Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts

Jaturong Jitputti a, Boonyarach Kitiyanan a,*, Pramoch Rangsunvigvit a, Kunchana Bunyakiat a, Lalita Attanatho b, Peesamai Jenvanipanjakul b

a The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand
b Thailand Institute of Scientific and Technological Research, Bangkok, Thailand

Received 15 April 2005; received in revised form 11 August 2005; accepted 28 September 2005

Abstract

This work reports on the preliminary results of using several acidic and basic solids, such as ZrO2, ZnO, SO4 2−/SnO2, SO4 2−/ZrO2, KNO3/Zeolite and KNO3/ZrO2 as heterogeneous catalysts for crude palm kernel oil (PKO) and crude coconut oil (CCO) transesterification with methanol. It was found that ZnO and SO4 2−/ZrO2 exhibited the highest activity for both PKO and CCO transesterification. In the case of SO4 2−/ZrO2, only 1 wt.% of this acidic solid was needed to catalyze the reaction, and resulted in fatty acid methyl esters content higher than 90%. Moreover, a study of the catalyst’s recyclability indicated that the spent SO4 2−/ZrO2 cannot be directly reused for the transesterification. However, this spent catalyst can be easily regenerated and the same activity can be obtained.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Transesterification; Biodiesel; Palm kernel oil; Coconut oil; Solid catalysts

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 [1]. However, the direct use of vegetable oils in an diesel engine can lead to a number of problems such as poor fuel atomization, poor cold engine start-up, oil ring sticking, 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, with the transesterification of triglycerides to fatty acid alkyl esters showing the most current promise.

Transesterification, often called alcoholysis [2], is the reaction of a fat or oil with an alcohol to form esters and glycerol as shown in Scheme 1, which has been widely used to reduce the viscosity of vegetable oils (triglycerides). In transesterification, triglycerides in vegetable oil react with alcohol to form a mixture of glycerol and fatty acid alkyl esters, called biodiesel. Biodiesel produced from vegetable oils can be used as an alternative to diesel fuels because its characteristics are similar to those of petroleum-based diesel fuels. For example, they have a viscosity close to that of petroleum-based diesel fuel, their volumetric heating values are a little lower, but they have high cetane and flash points [1]. Many types of alcohols such as methanol and ethanol can be used in the transesterification. If methanol is used, the resulting biodiesel is fatty acid methyl ester (FAME), which has proper viscosity, boiling point and high cetane number [3].

Transesterification can be catalyzed by both acidic- and basic-catalysts. An acidic catalyst such as sulfuric acid slowly catalyzes the transesterification of triglyceride. Alkaline metal hydroxides (e.g. KOH and NaOH) are preferred as the basic 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 as a result, soap is formed (Scheme 2). The formation of soap reduces the biodiesel yield, and causes significant difficulty in product separation (ester and glycerol).

* Corresponding author at: The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Road, Bangkok 10330, Thailand.
Tel.: +66 2 218 4143; fax: +66 2 213 4439.
E-mail address: Boonyarach.Kitiyanan@chula.ac.th (B. Kitiyanan).

1385-8947/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
To avoid the problem of products separation, it has been proposed to replace the homogeneous catalyst by a heterogeneous catalyst [4], suggesting that the production of alkyl esters will be simplified when heterogeneous catalysts are utilized.

In this work, the production of biodiesel using heterogeneous catalysts was investigated, using six types of catalyst (ZrO2, ZnO, SO4\textsuperscript{2-}, SnO2, SO4\textsuperscript{2-}/ZrO2, KNO\textsubscript{3}/KL zeolite), which were prepared and applied for the transesterification of crude palm kernel oil and crude coconut oil.

2. Experimental

2.1. Materials and catalysts preparation

Crude palm kernel oil was obtained from Chumporn Palm Oil Industry Public Company Limited (Chumporn Province, Thailand). Crude coconut oil was obtained from Thai Taksin Company (Prachuap Kirikun Province, Thailand). Both oils were used as received.

Potassium nitrate (KNO\textsubscript{3}) and zinc oxide (ZnO with purity higher than 99.0%) and stannous chloride (SnCl\textsubscript{2}) 98% were purchased from Fluka. Zirconium oxide (ZrO\textsubscript{2}) and anhydrous sodium sulfate 99.0% were received from Riedel-de Haen. Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) 96%, methanol 99.8%, HPLC grade ace- tonitrile and acetone were purchased from Labscan (Bangkok, Thailand). Ammonium hydroxide (28–30% A.C.S. Reagent) was obtained from J.T. Baker.

The methyl esters used as standards for HPLC were methyl arachidate, methyl caprate, methyl caprylate, methyl laurate, methyl linoleate, methyl linolenate, methyl myristate, methyl oleate, and methyl palmitate (all purchased from Fluka).

Sulphated zirconia was prepared by the method outlined by Miao and Gao [6]. Zirconia powder was immersed in a 0.5 M H\textsubscript{2}SO\textsubscript{4} solution for 30 min, then, filtered and dried at 110°C for 24 h yielding the sulphate salt (SO\textsubscript{4}\textsuperscript{2-}/ZrO\textsubscript{2}). Finally, it was calcined at 500°C for 2 h.

KNO\textsubscript{3}/KL zeolite was prepared by the impregnation method with an aqueous solution of KNO\textsubscript{3}. It was reported that 21% KNO\textsubscript{3}/KL zeolite exhibited the highest basic strength [7]. The KL zeolite (40 g) was impregnated with KNO\textsubscript{3} solution and followed by drying at 100°C. The KNO\textsubscript{3}/KL zeolite was, then, calcined at 600°C for 2 h.

Zirconia-supported potassium nitrate was prepared using the method outlined by Wang et al. [8]. A 26% KNO\textsubscript{3}/ZrO\textsubscript{2} was prepared by grinding 40 g of ZrO\textsubscript{2} with 8 g of KNO\textsubscript{3}, followed by the addition of 24 ml of distilled water. The paste was kneaded and then dried at 110°C for 12 h, which was then calcined at 600°C for 2 h.

2.2. Transesterification reaction

One mole of vegetable oil, six moles of methanol, and a desired amount of catalyst were placed in a 300 ml stainless steel reactor (Parr series reactor). The reactants were stirred at 350 rpm, which was sufficient to keep system uniform in temperature and suspension. The reactor temperature was controlled by a heater with a programmable PID temperature controller. The system temperature was raised to 200°C for the desired reaction time, and then the reactor was cooled to room temperature. After cooling, the catalyst was separated from the product mixture by filtration. Phase separation of the filtrate resulted in the isolation of the methyl esters and the glycerol. The glycerol phase (bottom layer) was removed and kept in a separate container. Afterwards, the methyl esters biodiesel phase (top layer) was washed with 50°C distilled water [9], and dried by adding sodium sulfate (25% based on the weight of washed methyl esters product).

The biodiesel products were analyzed by high-pressure liquid chromatography (HPLC) using a Perkin-Elmer Series 200 LC-pump and a refractive index Series 200 detector and controlled by a PC with a software package (PerkinElmer Turbochrom Navigator). A Zorbax Eclipse XDB-C18 column (4.6 mm × 250 mm × 5 μm) was used and the mobile phase was acetone/acetone mixture (70:30 v/v) at a flow rate of 0.7 ml/min. The biodiesel samples were diluted with acetone (HPLC grade) and the injection volume was 20 μl.

The amount of methyl esters in each sample was quantified by comparing the signal for each methyl ester of the HPLC chromatogram of biodiesel products with the signal of each of standards.

The methyl esters content and methyl esters yield in each experiment were calculated from their content in the biodiesel as analyzed by HPLC. The content (or purity) was defined as a ratio of the weight of methyl esters, obtained from HPLC, to the total weight of the top phase. The yield was defined as a ratio of the weight of methyl esters, determined by HPLC, to the weight of vegetable oil used.
3. Results and discussion

3.1. Characterization of vegetable oils

The vegetable oils used in this study were crude palm kernel oil and crude coconut oil. Some of their properties such as density, kinematic viscosity, free fatty acid, and moisture content were determined, and are summarized in Table 1.

3.2. Investigation of heterogeneous catalysts for transesterification

Six solid catalysts (ZrO$_2$, ZnO, SO$_4^{2−}$/SnO$_2$, SO$_4^{2−}$/ZrO$_2$, KNO$_3$/KL zeolite and KNO$_3$/ZrO$_2$) were tested for the transesterification of crude palm kernel oil and crude coconut oil. The experiments were performed at a methanol:oil molar ratio of 6:1, using a 3 wt.% of the catalyst (based on the weight of the vegetable oil), pressure at 50 bars under nitrogen atmosphere, temperature of 200 °C, and the 350 rpm stirrer.

3.2.1. Crude palm kernel oil transesterification

Table 2 summarizes the methyl esters content and yield from the crude palm kernel oil transesterification with the prepared solid catalysts. Run 1 shows that, if there is no catalyst, the purity and amount of methyl esters is relatively low, even if the reaction is performed at high temperature (200 °C) with a long reaction time (4 h). However, when the solid catalysts are added, the methyl esters content and yield in the product are significantly increased. This indicates that the solid catalysts considerably increase the level of the transesterification of crude palm kernel oil.

Among the investigated solid catalysts, SO$_4^{2−}$/SnO$_2$ and SO$_4^{2−}$/ZrO$_2$ provide the highest yield of methyl esters at 90.3 wt.% based on crude palm kernel oil. Moreover, the purities of methyl esters (or methyl esters content) from these two catalysts are relatively high (95.4 wt.% for SO$_4^{2−}$/SnO$_2$ and 95.8 wt.% for SO$_4^{2−}$/ZrO$_2$, respectively). However, the ester content is the highest (98.9 wt.%) with ZnO. The solid base catalysts (KNO$_3$/KL zeolite and KNO$_3$/ZrO$_2$) are moderately active. The methyl esters content of 78.3 wt.% is obtained if the KNO$_3$/ZrO$_2$ is used as the catalyst, whereas methyl esters content of 77.8 wt.% is obtained with the KNO$_3$/KL zeolite. Both of them give methyl esters yield higher than 70 wt.% Among the tested catalysts, ZrO$_2$ gives the lowest amount of methyl esters content and yield.

For crude palm kernel oil, all investigated catalysts show potential to be used as heterogeneous catalysts for the transesterification with methanol. Moreover, soap formation was not observed when the solid catalysts were used. Based on the above results, the yield of methyl esters from solid catalysts is in the following order: SO$_4^{2−}$/ZrO$_2$ and SO$_4^{2−}$/SnO$_2$ > ZnO > KNO$_3$/ZrO$_2$ > KNO$_3$/KL zeolite > ZrO$_2$.

3.2.2. Crude coconut oil transesterification

As shown in the Table 3, SO$_4^{2−}$/ZrO$_2$ provides highest methyl ester content (93.0%) and yield (86.3%), followed by SO$_4^{2−}$/SnO$_2$, ZnO, KNO$_3$/KL zeolite, KNO$_3$/ZrO$_2$ and ZrO$_2$.

The zirconia (ZrO$_2$) catalyst possesses both acidic and basic properties. It has been used in several chemical reactions, such as hydrogenation and esterification. In this study, ZrO$_2$ exhibits the lowest catalytic activity. It can only catalyze the transesterification of crude palm kernel oil and crude coconut oil to yields of methyl esters 64.5 and 49.3 wt.% respectively.

On the other hand, ZnO has shown the potential to catalyze the transesterification of both crude palm kernel oil and crude coconut oil. Stern et al. reported ZnO and mixture of ZnO with Al$_2$O$_3$ as the heterogeneous catalysts for the production of alkyl esters from vegetable oils or animal oils with alcohols [10]. For crude palm kernel oil transesterification, ZnO gave a high methyl esters content up to 98.9 wt.% and a methyl esters yield of 86.1%.

In comparison with SO$_4^{2−}$/SnO$_2$ and SO$_4^{2−}$/ZrO$_2$, ZnO gives a higher methyl ester content, but a lower methyl ester yield. However, for crude coconut oil transesterification, ZnO also gives methyl esters content and yield of 83.2 and 77.5%, respectively, which are lower than the cases of using SO$_4^{2−}$/SnO$_2$ and SO$_4^{2−}$/ZrO$_2$.

Both sulfated stannous oxide (SO$_4^{2−}$/SnO$_2$) and sulfated zirconia (SO$_4^{2−}$/ZrO$_2$) can be considered as superacid solids, which have high acid strength [5,6], and as expected, both show...
high catalytic activity for both types of oil. The amount of methyl esters produced from crude palm kernel oil is slightly greater than that from crude coconut oil. This may be due to the higher levels of free fatty acid and water content of crude coconut oil, which may have an effect on the reaction.

Sulfated zirconia has shown promising results when used as a heterogeneous catalyst for transesterification since it gives high methyl esters contents and yields. When compared to the transesterification of crude palm kernel oil and crude coconut oil catalyzed by ZrO₂, the methyl esters produced from SO₄²⁻/ZrO₂ is much higher than that when using unsulfated ZrO₂.

Sulfated stannous oxide is another solid, which can be used as a catalyst for transesterification of crude palm kernel oil and crude coconut oil. From the above results, SO₄²⁻/SnO₂ shows relatively high activity, producing methyl esters content and yield of about 95.4 and 90.3 wt.% in the case of crude palm kernel oil, and 88.3 and 80.6 wt % for crude coconut oil. This demonstrates that SO₄²⁻/SnO₂ is also a promising heterogeneous catalyst to be used in crude palm kernel oil and crude coconut oil transesterification.

The base catalyzed transesterification reaction using KNO₃ doped on KL zeolite and on ZrO₂ give moderate methyl esters content and yield for both crude palm kernel oil and crude coconut oil as shown in Tables 2 and 3.

Most investigated solid catalysts show great potential for use as heterogeneous catalysts for transesterification. Among them, SO₄²⁻/ZrO₂ exhibited the highest catalytic activity for the crude palm kernel oil and crude coconut oil transesterification, and the highest methyl esters content and yield can be obtained when SO₄²⁻/ZrO₂ was used as the heterogeneous catalyst. Therefore, it is interesting to further investigate the parameters affecting the transesterification catalyzed by SO₄²⁻/SnO₂ and SO₄²⁻/ZrO₂, and since the former shows better catalytic activity than latter, SO₄²⁻/ZrO₂ was, therefore, selected for further investigation.

3.2.3. Transesterification catalyzed by SO₄²⁻/ZrO₂

The results of catalytic (with SO₄²⁻/ZrO₂) and non-catalytic crude palm kernel oil transesterification are shown in Fig. 1. The methanol to oil molar ratio was kept constant at 6:1. Initially, the mixture of reactants and the sulfated zirconia solid catalyst was at room temperature and it was, then, heated to the desired reaction temperature at 200 °C over 15 min.

Interestingly, 84.1 wt.% of methyl esters was already observed after heating the mixture from room temperature to 200 °C in the test containing SO₄²⁻/ZrO₂. However, for the blank run, only 3.7 wt.% of methyl esters was observed. These results indicate that the SO₄²⁻/ZrO₂ catalyst significantly enhances the rate of transesterification.

After the reactor temperature reached the desired temperature, the methyl esters content slowly increased with increasing reaction time for both the catalytic and the non-catalytic reaction. At 60 min, 95.0 wt.% of methyl esters was produced from catalytic reaction, while non-catalytic reaction has methyl esters content only 16.7 wt %.

After 60 min, the amount of methyl esters produced from catalytic reaction was relatively constant at around 95 wt %, which may be due to catalyst deactivation. Further investigation is needed to examine the precise reason for this phenomenon. In case of the non-catalytic reaction, the rate of transesterification was faster during the first 30 min than after 1 h, however, the methyl esters content still increased slowly with increasing reaction time. This is due the rate constants for the conversion of di- and monoglycerides to monoglycerides and glycerol being very low compared to the rate constants for conversion of triglycerides to diglycerides [11].

The crude coconut oil transesterification catalyzed by SO₄²⁻/ZrO₂ was also performed to study the effect of the reaction time on the methyl esters content. As shown in Fig. 2, the transesterification of crude coconut oil catalyzed by SO₄²⁻/ZrO₂ occurs in the same manner as that of crude palm kernel oil transesterification. After the temperature reached 200 °C, 82.9 wt % of methyl esters is achieved when.
SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} is used as the catalyst. As can be seen, a large amount of coconut methyl esters is produced during the heating period, attributable to the high activity for transesterification of SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2}. The methyl esters content reaches 92.8 wt.% at a reaction time 60 min and this is relatively constant after this reaction period. However, the methyl esters produced from crude palm kernel oil is slightly higher than that from crude coconut oil, which is probably due to the higher amount of free fatty acid and water content in the crude coconut oil. It was previously observed in homogeneous catalytic systems that crude vegetable oils yielded lower methyl ester than refined vegetable oils due to the high free fatty acid content in the crude vegetable oils [12].

In the case of homogeneous catalysts, it has been revealed that the amount of catalysts has a strong influence on the conversion of vegetable oil to ester [2,12,13]. Thus, the effect of the SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} loading on the transesterification of crude palm kernel oil and crude coconut oil was studied. The reaction was carried out with a methanol:oil molar ratio of 6:1, under nitrogen atmosphere at pressure of 50 bars, at a temperature 200°C with a stirrer speed of 350 rpm. The effect of the amount of SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} on the methyl esters content is shown in Fig. 3.

In the case of crude palm kernel oil, after 4 h, 77.8 wt.% of methyl esters respectively were 93.0 and 93.5%.

It can be concluded that 1 wt.% of SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} (based on the weight of vegetable oil) was sufficient to catalyze the transesterification of crude palm kernel oil and crude coconut oil. It is probably further concluded that, when more than 1 wt.% of SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} was used, the maximum methyl ester content is probably limited by the equilibrium of transesterification, since the amount of ester was relatively constant when greater than 1 wt.% of SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} was added.

As shown in Table 4, the reaction catalyzed by spent SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} catalyst was fully deactivated. The spent SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} catalyst is recovered by filtering the product mixture through a nylon membrane. The recovered catalyst is then dried at 100°C and directly added to the reactor to test for the transesterification of crude palm kernel oil.

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst</th>
<th>Methyl esters content (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fresh SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2}</td>
<td>95.8</td>
</tr>
<tr>
<td>2</td>
<td>Spent SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2}</td>
<td>27.7</td>
</tr>
<tr>
<td>3</td>
<td>Regenerated SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2}</td>
<td>95.9</td>
</tr>
</tbody>
</table>

However, the spent SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} can be regenerated by immersion in a 0.5 M H\textsubscript{2}SO\textsubscript{4} solution for 30 min, filtered, and dried at 110°C for 24 h to re-form the sulfated sample (SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2}). The regenerated catalyst is calcined at 500°C for 2 h prior to use. As expected, the recycled SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} gave a high amount of methyl esters content (95.9 wt.%) as in the case of freshly prepared SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} catalyst (95.9 wt.%). This shows that the spent SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} from the transesterification can be easily regenerated and results in the same activity as that of the fresh catalyst.

It was reported that, in the transesterification of soybean oil with methanol, guanidines supported on poly(1,4-divinylbenzene) were slowly leached out from the polymer support [14]. However, in this study, the spent SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} was unable to catalyze the reaction, while the undoped ZrO\textsubscript{2} moderately catalyzed the reaction as shown in Tables 2 and 3. If the deactivation of the catalyst comes merely from the acid leaching, the spent SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} should be able to catalyze the reaction as in the case of the undoped ZrO\textsubscript{2}, but the spent SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} shows much lower activity. This suggests that the catalyst deactivation is more complicated, probably due to a combination of catalysts leaching and other phenomena, such as the blocking of the active sites by the products or unreacted starting materials.
A detailed study of the catalyst deactivation is currently under investigation.

4. Conclusions

All of the investigated solid catalysts (ZrO$_2$, ZnO, SO$_4^{2-}$/SnO$_2$, SO$_4^{2-}$/ZrO$_2$, KNO$_3$/KL zeolite and KNO$_3$/ZrO$_2$) have shown potential to be used as heterogeneous catalysts for the transesterification of crude palm kernel oil and crude coconut oil. Based on the methyl esters yield, SO$_4^{2-}$/ZrO$_2$ acid solid catalyst provides the highest yield when compared with the other solid catalysts. The order of activity of the solid catalysts for crude palm kernel oil transesterification is SO$_4^{2-}$/ZrO$_2$ > SO$_4^{2-}$/SnO$_2$ > ZnO > KNO$_3$/ZrO$_2$ > KNO$_3$/KL zeolite > ZrO$_2$. In the case of crude coconut oil, the activity can be shown from highest to lowest as follows: SO$_4^{2-}$/ZrO$_2$ > SO$_4^{2-}$/SnO$_2$ > ZnO > KNO$_3$/KL zeolite > KNO$_3$/ZrO$_2$ > ZrO$_2$. The SO$_4^{2-}$/ZrO$_2$ system can yield up to 90.3 wt.% of methyl esters from crude palm kernel oil and 86.3 wt.% from crude coconut oil.

A study into the effect of the reaction time for the transesterification of crude palm kernel oil and crude coconut oil was performed using SO$_4^{2-}$/ZrO$_2$, which it can be concluded that 1 h reaction time is sufficient for the amount of methyl esters to reach its maximum. In addition, only 1 wt.% of SO$_4^{2-}$/ZrO$_2$, based on weight of vegetable oil is adequate to catalyze the transesterification. Moreover, the preliminary study of re-used catalysts indicates that the spent SO$_4^{2-}$/ZrO$_2$ is fully deactivated and cannot be directly reused for transesterification. However, the spent SO$_4^{2-}$/ZrO$_2$ can be easily regenerated and results in the same activity as in fresh catalyst.

Acknowledgments

We gratefully acknowledge the Grants for Development of New Faculty and Staff, the Research Unit for Petrochemical and Environmental Catalysts, Ratchadapisek Somphot Endowment Fund, Chulalongkorn University, and the Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PIT consortium).

References