were added. After that, start agitation with 650 rpm to have a good mixing of the compounds and to eliminate possible mass transfer problems, this was represent the beginning of the reaction. Reaction was continued for 2 h, during this period samples were taken every (15 or 30 min) and centrifuged (for heterogeneous catalyst) to separate catalyst from organic phase and added 3 drops of phenolphthalein as indicator and 2 ml ethanol for dilution and titrate with 0.1M KOH in order to obtain FFA conversion to biodiesel and the acidity was calculated using the following equation:

$$a = \frac{V \cdot 1000 \cdot \text{Mwt} \cdot C}{W} \quad (1)$$

where a: acidity index; V: volume of KOH solution employed for titration, ml; Mwt.: molecular weight of KOH, g/mol; C: concentration of the solution used for titration, mol/l; W: weight of the sample taken to analyzed, g. Using the following equation, the conversion of free fatty acid was calculated:

$$X = \frac{a_i - a_f}{a_i} \quad (2)$$

Where a_i is the initial acidity of the mixture and a_t is the acidity at "t" time.

2.3 Preparation of Zirconium Sulfate (SZ)

(a) Preparation of SZ by the Solvent-Free Method

SZ by the solvent free method (SF) was prepared by grinding $(\text{NH}_4)_2\text{SO}_4$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ at a molar ratio of 6:1 in an agate mortar for 20 min at room temperature. After that calcined at 600°C for 5 h (Sun, *et al*, 2005).

(b) Preparation of SZ by the Conventional Method

Zirconium oxy-chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) of 20 g was dissolved in 200 ml water, then the solution reached to pH of 9 using 25% w/w NH_3 solution and constant mixing to permit zirconium hydroxide to precipitate. The precipitation of zirconium hydroxide was washed to remove chloride salts, then filtered with a Buchner funnel. In the next step, the zirconium hydroxide was dried for 24 h at 100°C and impregnated with 1 M H_2SO_4 under constant mixing for 30 min. Then, the $\text{SO}_4^{2-}/\text{ZrO}_2$ was dried at 100°C for 24 h and calcined in air for 3 h at 650°C (Yadav and Nair, 1999).

(c) Preparation of Modified SZ Catalyst

50 g of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) supplied from local market was dissolved in 500

ml water, then zirconium hydroxide allowed to precipitate at pH of 9 using 25% w/w NH₃ solution under constant mixing for 30 min. The white precipitation was washed with water to remove the chloride salts until the pH of the solution reached 7, then filtered with conical funnel.

In the next step, the zirconium hydroxide dried at 110°C for 18 h, then impregnated with 1 M H₂SO₄ under constant mixing for 8 h. After precipitation for 24 h, the SO₄/ZrO₂ was dried for 24 h at 110°C and then calcined in air for 3 h at 650°C.

(d) Reused Catalyst

Catalyst reusability was investigated by filtration of the used solid catalyst. After drying for 24 h at 100°C, nearly 0.3 g of the used catalyst was stirred with 50 ml distilled water for 3 h. Finally the suspensions were filtrated and dried at 100°C for 24 h and calcined at 650°C for 3 h (Rattanaphra *et al*, 2010).

2.4 Characterization of Modified Catalyst

X-Ray Diffraction (XRD)

The powder X-ray diffraction patterns of sample was recorded using a Shimadzu XRD-6000 diffractometer with Ni filtered CuK α radiation ($\lambda = 0.154$ nm) in the range of $2\theta = 10$ -60°. It has been generally realized that the crystalline phase of the SZ catalysts plays a very important role in catalytic activity and zirconia with tetragonal structure showing a higher catalytic activity than that of monoclinic ZrO₂. Fig. 1 displays the XRD for S/ZrO₂. The S/ZrO₂ sample reveal well crystalline structure. The phase shown for sulfated zirconia was orthorhombic at $2\theta = 25.35, 27.59, 29.55, 32.88$ and 36.32° .

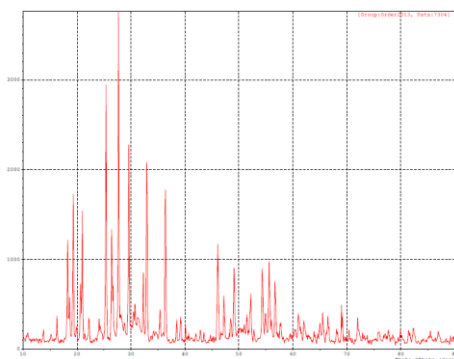


Fig. 1 XRD of modified sulfated zirconia

Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 2 shows FTIR of sulfated zirconia. The band at 1332.72cm⁻¹ is due to the splitting of the S=O asymmetric stretching, which implies the

existence of sulfate species. While the band at 790 and 710 due to S-O stretching vibration. The bands at 1138 and 1267.14cm⁻¹ are normally stands for chelating bidentate sulfate ions coordinated to the zirconium cation. The peaks of t-ZrO₂ has also been observed at 649.97, 613.32, 588.25cm⁻¹.

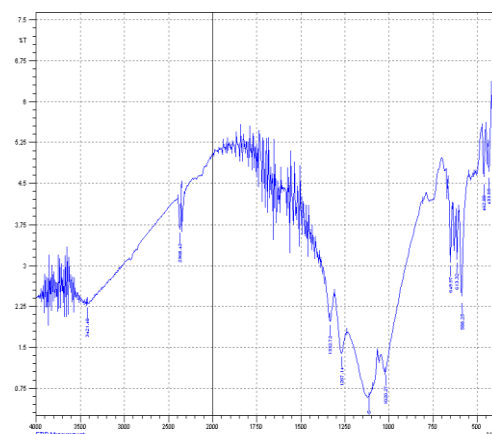


Fig. 2 FTIR of modified sulfated zirconia

Thermal Gravimetric Analysis (TGA)

The TGA/DTA analysis was performed with an EXSTAR 6000 series instrument and shown in Fig. 3. A 34.541 mg of sample was heated in the air (20 °C/min) from 50 to 900 °C. The weight loss and heat flow were measured as a function of temperature. Thermal analysis results for SZ catalyst after calcination was depicted in Fig. 3. TGA showed that SO₄/ZrO₂ was thermally stable. There was no weight loss observed from 50 to 670°C but for higher temperature 670-800°C weight loss approximately 20% due to decomposition of sulfate. The beak in DTA curve due to phase transition hence, the sample was calcinated at 650°C.

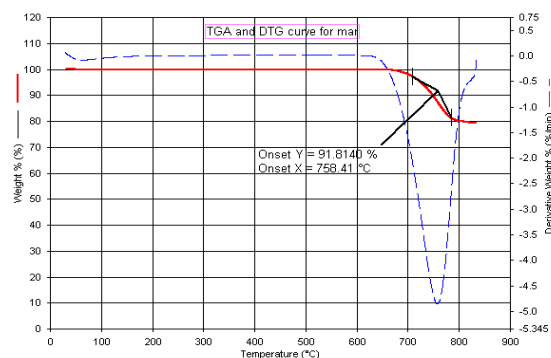


Fig. 3 TGA of modified sulfated zirconia

Scanning Electron Microscopy (SEM)

The SEM of SO₄/ZrO₂ is shown in Fig.4. The SEM of SO₄/ZrO₂ showed that the surface of ZrO₂ was distinctly altered, exhibiting considerable surface shining after sulfation. SEM images taken at

higher magnification clearly showed the alternation and shining of the surface. This may be due to the presence of highly charged species, i.e. sulfate ions.

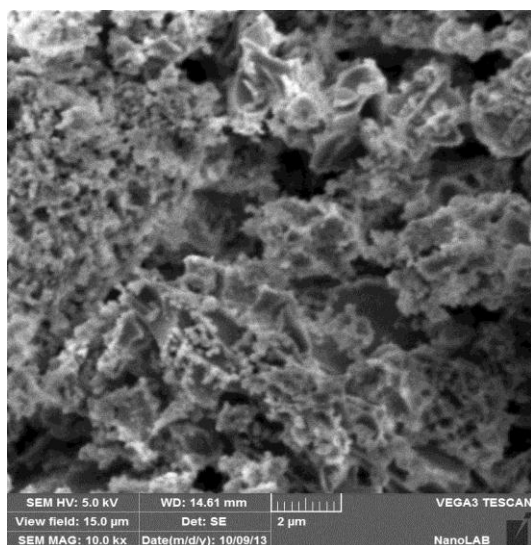


Fig. 4 SEM of modified sulfated zirconia

The textural properties were determined from the nitrogen adsorption isotherm determined after degassing at 200°C under vacuum at 5 – 10 mbar. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation and the pore volume was determined at a relative pressure of 0.98. The most important results are given in Table 1. In principle, the specific surface area depends on the calcination temperature.

Table 1 Textural properties of modified sulfated zirconia

Parameter	Value
Surface area (m ² /g)	125.23
Pore volume (cm ³ /g)	0.063
Bulk density (g/ml)	1.994
SO ₄	8.3%
S/SZ	2.77%

3. Results and Discussion

3.1 Effect of Mixing Speed

Fig.5 illustrates the relationship between conversion of lauric acid with time at different mixing speeds (500-900 rpm) using a homogeneous catalyst of concentration 1wt%, reaction temperature of 130°C and lauric acid:2-ethylhexanol molar ratio of 1:1. The results obtained here, showed that the conversion increased from 91.78% to 96.55% for mixing speed of 500 to 650 rpm respectively, then decreasing to 93.97% for mixing speed of 900 rpm after 10 min. Also, it can be seen that reaction rate at 900 rpm lower than 650 rpm at reaction time 30 min while after that time there is no effect of mixing speed.

When the speed is higher than the desired one which gave high conversion, there was a negative effect because of the formation of very small droplet that behave as rigid drop, causing the molecules inside the drop could not move and transferred from center of drop to surface to be converted, therefore the reaction and conversion took place only on the surface which gave lower conversion.

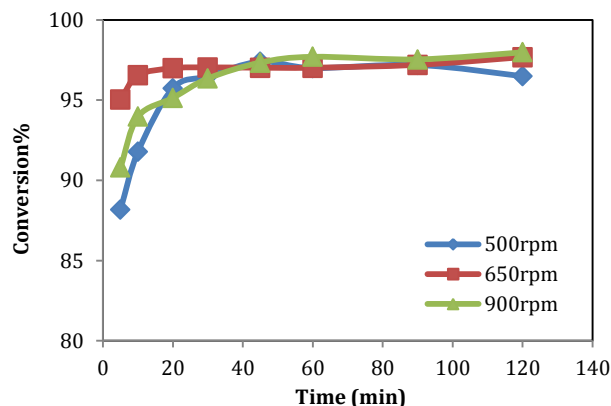


Fig. 5 Effect of mixing speed on conversion of lauric acid

[Operating conditions: molar ratio of free fatty acid: alcohol was 1:1, reaction temperature 130°C and concentration of sulfuric acid 1wt%]

For heterogeneous catalyst, experiment for lauric acid was conducted at variable mixing speed, keeping other variables constants, temperature of 130°C, the molar ratio of acid:alcohol of 1:1 and concentration of SZ catalyst of 2wt%. The results was shown in Fig.6. From this Figure, results indicate the conversion of lauric acid increased from 74% at 500 rpm to 80.2% at 650 rpm after 20 min reaction time. it can be seen that mixing speed has little effect on conversion rather but still speed 650 rpm is better for the first period and then all speed has approximately the same effects.

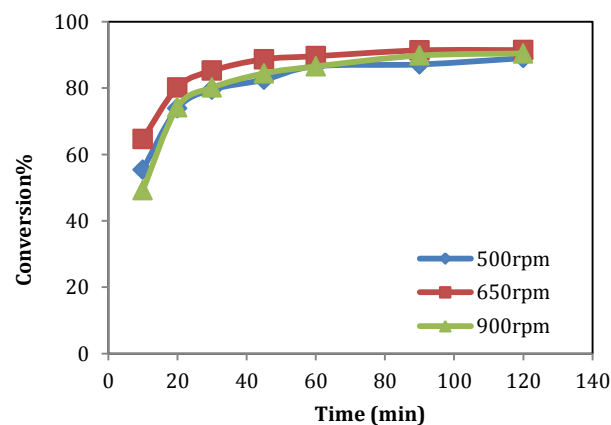


Fig. 6 Effect of mixing speed on conversion of lauric acid

[Operating conditions: molar ratio of fatty acid: alcohol was 1:1, reaction temperature 130°C and concentration of sulfated zirconia 2wt%]

Mass transport depends on the stirring speed, i.e. eddy diffusion that renewal the molecules attached to catalyst surface and then increase the conversion due to reduce the resistance on the surface. Moreover, sufficiently speed of mixing led to decrease the resistance of external mass transfer to the lowest limit that permit the reactants molecules to transfer freely and reaching solid catalyst surface easily.

3.2 Effect of Reaction Temperature

For lauric acid and 2-ethylhexanol and homogeneous catalyst, Fig.7 shows the conversion of lauric acid at different temperatures (100 to 130°C) with alcohol: lauric acid molar ratio of 1:1, 1wt% of sulfuric acid as catalyst and mixing speed of 650 rpm.

The results indicated that reaction rate at 100°C was lower than at 130°C. The conversions of lauric acid were 82.5% and 91.7% at temperature 100°C and 130°C and reaction time of about 120 min and 60 min respectively.

Since the esterification reaction is endothermic, increasing reaction temperature led to increasing conversion. The high temperature cause increase in activity of molecules which mean more molecules have more energy, therefore the probability of molecules to react increased.

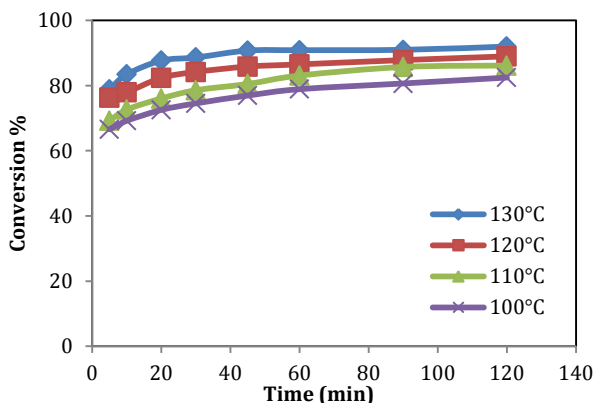


Fig.7 Effect of temperature on lauric acid conversion

[Operating conditions: molar ratio of alcohol: FFA of 1:1, homogeneous catalyst of concentration 1wt% (H₂SO₄) and mixing speed 650 rpm

For lauric acid esterification with 2-ethylhexanol using heterogeneous catalyst, the results were illustrated in Fig.8. This Figure illustrates the change of conversion with time at different temperatures and constant alcohol: lauric acid molar ratio 1:1, concentration of heterogeneous catalyst 2wt % and mixing speed 650 rpm.

For reaction temperature of 130°C, the conversion almost doubled at time 20 min compared to that at 100°C, i.e. it was 80.22% and 42.99% at 130°C and 100°C respectively at that time. Then the conversion

increased to 89.62% and 72.22% after 120 min reaction time at the same conditions. The primary advantage of higher temperature is a shorter reaction time.

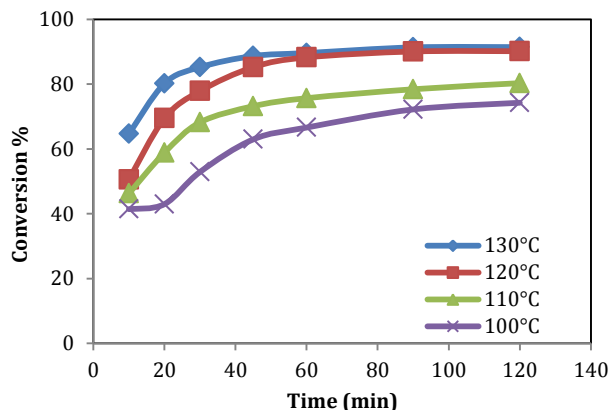


Fig.8 Effect of temperature on lauric acid conversion

[Operating conditions: molar ratio of alcohol:FFA 1:1, heterogeneous catalyst of concentration 2wt% (SZ) and mixing speed 650 rpm]

3.3 Effect of Alcohol to Free Fatty Acid Molar Ratio

In this study, biodiesel was produced from lauric acid which esterified with 2-ethylhexanol at various molar ratios of 2-ethylhexanol: lauric acid from 1 to 3. The results illustrated in Fig. 9 at constant temperature of 130°C and homogeneous catalyst of concentration 1wt% H₂SO₄.

From this figure, it can be seen as the molar ratio increase, the conversion increased also but this increment was little. It increases from 90.72% to 98% as ratio increased from 1 to 2 after 45 min. Therefore, economically, molar ratio of 1:1 will give the desired conversion. When the ratio increased to 3 the conversion decreased to 96.73% after 45 min reaction time as a result of dilution of sulfuric acid by excess 2-ethylhexanol.

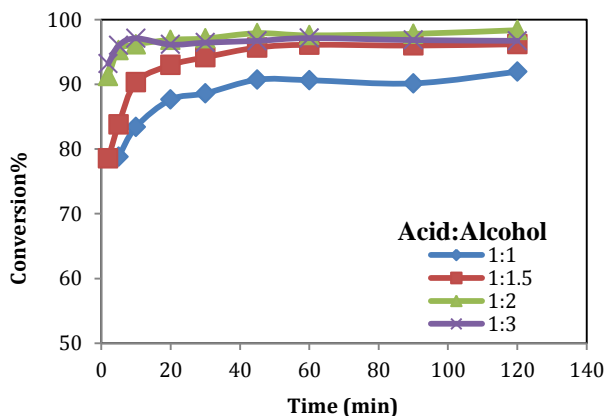


Fig. 9 Effect of acid: alcohol molar ratio on lauric acid conversion

[Operating conditions: reaction temperature 130°C, concentration of homogeneous catalyst 1wt% (H₂SO₄) and mixing speed 650 rpm]

The same behavior was shown when using SZ catalyst (i.e heterogeneous catalyst) as demonstrated in Fig.9. This figure shows the effect of molar ratio 2-ethylhexanol:lauric acid on conversion of lauric acid at temperature 130°C, concentration of catalyst of 2wt% and mixing speed of 650 rpm.

As the molar ratio increased, the conversion increased but slightly. It reached maximum conversion of 97% after nearly 30 min for molar ratio of 3 while for stoichiometric ratio it reached 89.62% conversion after 60 min.

Thus with low 2-ethylhexanol to lauric acid molar ratio, i.e higher mixture viscosity, a diffusion limiting process towards the solid SZ particles in the mixture was observed.

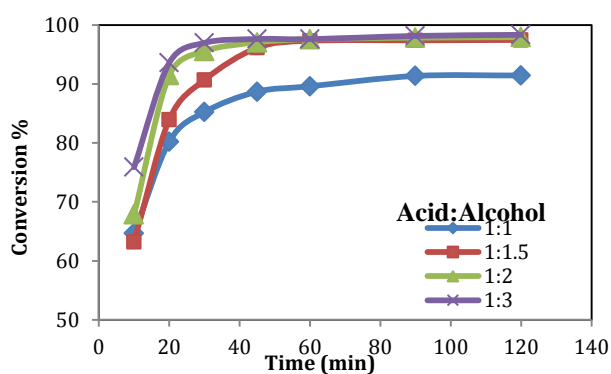


Fig. 9 Effect of acid: alcohol molar ratio on lauric acid conversion

[Operating conditions: reaction temperature 130°C, concentration of heterogeneous catalyst 2wt% (SZ) and mixing speed 650 rpm]

3.4 Effect of Catalyst Concentration

The relationship of conversion with catalyst concentration for lauric acid displayed in Fig. 10 at a constant reaction temperature 130°C and 2-ethylhanol:lauric acid molar ratio of 1:1.

Firstly, as expected in the absence of any acid catalysts, very low conversion to 2-ethylhexyl laurate was obtained, it gave 58.6% after 120 min. Conversely, in the presence of acid catalysts, a different results were observed. Therefore the conversion increased to reach 84% and 90.7% when the reaction catalyzed by 0.2wt% and 1wt% sulfuric acid respectively after 60 min. Although this increment is slight relative to catalyst concentrations but it is in agreement with the Kusmiyati and Sugiharto, 2010 results, who used four different concentration of catalyst (0.5, 1, 1.5 and 2wt% H₂SO₄) to esterify oleic acid with methanol at ratio 1:8 and temperature 130°C during 90 min. Their results showed the most effect of catalyst concentration was obviously seen below 1wt%, however the further added above 1wt% did not give significant increasing in conversion.

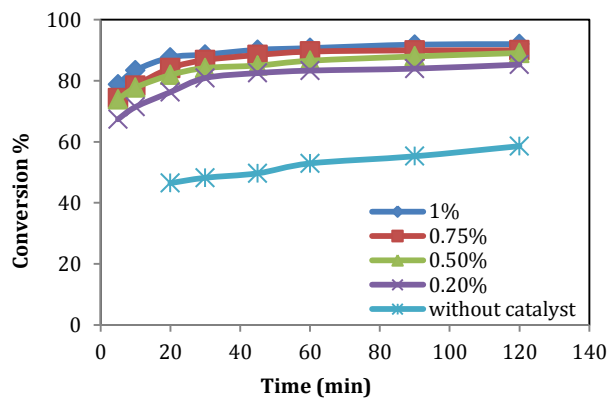


Fig. 10 Effect of homogeneous catalyst concentration on lauric acid conversion

[Operating conditions: reaction temperature 130°C, molar ratio of 2-ethylhexanol:lauric acid 1:1 and mixing speed 650 rpm]

The same behavior was seen for lauric acid conversion that demonstrates in Fig. 11. This figure shows the effect of SZ concentration on lauric acid conversion at a temperature 130°C and 2-ethylhexanol:lauric acid molar ratio of 1:1.

The conversion of LA was 58.6% after 2 h reaction time for uncatalyzed esterification reaction compared to catalyzed reaction which gave 85.25% conversion after 30 min reaction time with catalyst concentration of 2wt%. The conversion increase with increasing catalyst concentration, this is due to increase in the total number of active sites available for reaction. The increase in catalyst concentration considerably shortened the reaction time needed to reach the equilibrium.

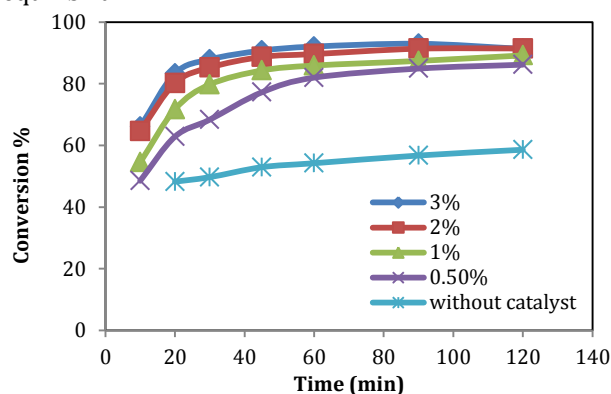


Fig. 11 Effect of heterogeneous catalyst concentration on lauric acid conversion

[Operating conditions: reaction temperature 130°C, molar ratio of 2-ethylhexanol:lauric was 1:1 and mixing speed 650 rpm]

3.5 Effect of Catalyst Preparation Method

According to preparation method, SZ activity effect the esterification reaction. The performance of various SZ was tested at constant reaction temperature of 130°C,

alcohol: acid of 3:1, concentration of SZ of 2wt% and mixing speed of 650 rpm and the results depict in Fig. 12.

The modified and commercial SZ have the same efficiency for esterification reaction and gave approximately 97% conversion of lauric acid after about 30 min which was higher than that achieved with other types of catalysts. The conventional catalyst, solvent free catalyst and reused catalyst gave nearly 85%, 90.5% and 81.3% conversion respectively after 2 h reaction. Therefore, it can be concluded that solvent free catalyst better than conventional catalysts for this system and reused catalyst is lowest one.

The activity of modified method may be due to the strength and number of sites and Bronsted acidity. This result of modified and commercial SZ agreed with Neji *et al.*, 2009 who showed no relationship was found between surface area, average pore diameter with the esterification activity of the catalysts.

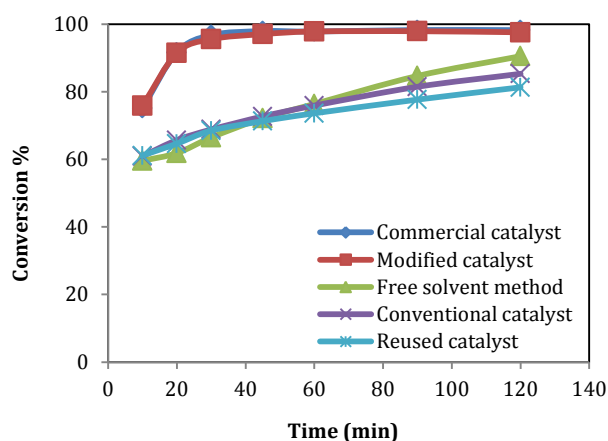


Fig. 12 Different types of SZ catalysts for lauric acid conversion

[Operating conditions: molar ratio of lauric acid:2-ethylhexanol 1:3, reaction temperature 130°C, catalyst concentration 2wt% (SZ) and mixing speed 650 rpm]

3.6 Comparison between Homogeneous and Heterogeneous Reactions

Sulfuric acid as homogeneous catalyst and sulfated zirconia as a heterogeneous catalyst were used in this study to indicate how they accelerate the reaction rate since these substances affect only reaction speed. The results were demonstrated in Figs. 13 to 15.

Fig. 13 depicts the effect of catalyst type on conversion of oleic acid at molar ratio of oleic acid:2-ethylhexanol of 1:1 and temperature of 130°C. It could be seen that sulfuric acid gave a higher conversion than sulfated zirconia at first 30 min, then the difference decrease until they equal in their performance. It was indicated that conversions were 88.61% and 79.76% at 30 min for homogeneous and heterogeneous respectively, finally, they all nearly reach to the end with 90% conversion after 120 min.

In general, homogeneous catalyst gave higher conversion than that for heterogeneous catalyst, this may be due to better contact will happen for homogeneous catalyst that the reaction occur in entire volume of reactor, while only on active sites for heterogeneous catalyst.

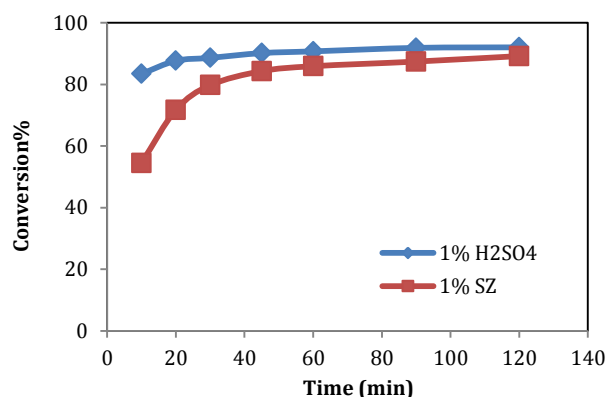


Fig. 13 Effect of catalyst type on lauric acid conversion

[Operating conditions: molar ratio of lauric acid:2-ethylhexanol of 1:1, reaction temperature 130°C and catalyst concentration of 1wt%]

For lauric acid with lower concentration of sulfated zirconia (0.5wt%), reaction temperature of 130°C and lauric acid:2-ethylhexanol molar ratio of 1:1, the results were compared with homogeneous reaction (0.5wt% H₂SO₄). These results illustrated in Fig.14.

A gradual increase of conversion was observed for heterogeneous reaction in the first reaction period until nearly 60 min, then, conversion rate decreases till the end. The corresponding conversion was increased from 48.51% after 10 min to reach 86% at 120 min, whereas for homogeneous reaction, the increasing is slower, start with 77.77%, reaching 89.12% after 120 min reaction time but still their conversion higher than that of heterogeneous.

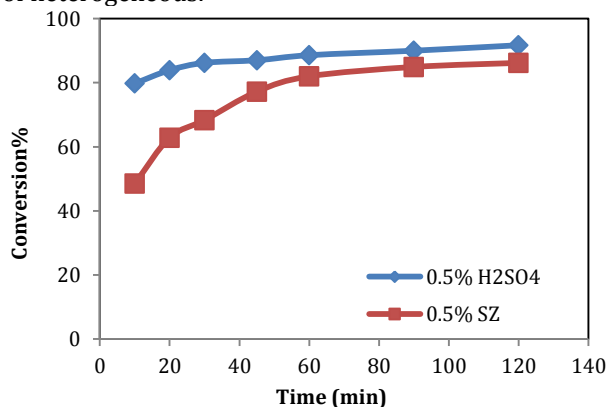


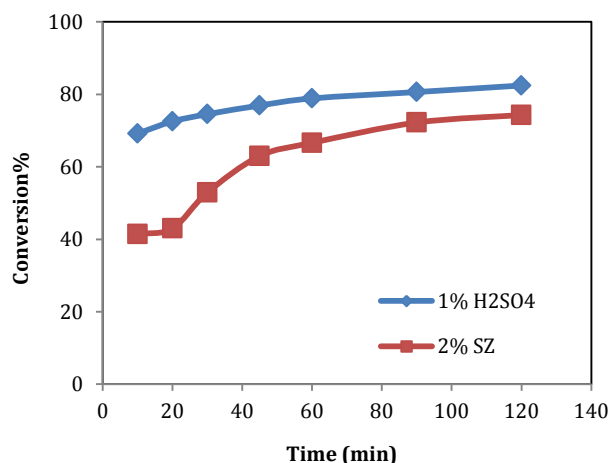
Fig.14 Effect of catalyst type on lauric acid conversion

[Operating conditions: molar ratio of lauric acid:2-ethylhexanol of 1:1, reaction temperature 130°C and catalyst concentration of 0.5wt%]

Table 2 Biodiesel vs. Petroleum diesel

Fuel properti-es	2-ethyl hexyl laurate using H ₂ SO ₄ calatyst	2-ethyl hexyl laurate using SZ calatyst	Biodiesel (Lotero <i>et al.</i> , 2005)	Diesel (Lotero <i>et al.</i> , 2005)
Flash point °C	160	106	100-170	60-80
Boiling point° C	203	291	182-338	188-343
Pour point °C	-9	-5	-15 to 10	-35 to -15
Cloud point° C	-6	-2	-3 to 12	-15 to 5
Viscosity @40°C c.st	4.6756	5.2454	1.9-6	1.3-4.1
Density g/ml	0.8685	0.8683	0.88	0.85
Carbon residue %	0.836	0.823		
API	31.42	31.46		
Heat of combust-ion (cal/g)	10815.97	10816.71		

The comparison was done also at low temperature (100°C) but with double concentration of sulfated zirconia because it was expected that high temperature need low quantity of catalyst as a result of high activation energy. The result of lauric acid was shown in Fig. 15 at 1wt% concentration for sulfuric acid and twice this concentration (2wt%) for sulfated zirconia. The inverse relationship of conversion was observed, in which the conversion by using sulfuric acid at 60 min approximately 20% higher than that when sulfated zirconia was used although its concentration was higher. Also the conversion at 120 min was 82% for sulfuric acid while for sulfated zirconia was 75.78%.

**Fig. 15** Effect of catalyst type on lauric acid conversion

[Operating conditions: molar ratio of lauric acid:2-ethylhexanol of 1:1 and reaction temperature 100°C]

Testing of Biodiesel Obtained from Lauric Acid

Biodiesel obtained from lauric acid was analyzed by ASTM (American Standard for Testing Material). Table 2 shows biodiesel from this experiment.

Conclusions

1) Modified SZ catalyst that prepared with new certain conditions exhibited a large similarity with commercial one, both considered as a preferable to the esterification reaction of lauric acid with 2-ethylhexanol.

- In general, homogeneous catalyst (H₂SO₄) gave better performance than heterogeneous catalyst (SZ). Higher conversion achieved for homogeneous catalyst (H₂SO₄) was 98.38% that achieved at operating conditions of molar ratio of alcohol: acid of 2:1 reaction temperature of 130°C, concentration of catalyst 1wt% and mixing speed of 650 rpm.
- Biodiesel properties such as viscosity, flash point, density and pour point obtained from the present work show that the biodiesel formed can be used as fuel.
- The mixing speed has slight effect for homogeneous system while, it has largest effect on heterogeneous reaction.
- As the temperature increased the conversion of free fatty acid increased this indicate that esterification reaction was endothermic. In general, esterification process as an endothermic reaction dependent largely on reaction temperature.
- The molar ratio of alcohol to FFA higher than stoichiometric (1:1) very important for biodiesel production. While, has no effect for reactive distillation technique.

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