



## Potential of $\text{LiNO}_3/\text{Al}_2\text{O}_3$ Catalyst for Heterogeneous Transesterification of Palm Oil to Biodiesel

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### Abstract

Production of biodiesel through transesterification process using heterogenous catalysts in order to avoid the saponification problem was studied. In this process, palm oil reacted with methanol to form a mixture of glycerol and biodiesel over a solid basic catalyst. One type of the catalysts used in this research is basic catalyst of  $\text{LiNO}_3/\text{Al}_2\text{O}_3$ . The parameters studied in this research are concentration of  $\text{LiNO}_3$  loading on  $\text{Al}_2\text{O}_3$  and effect of different reaction time. The products was analyzed using Gas Chromatography to determine composition and yield of resulted methyl esters as well as conversion of palm oil to biodiesel. The major products in this transesterification reaction were biodiesel and glycerol. It can be concluded that the 20 wt%  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  catalyst is potential for producing biodiesel from palm oil over transesterification reaction. Advantages of the usage of this catalyst is that the soap formation was not observed in this research. © 2010 BCREC UNDIP. All rights reserved

*Keywords:* Biodiesel; heterogenous catalyst; superbasic catalyst; transesterification; palm oil

### 1. Introduction

Due to the increase in crude oil prices and environmental concerns, a search for alternative fuels has gained recent significant attention. Among the different possible resources, diesel fuels derived from triglycerides of vegetable oils and animal fats have shown potential as substitutes for petroleum-based diesel fuels. However, the direct use of vegetable oils in diesel engine can lead to a number of problems such as poor fuel atomization, poor cold engine start-up, oil ring stickening and the formation of gum and other deposits. Consequently, considerable efforts have been made to develop alternative diesel fuels that have the

same properties and performance as the petroleum-based fuels [1]. In addition, biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability.

The direct usage of vegetable oils as biodiesel is possible by blending it with conventional diesel fuels in a suitable ratio. But direct usage of these triglyceride esters (oils) is unsatisfactory and impractical for long term usages in the available diesel engines due to high viscosity, acid contamination, free fatty acid formation resulting in gum formation by oxidation and polymerization and carbon deposition. Hence vegetables oils are processed so as to acquire properties (viscosity and

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volatility) similar to that of fossil fuels and the processed fuel can be directly used in the diesel engines available. Three processing techniques are mainly used to convert vegetable oils to fuels form, they are pyrolysis, microemulsification and transesterification [2-5].

There are four primary ways to make biodiesel which are direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification. The most common way to produce biodiesel is by transesterification. In the transesterification, triglycerides in vegetable oil react with alcohol to form a mixture of glycerol and fatty acid alkyl esters, called biodiesel. If methanol is used, the resulting biodiesel is fatty acid methyl ester (FAME), which has proper viscosity, boiling point and high cetane number. Methanol is the commonly used alcohol in this process, due to its low cost.

Transesterification can be catalyzed by both acidic-and basic-catalysts. Currently from the literature review, most of the biodiesel are synthesized using alkaline catalysts because the transesterification reaction by an acid catalyst is much slower than that by the alkaline catalysts. However, in the alkaline metal hydroxide-catalyzed transesterification, even if a water-free vegetable oil and alcohol are used, a certain amount of water is produced from the reaction of the hydroxide with alcohol. The presence of water leads to the hydrolysis of the esters and formed a lot of soap. The formation of soap reduces the biodiesel yield and causes significant difficulty in product separation (ester and glycerol). To avoid the problem of products separation and reduces the biodiesel yield, it has been proposed to replace the homogeneous catalysts by a heterogeneous catalysts. The second conventional way of producing biodiesel is using an acid catalyst instead of a base. Any mineral acid can be used to catalyze the process; the most commonly used acids are sulfuric acid and sulfonic acid. Although yield is high, the acids, being corrosive, may cause damage to the equipment and the reaction rate was also observed to be low [3].

This research is purposed to study the transesterification of palm oil into biodiesel using  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  heterogeneous catalyst. The production of biodiesel was investigated in this research using basic solids catalyst as heterogeneous catalysts. The usage of heterogeneous catalysts in the biodiesel production may result in high content, high yield of methyl esters and conversion of oil. The soap formation was not observed which will increase the production of biodiesel.

## **2. Materials and Methods**

### **2.1. Materials of Research**

The materials used in these experiments are methanol, cooking oil, lithium nitrate and aluminium oxide. Cooking oil was supplied by Swalayan Ada (Bimoli). The average molecular weight of palm oil was taken as 820 g/mol and density as 0.88 g/ml at 20 °C. Methanol (99%) was purchased from Grade AR while lithium nitrate (99.995 %) and aluminium oxide were supplied by Merck.

### **2.2. Catalyst Preparation**

The  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  catalyst was prepared by impregnation method. A certain amount of lithium nitrate was dissolved in distilled water to be a 1 N solution. A certain amount of powdery aluminium oxide was immersed into an aqueous solution of lithium nitrate for 2 h at ambient temperature. The mixed chemicals was dried overnight in an oven (Memmert) at 393 K. Next, the powder was calcined at 1123 K in a muffle furnace (Carbolite) for 4 h and then crushed into the desired size (45–60 mesh).

### **2.3. Catalyst Testing**

The transesterification reaction carried out in a 500 cm<sup>3</sup> reactor vessel. The oil, the methanol and the catalyst were filled in the reactor. The mixed reactants were stirred which sufficient to keep uniform in temperature and catalyst distribution. The reactor temperature was controlled by a temperature controller. The system temperature was raised to 60 °C and maintained at this temperature for the needed reaction time. Thus, the reactor was cooled to room temperature. After cooling, the catalyst was separated from the product mixture by vacuum filtration. The glycerol phase (bottom layer) and the methyl esters biodiesel phase (top layer) were separated and put in a separate container.

The biodiesel products were analyzed in a gas chromatography mass spectrometry (GC-MS), equipped with a capillary column (Agilent 1901 S-433, 30 m x 250 μm x 0.25 μm) and a mass selective detector (MSD). This GC-MS was controlled by a PC with a software package (MSD Chemstation). Helium was used as a the carrier gas with the flowrate at 2.2 ml/min. The injector temperature is at 80 °C and the maximum oven temperature is 300 °C. Analysis of biodiesel for each sample was carried out by dissolving 1 ml of biodiesel sample into 5 ml of n-hexane and

injecting 0.2  $\mu\text{l}$  of this solution in GC. The methyl esters content, methyl esters yield and conversion in each experiment were calculated from their content in biodiesel as analyzed in GC.

### 3. Results and Discussion

#### 3.1. Product of Transesterification of Palm Oil

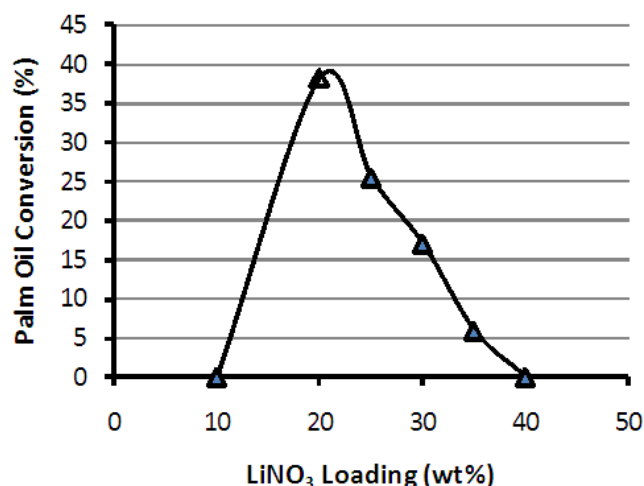
Transesterification process of palm oil to biodiesel over  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  catalyst produced liquid products consisted of two layers. The bottom layer is a glycerol, while the top one is a methyl ester. Figure 1 shows the two layer of reaction product of transesterification process. This two phases were separated depends on their layer.



**Figure 1.** Product of transesterification process of palm oil and methanol

#### 3.2. Effect of $\text{LiNO}_3$ Loading on Oil Conversion

On account of the high activity of the catalysts in the transesterification reaction of palm oil, influence of loading amount of  $\text{LiNO}_3$  on conversions of triglycerides were studied to find a higher catalytic catalyst. Figure 2 shows the effect of the loading amount of  $\text{LiNO}_3$  on the conversion of palm oil at the loading amount range 10 to 40 wt%. Loading of  $\text{LiNO}_3$  onto the  $\text{Al}_2\text{O}_3$  produced a dramatic increment of basic strengths on the  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  leading to enhancing transesterification mechanism and increasing methyl esters formation.



**Figure 2.** Effect of  $\text{LiNO}_3$  loading of oil conversion. Reaction conditions : methanol/oil molar ratio 6:1, catalyst amount = 1%, reaction time = 1 h, reaction temperature = 60  $^{\circ}\text{C}$ .

As shown in Figure 2, when the loading amount of  $\text{LiNO}_3$  increased, the conversion of 38.4 % was registered at loading of 20 wt%. However, if the loaded  $\text{LiNO}_3$  was over 20 wt%, the conversion decreased. The conversions of 25.5 %, 17.06 % and 5.9 % were obtained for 25 wt%, 30 wt% and 35 wt% of  $\text{LiNO}_3$  loading, respectively. Meanwhile, the conversions of 0% were obtained at loading  $\text{LiNO}_3$  of 10 wt% and 40 wt%. It is very likely that dispersion of  $\text{LiNO}_3$  on  $\text{Al}_2\text{O}_3$  support weakens the combination of  $\text{Li}^+$  and  $\text{NO}_3^-$  ions due to the interaction between  $\text{LiNO}_3$  and the surface of support, which is beneficial for the decomposition of  $\text{LiNO}_3$ . At low loading of  $\text{LiNO}_3$  which is 10 wt%, the sample did not present any catalytic activity, due to the lack of strong basic sites on which methanolysis reaction could occur.

When the amount of  $\text{LiNO}_3$  loadings were increased more than 10 wt%, the active basic sites are more dispersed on the alumina surface and strong adsorption of reactant may occur at unreactive surface sites [6]. However, if alumina was loaded too much with  $\text{LiNO}_3$ , the component cannot be well dispersed. The amount of loaded  $\text{LiNO}_3$  higher than 20 wt% resulted in agglomeration of the active  $\text{LiNO}_3$  phase and the cover basic sites by the exceeded  $\text{LiNO}_3$ , hence lower the surface areas of active components. The excess  $\text{LiNO}_3$  cause a lowered catalytic activity. Therefore, it seemed that the catalytic activity was proportional to the total loading amount of  $\text{LiNO}_3$ . Among this investigation, the loading of 20 wt%  $\text{LiNO}_3$  on alumina has shown promising results

when used as a heterogeneous catalyst for the transesterification of palm oil with methanol since it gives higher methyl esters contents and yields. Hence, the loading of 20 wt% of  $\text{LiNO}_3$  on alumina would be needed for further investigation particularly for catalyst characterization.

### 3.3. Effect of $\text{LiNO}_3$ Loading on Methyl Ester Content and Yield

Figure 3 shows methyl esters content as function of  $\text{LiNO}_3$  loading, while Figure 4 presents yield of methyl esters over the variation of  $\text{LiNO}_3$  loading on alumina. The methyl ester was not observed when 10 wt% of  $\text{LiNO}_3$  supported into alumina was used in this transesterification. This is also similar as in the case using 40 wt% of  $\text{LiNO}_3$  loading on alumina. From the figure, 20 wt% of  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  provides the highest content of methyl ester closes to 97.8 wt%. In comparison with 25 wt%, 30 wt% and 35 wt% of  $\text{LiNO}_3$  loading, the loadings give the lower methyl ester content. The methyl ester content of 35.89 wt% was obtained if 25 wt% of  $\text{LiNO}_3$  loading was used. Whereas methyl ester content of 28.13 wt% was obtained using 30 wt% and 9.2 wt% was obtained using 35 wt% of  $\text{LiNO}_3$  supported on alumina. Therefore, the experimental run using 20 wt% of  $\text{LiNO}_3$  loading on alumina at 1 hour of reaction time and 60 °C of reaction temperature gives a promising biodiesel product. The potential performance occurs may be due to the good formation of strong basic sites on the catalyst therefore soap formation did not occur in the product of methyl ester. It can be concluded that 1 hour of reaction time is sufficient to purify the methyl ester product.

The results of methyl ester yield were shown in Figure 4. Trend of the graph is similar with methyl ester content which is the upward trend in the methyl ester yield if the loading bigger than 10 wt% and the downward trend is observed if the loading bigger than 20 wt% of  $\text{LiNO}_3$ . The methyl ester yield of 0 wt% was observed when the transesterification were run using below 10 wt% and higher than 40 wt% of  $\text{LiNO}_3$  loadings.

The highest methyl ester yield of 40.86 wt% was obtained using 20 wt% of  $\text{LiNO}_3$  loading on alumina compared with another one. This is similar with the result of methyl ester content where 20 wt% of  $\text{LiNO}_3$  loading gives the highest methyl ester content. The methyl ester yield for 25 wt% loading is 25.2 % whereas the yield of 18.02 wt% and 6.4 wt% is obtained for 30 wt% and 35 wt% of  $\text{LiNO}_3$  loading, respectively.

From the result, there is no catalytic activity for  $\text{LiNO}_3$  loading of less than 10 wt% and higher than

40 wt% due to lack of strong basic sites. The parent of alumina is slight acidic and when the amount of  $\text{LiNO}_3$  is loaded, the catalyst basicity is increased. However, when the loaded  $\text{LiNO}_3$  is over 20 wt%, the yield is decreased which may be due to the  $\text{LiNO}_3$  cannot be well dispersed on alumina support. The excess  $\text{LiNO}_3$  loading could cover the basic sites on the surface of composite and cause a lowered catalytic activity. Therefore, it seems that the catalytic activity is proportional to the amount of decomposed  $\text{LiNO}_3$  instead of the total loading amount of  $\text{LiNO}_3$  [6].

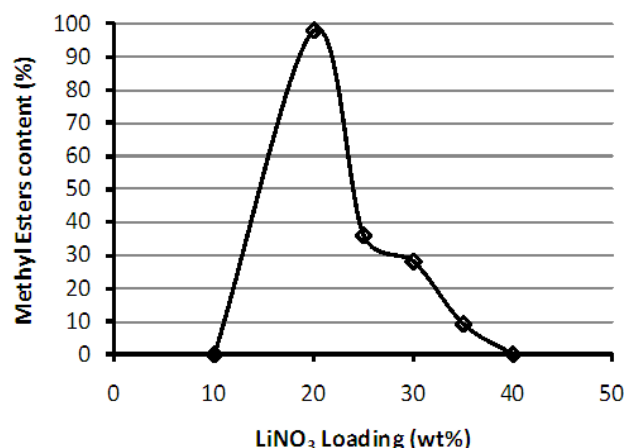


Figure 3. Effect of  $\text{LiNO}_3$  loading on methyl esters contents. Reaction conditions: reaction time = 1 h, reaction temperature = 60 °C

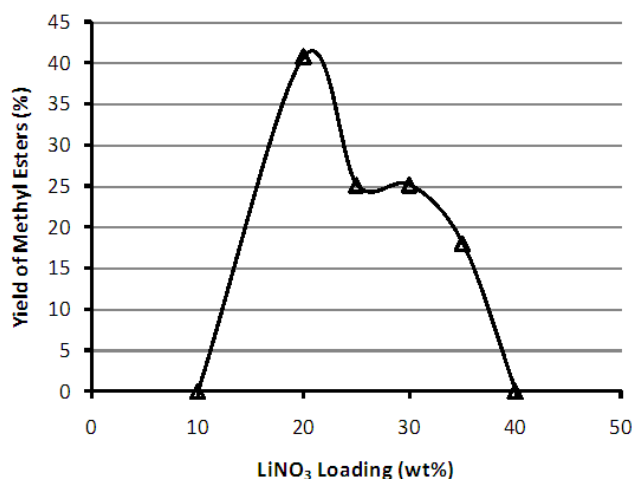


Figure 4. Effect of  $\text{LiNO}_3$  loading on yield of methyl esters. Reaction conditions: reaction time = 1 h, reaction temperature = 60 °C

Among this investigation whereby the influence of loading amount of  $\text{LiNO}_3$  on the methyl ester content and yield to find a higher catalytic activity, the loading of 20 wt%  $\text{LiNO}_3$  on  $\text{Al}_2\text{O}_3$  shown promising results closely matching the effects of  $\text{LiNO}_3$  loading on the conversion of triglycerides. Therefore, it is interesting to further investigate the parameters affecting the transesterification catalyzed by 20 wt% of  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  including all parameters interaction.

### 3.4. Effect of Reaction Time on Oil Conversion and Methyl Esters Yield

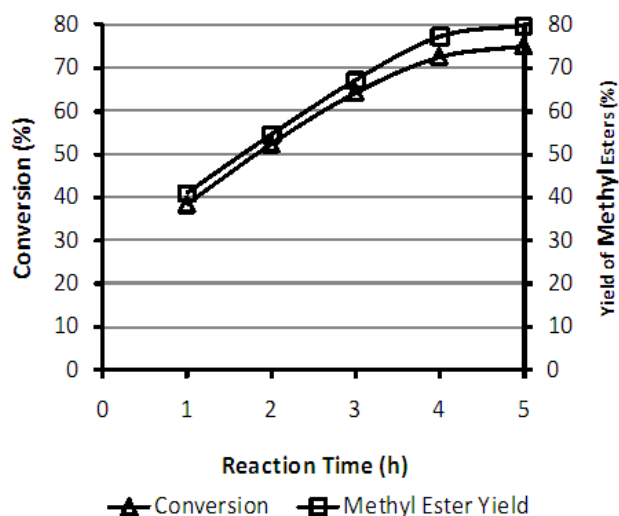
As shown in Figure 5, trend of reaction time on oil conversion is similar with that towards yield of methyl ester. By using the 20 wt%  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  catalyst, the conversion reaches nearly constant after 4 hours reaction time. Based on Xie et al. [6], transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst was studied. This paper reported that the conversion is increased in the reaction range between 1 and 7 hours, and thereafter remained nearly constant. That's mean the results is similar with the results of Xie et al. [6].

The reaction was very fast in the first few hours where the conversion increased rapidly and a product of closed to 100 % of ester content was formed within first 3 hours. After that, the reaction slowed down and entered a slow rate stage till the reaction equilibrium was reached eventually. According to Ma and Hanna [7], conversion increases with reaction time. It can be concluded that reaction time is also a controlling factor of product yield and extending the reaction time has a positive effect on the product yield in term of heterogenous catalytic transesterification.

From Figure 5, the methyl ester content closed to 100% at a reaction time of 1 hour and then remained relatively constant with increasing further reaction time. The purity of biodiesel reached equilibrium after 1 hour reaction time using 20 wt% of  $\text{LiNO}_3$  on  $\text{Al}_2\text{O}_3$ . The constant value obtained is due to the reaction will proceed to near completion even at room temperature if given enough time [8]. In term of methyl esters yield, increasing yield during the first hour to 4 hours is due to the mixing and dispersion of methanol into oil and then the reaction proceed to near completion. It can be concluded that the ester yield slightly increases as the reaction time increases.

Ma [9] studied the effect of reaction time on the transesterification of beef tallow with methanol. He reported that the reaction is very slow during the first minute due to the mixing and dispersion

of methanol into beef tallow but from one to five minutes, the reaction proceeded very fast.



**Figure 5.** Effect of reaction time on oil conversion and methyl esters yield. Reaction conditions : methanol/oil molar ratio 6:1, catalyst amount = 1%, reaction temperature = 60 °C,  $\text{LiNO}_3$  loading = 20 wt%

### 3.5. Characterization of Biodiesel Product

Further investigations on the physical properties of biodiesel were studied. The highest yield of biodiesel obtained from these experiments which are reaction time at 5 hours, reaction temperature at 60 °C and using 20 wt%  $\text{LiNO}_3/\text{Al}_2\text{O}_3$  was taken a sample for product characterization. The properties of this sample was compared with biodiesel standards. The characterization result is presented in Table 1.

Viscosity value of standard is specified by ASTM D 445 method, while density and iodine values are specified by DIN 51606 method. From the table, the viscosity value of the sample was 0.72  $\text{mm}^2/\text{s}$ , while the range of biodiesel standard is around 1.9-6.0  $\text{mm}^2/\text{s}$  which means it is not under the range of biodiesel standard. The density value obtained was 0.79  $\text{kg}/\text{l}$  while for biodiesel standard is around 0.875-0.9  $\text{kg}/\text{l}$  which is also not within the limit of biodiesel standard. Meanwhile, the iodine value was 3.8  $\text{mg I}_2/\text{g}$  which is within the range of biodiesel standards.

From the value of viscosity, it can be said that this sample is good due to the lower viscosity because high viscosity leads to poorer atomization of the fuel spray and less accurate operation of the

fuel injectors. The density value obtained from this experiment was much lower than the standards. Demirbas [10] reported that the density values of vegetable oil methyl esters considerably decreases via transesterification process.

In this research, the iodine value obtained was 3.81 g I<sub>2</sub>/g sample which is under the biodiesel standard value. Since the iodine value was only dependent on the origin of the vegetable oil, the biodiesel esters obtained from the same oil should have similar iodine values. The iodine value of the conventional diesel fuel is approximately 10. Therefore, the biodiesel has a significantly higher degree of unsaturation than diesel fuel. From the results obtained, we can conclude that the viscosity and the density values of this sample were not meet the requirement of the biodiesel standards while the iodine value was meet the requirement.

**Table 1:** Comparison of physical properties of sample biodiesel with standard biodiesel

Parameters	Method	Biodiesel (Standard)	Biodiesel (Sample)
Viscosity @ 40 °C (mm <sup>2</sup> /s)	D 445	1.9 - 6.0	0.72
Density (kg/m <sup>3</sup> )	DIN 51606	0.875 - 0.9	0.79
Iodine Value (mg I <sub>2</sub> /g)	DIN 51606	<15	3.81

The major fatty acid methyl ester components were detected by GC-MS which are palmitic acid, oleic acid, stearic acid and linoleic acid.

#### 4. Conclusion

The results indicated that biodiesel could be produced via transesterification of palm oil using basic solid catalyst which based on LiNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> as heterogenous catalyst. The soap formation was not observed in this research, which reduces the production of biodiesel. The 20 wt% loading of LiNO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> was sufficient for producing methyl ester content with promising yield. The 5 hours of reaction time gave the highest methyl ester yield and conversion of oil to biodiesel. The major fatty acid methyl ester components were detected by GC-MS which are palmitic acid, oleic acid, stearic acid and linoleic acid.

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