The Effect of Reaction Temperature and Reaction Time on the Transesterification of Palm Olein using NaOH/ZnO Heterogeneous Catalyst

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Abstract. The transesterification of palm olein to fatty acid methyl esters was studied using NaOH/ZnO catalyst. The catalyst was prepared by impregnation with the loading of NaOH 25% w/w NaOH on ZnO calcined at 600 °C for 6 hours. Biodiesel samples were first analyzed using gas chromatography according to ASTM methods. The influence of reaction temperature and reaction time on transesterification was examined. Optimum reaction condition was achieved at reflux of methanol (65°C K) for about 120 minute. The conversion of vegetable oil was found to be 99.7%. A reducible catalyst was also studied. The catalyst showed high activity, with oil conversion being obtained under mild conditions (reflux temperature of methanol).
Keywords: biodiesel, transesterification, heterogeneous catalyst, zinc oxide

1 Introduction

Nowadays, biodiesel has become a particularly attractive renewable fuel because of its environmental benefits and because it is made from renewable resources. Biodiesel can be used in existing engines and it is environmentally friendly because it can reduce the combustion emission of carbon monoxide, particulate matter, and sulfur compounds, as well as limit greenhouse emissions. Transesterification is the process used to make biodiesel synthesized from animal fats and vegetable oils by reaction of the oils and methanol.

A sharp increase in the production of this kind of biofuel is expected in the near future. Several commercial processes to produce fatty acid methyl esters from vegetable oils have been developed and are available today. Most of the commercial biodiesel is produced from transesterification of vegetable oils (mainly colza, soybean, sunflower, palm oil) using very effective homogeneous base catalysts such as NaOH or KOH, or acid catalyst such as sulfuric acid or hydrochloric acid which are soluble in methanol or ethanol [1].

The homogenous base catalysts have the advantage of gaining the fast reaction, but separation of the catalyst and the product is difficult and costly. Moreover, the washing operation is accompanied by formation of stable emulsion and saponification, resulting in not only the production loss but also in further contamination of the wastewater [2, 3]. Also, it is rather difficult to remove the homogeneous catalyst from glycerol which is the byproduct of the transesterification process. Although sulfuric acid or hydrochloric acid can also catalyze the transesterification, but the reaction time is very long and a high molar ratio of methanol to oil is needed [3-5].

To address this problem, more and more research at present has focused on the use of heterogeneous catalysts [6, 7]. Heterogeneous catalysts have several advantages including easier operational procedures, catalyst separation, and reduction of environment pollutants, among others. It designed to give higher activity, selectivity and longer catalyst lifespan [8]. As the

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catalytic activity of basic catalysts is higher than that of acid solids, they have been preferably studied [9].

In the present work, NaOH-doped ZnO is prepared and characterized for biodiesel production from vegetable oil. The catalysts were prepared by an impregnation method followed by calcination at high temperature. The catalyst is then tested for the catalytic activities in the transesterification reaction of RBD palm olein terms of the conversion to methyl esters. A screening of the reaction conditions has been carried out by examining the effect reaction temperature and the reaction time and reusability of the catalyst was studied.

2 Materials and Methods

The chemicals and oils used in these experimental works are listed below: Sodium Hidroxide (NaOH), Zink Oxide (ZnO), Molecular Sieve, MSTFA and Methanol were from Aldrich corp. RBD Palm Olein (cooking oil) was purchased in a local food-store. All the employed materials were of analytical grade and were used as received without further purification. Biodiesel was analyzed with SRI gas chromatography equipped with FID detector using ASTM (D 6584) method.

Catalyst Preparation. NaOH/ZnO was prepared by impregnation method by using NaOH (Aldrich) as precursor impregnated to ZnO (Aldrich) at 25 wt.% NaOH loading. Prior to impregnation the ZnO powder was preheated in oven overnight at 120 °C to remove the moisture content. An aqueous NaOH slowly added to the support and stirred with an appropriate amount of the ZnO for 3 hours. The slurry was dried overnight in oven at 120 °C. Finally the catalyst precursor was calcined in air at 600 °C for 6 hours.

Transesterification Reaction. The experiment was carried out in 250 ml round bottom flask equipped with reflux condenser and a magnetic stirrer. The transesterification process was conducted with 10.0 g of the commercial grade palm olein (seri murni) purchased from local store and use as received. The transesterification reaction was conducted at varied reaction temperature and reaction time with 1:15 molar ratio oil/methanol by using 6 % wt catalyst.

The transesterification process was started by stirring the mixture using magnetic stirrer. Stirring the mixture helped the heterogeneous catalyst to be distributed and suspended freely throughout the reaction mixture, thereby catalyzing the transesterification process. The reaction was allowed to occur for 2 hours. After 2 hours, transesterification process was stopped by immersing the batch reactor into water (at room temperature ~25°C). The reaction stopped as the reaction mixture was cooled. Then, the heterogeneous catalyst was filtered out using filter paper and the reacted mixture was poured into the separating funnel. The top methyl esters (biodiesel) phase was then separated from the bottom glycerol phase and the excess alcohol was removed using warm water (at temperature ~60°C).

Before analyzing this biodiesel sample, it was dried using molecular sieve. Biodiesel was analyzed with SRI gas chromatography equipped with FID detector using ASTM (D 6584) method. Prior to analyzing the methyl ester content of the samples, 0.1 mg of the reaction mixture were weight and derivatized by exactly 100 micro-liter of MSTFA (Aldrich) in a 10mL septa vial at room temperature for 30 minute, and dissolved at 8 ml n-Heptane and shaked. 1 micro-liter of the reaction mixture was injected into the cool-on-column port and analysis started. Mono-, di-, and triglycerides were determined by comparing to monoolein, diolein, and triolein standards. Chromatogram and peak integration report were obtained.

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3 Results and Discussion

NaOH/ZnO with the compositions of 25%w NaOH was calcined at 600°C is used for the biodiesel production by transesterifcation using methanol. The reaction parameters are optimized to get maximum conversion including reaction temperature and reaction time.

Effect of Reaction Temperature.

Figure 1 graphically illustrates the change of the conversion as a function of reaction temperature. The figures show that the conversion is increased as the reaction temperature increased from 55°C to 65°C, after that temperature the conversion of biodiesel reduced. The maximum yield is 99,7% at temperature 65°C)

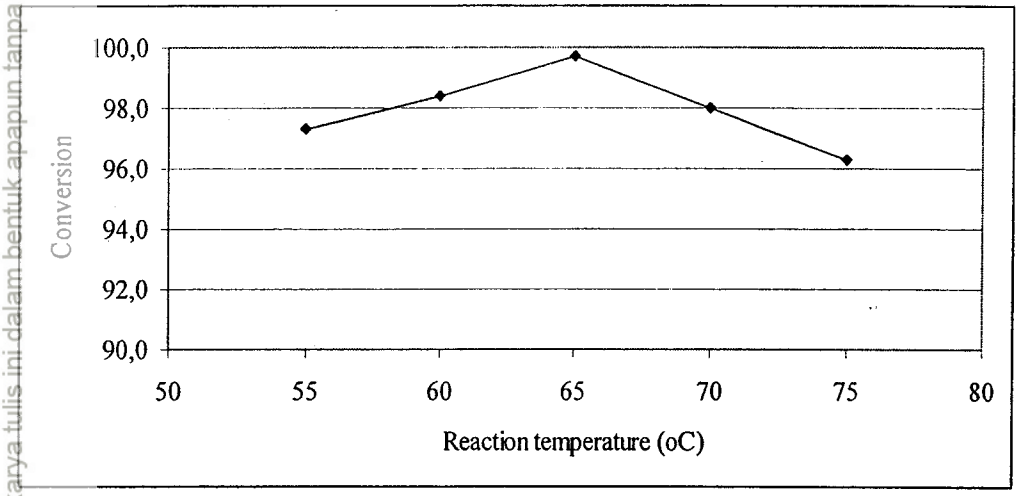

Figure 1. Conversions of RBD palm olein as a function of reaction temperature. Reaction conditions: catalyst amount 6 % (wt), mol oil/methanol ratio 1: 15, reaction time 120 minutes

Effect of Reaction Time.

Figure 2 graphically illustrates the change of the conversion as a function of reaction time. The figures show that the conversion is increased as the reaction time increased from 30 minutes to 120 minutes. The conversion is decreased when the reaction time further increased to 150 minutes. This could be due to the fact that transesterification is reversible reaction. After reaching the equilibrium the methyl ester could be reacted with glycerol to produce acylglycerol, resulting in the decreased in the conversion was decreased. The optimum reaction time for the reaction is considered to be around 120 minutes (99,7% biodiesel conversion).

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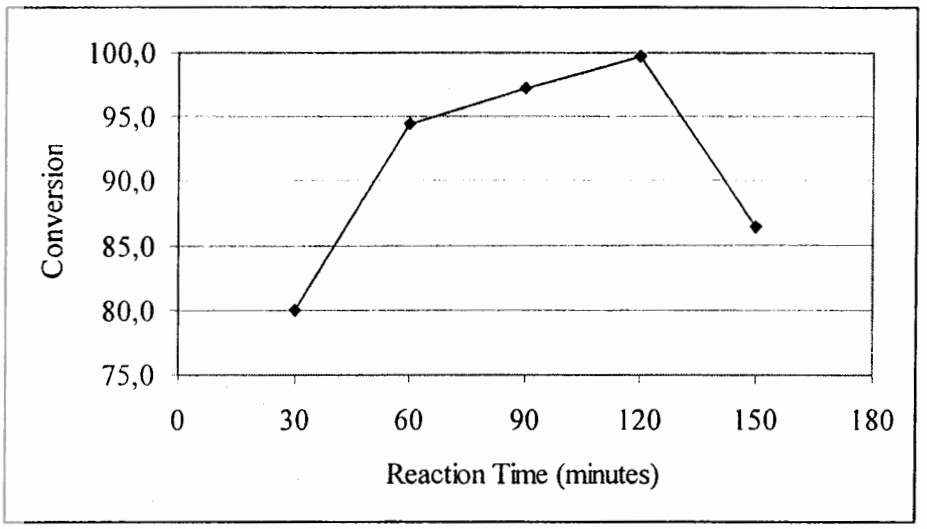

Figure 2. Conversions of RBD palm olein as a function of reaction time. Reaction conditions: catalyst amount 6 % (wt), mol oil/methanol ratio 1: 15, reaction temperature 65 °C.

Catalyst reusability.

The catalyst was recycled to study reusability. After the first run, the catalyst was filtered, washed with methanol and dried. Then the catalyst was used in the second run, *etc.* In the first run, the conversion is 99.7% and in the second run it decreases to 93.0%. In the third run the conversion is 80.7%. In the fourth run, the conversion decreases to 71.7%. So we can use the same catalyst at least three times even without a high temperature treatment of the catalyst to recover its activity. The decreased activity after subsequent runs raised the question of leaching. In order to clarify this, reusability tests was also repeated after activation at 600 °C for 2 h. This was done to ensure the complete removal of any contaminants that may block the active sites of the catalyst, which has a poisoning effect. Up to the 4th cycle there was only a minute decrease in activity as seen from the results shown in Table 1, whereas in the 5th cycle there is 7.6% decrease in activity. Thus the present catalyst can be effectively used at least for four repeated cycles without much change in activity.

Table 1. Reusability results of the catalyst calcined at 600°C under optimum conditions

No of cycle	% Conversion
1st	99,7
2nd	93,0
3rd	80,0
4th	71,5
5th	7,6

Conclusions

A promising heterogeneous catalyst is proposed for biodiesel production by transesterifcation of palm oils with methanol. The NaOH impregnated on ZnO with amount loading of NaOH 25% wt, followed by calcination at 600 °C, appears to be an active catalyst in RBD palm olein transesterifications. The optimized reaction conditions for the transesterification at a reaction temperature of reflux methanol (65°C) and a reaction time 120 minutes, which resulted in a

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99.7.% conversion of RBD palm olein. There is little change in the catalytic activity of the reused catalyst even after four repeated cycles. The major advantages of the present system include operational simplicity, mild reaction conditions, low reaction time, high conversion and reusability.

The NaOH impregnated on ZnO with amount loading of NaOH 25% wt, followed by calcination at 600 °C, appears to be an active catalyst in RBD palm olein transesterifications. The optimized reaction conditions for the transesterification were 6 wt.% NaOH/ZnO catalyst, a molar ratio of oil to methanol of 1:15 and a reaction time 120 minutes, which resulted in a 99.7.% conversion of RBD palm olein at reflux of methanol (65 °C).

Acknowledgement

The authors acknowledge the I-MHERE (Indonesian Higher Education for Relevance anad Efficiency) Directorat pendidikan Tinggi Departemen Pendidikan Nasional Jakarta for their financial supports.

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