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Transesterification of Palm Kernel Oil and Coconut Oil by Difference Solid Catalysts

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Abstract: Several acid and basic solids, such as ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2, were tested as heterogeneous catalysts for palm kernel oil (PKO) and coconut oil (CCO) transesterification with methanol. It was found that ZnO and SO_4^{2-}/ZrO_2 exhibited the highest activity for both PKO and CCO transesterification. In the case of using SO_4^{2-}/ZrO_2, only 1% by wt of this super acid solid is sufficient to catalyze the reaction and results in fatty acid methyl esters content higher than 90%. Moreover, the preliminary study of re-used catalysts indicates that spent SO_4^{2-}/ZrO_2 cannot be directly reused for transesterification. However, this spent catalyst can be easily regenerated and results in the same activity as fresh catalyst

Keywords: Transesterification, Biodiesel, Palm Kernel Oil, Coconut Oil, Heterogeneous Catalysts.

Introduction

Due to the increase in crude oil prices and environmental concerns, a search for alternative fuels have gain significant attention over the years. Among different possible resources, diesel fuels derived from triglycerides of vegetable oils and animal fats present a promising alternative to substitute petroleum-based diesel fuels.

A number of studies have shown that triglycerides of vegetable oils can be used as diesel fuels [1]. 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, gum and other deposit formation. Consequently, considerable efforts have been made to develop alternative diesel fuels that have the properties and performance as the petroleum-based diesel fuels, and the most promising way is the transesterification of triglycerides to fatty acid alkyl esters.

Transesterification, also called alcoholysis, is the reaction of a fat or oil with an alcohol to form esters and glycerol [2]. This process has been widely used to reduce the viscosity of vegetable oils (triglycerides). In transesterification, triglycerides in vegetable oil will react with alcohol to form mixture of fatty acid alkyl esters and glycerol. The fatty acid alkyl esters produced from this process is called biodiesel which has become more attractive recently because of its environmental and economic benefits.

Biodiesel produced from vegetable oils can be used as an alternative to diesel fuels because the characteristics of biodiesel are close to petroleum-based diesel fuels. Several works have shown that biodiesel produced from various vegetable oils have viscosity close to petroleum-based diesel fuel. Their volumetric heating values are a little lower, but they have high cetane and flash points [1]. If methanol is used in transesterification, the obtained biodiesel will be fatty acid methyl esters (FAMEs). FAMEs have proper viscosity and boiling point and high cetane number [3].

Transesterification reaction can be catalyzed by both acidic catalysts and basic catalysts. In general, homogeneous catalysts such as minerals acids, metal hydroxide and metal alkoxide are usually used in transesterification reaction. However, the replacement of homogeneous catalysts by heterogeneous catalysts would have several advantages such as easy catalyst separation and reduction of environmental pollutants [4]. There are prospects that the technology of production of alkyl esters will be simplified when heterogeneous catalysts are utilized.

In this work, the production of biodiesel by using heterogeneous catalysts was investigated. Six types of catalyst (ZrO2, ZnO, SO4 2-/SnO2, SO4 2-/ZrO2, KNO3/KL zeolite, and KNO3/ZrO2) were prepared and applied for the transesterification of crude palm kernel oil and crude coconut oil.

Experimental

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_3) and Zinc Oxide (ZnO with purity higher than 99.0 % and Stannous Chloride (SnC_{l2}) 98 % were purchased from Fluka. Zirconium Oxide (ZrO_2) and Anhydrous Sodium Sulfate 99.0% were received from Riedel-deHaën. Sulfuric Acid (H_2SO_4) 96 %, Methanol 99.8 %, HPLC grade Acetonitrile and Acetone were purchased from Labscan. Ammonium Hydroxide was 28-30% (A.C.S.Reagent) and obtained from J.T. Baker.

Methyl ester used as standard for HPLC were Methyl Arachidate, Methyl Caprate, Methyl Caprylate, Methyl Laurate, Methyl Linoleate, Methyl Linolenate, Methyl Myristate, Methyl Oleate, and Methyl Palmitate , and all of them were purchased from Fluka.

Sulphated Stannous Oxide ($SO^4{}_{2-}/SnO_2$) was prepared by using the method outlined by Chavan et al. [5]. Stannous chloride (22.56 g) was dissolved in 200-ml distilled water to get a clear solution. Aqueous ammonium hydroxide (25 ml) was gradually added into this solution until pH is 8. The precipitated yellowish solid was then obtained by filtering and washing with distilled water. Then it was dried at 110^{0}C for 12 hours to get stannous hydroxide. This dried hydroxide powder was then equilibrated with 25 ml of 2 N H_2SO_4 for 2 hours. It was then again dried and calcined at 500^{0}C for 4 hours.

Sulphated Zirconia was prepared by the method outlined by Miao and Gao [6]. Zirconium oxide powder was immersed in a 0.5 M H_2SO_4 solution for 30 min, then filtered and dried at 110^{0}C for 24 hours to form the sulphated sample ($SO^4{}_{2-}/ZrO_2$). Finally, it was calcined at 500^{0}C for 2 hours.

KNO_3/KL zeolite was prepared by impregnation KL zeolite with an aqueous solution of KNO3. It was reported that 21% KNO_3/KL zeolite exhibits the highest basic strength [7]. The KL zeolite (40 g) was impregnated with KNO_3 solution and followed by drying at 100°C. The KNO_3/KL zeolite was then calcined at 600^{0}C for 2 hours.

Zirconia-supported potassium nitrate was prepared using the method outlined by Wang et al. [8]. The 20%KNO_3/ZrO_2 was prepared by grinding 40 g of ZrO_2 with 8 g of KNO^3 and followed by adding 24 ml of distilled water. The paste was kneaded and then dried at 110°C for 12 hours. Finally, the 20%KNO_3/ZrO_2 was calcined at 600^{0}C for 2 hours.

Transesterification reaction

One mole of vegetable oil, six moles of methanol, and desired amount of catalyst were weighed and placed in a 300 ml stainless steel reactor (Parr series reactor). The reactor was placed in a heater and then heated to 200°C, controlled by a programmable PID temperature controller. The reaction was carried out until it reached the desired reaction time, and then the reactor was cooled down to room temperature. After cooling, the catalyst was separated from the product mixture by filtration. The filtered product mixture was then placed in a separatory funnel for the phase separation of the methyl esters and the glycerol. The glycerol phase (bottom phase) was removed and kept in a separate container. Afterwards the methyl esters phase (top phase) was washed with 50°C distilled water [9]. Finally, the methyl esters product (biodiesel) was dried by adding sodium sulfate (25% based on the weight of washed methyl esters product).

The biodiesel products was 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 (Perkin Elmer Turbochrom Navigator). A Zorbax Eclipse XDB-C18 column (4.6 mm x 250 mm x 5ɷm) was used and the mobile phase was acetone/ acetonitrile mixture (70:30 vol/ vol) at a flowrate 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 for each sample was quantified by comparing the RID signal for each methyl ester of the HPLC chromatogram of biodiesel product with the RID signal of each of methyl ester standard.

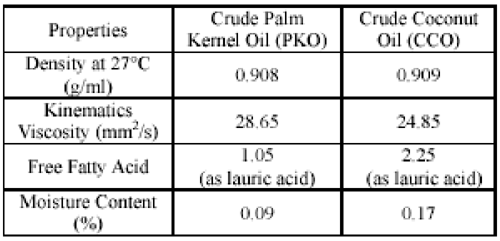
The methyl esters content and methyl esters yield in each experiment were calculated from the content in methyl esters of biodiesel as analyzed by HPLC. The methyl esters content (or purity) is defined as a ratio of weight of methyl esters, which was determined by using HPLC, to weight of methyl esters phase (top phase), which may contain mono-, di- and triglycerides. The methyl esters yield is defined as a ratio of weight of methyl esters, which was determined by using HPLC, to weight of vegetable oil used.

Results and Discussion

Characterization of vegetable oils

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

Table 1 Some physical properties of crude palm kernel oil and rude coconut oil



Properties	Crude Palm Kernel Oil (PKO)	Crude Coconut Oil (CCO)
Density at 27°C (g/ml)	0.908	0.909
Kinematics Viscosity (mm^2/s)	28.65	24.85
Free Fatty Acid	1.05 (as lauric acid)	2.25 (as lauric acid)
Moisture Content (%)	0.09	0.17

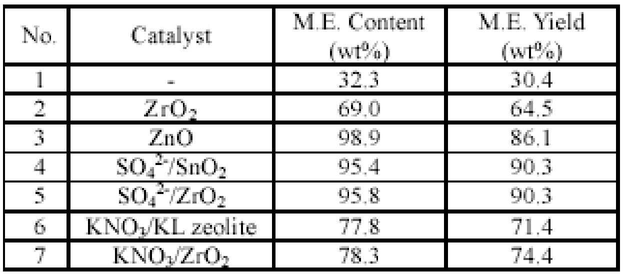
Investigation of heterogeneous catalysts for transesterification

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) have been tested for the transesterification of crude palm kernel oil and crude coconut oil to evaluate for their catalytic activity. The experimental conditions are set at methanol: oil molar ratio of 6:1, 3% by weight of catalysts (based on weight of vegetable oil), pressure at 50 bars under nitrogen atmosphere, temperature at 200°C, and the 350 rpm stirrer.

Crude Palm Kernel Oil Transesterification

Table 2 summarized the methyl esters (M.E.) content and methyl esters yield from crude palm kernel oil transesterification with the prepared solid catalysts. It can be seen that, when there is no catalysts present, the purity and amount of methyl esters are relatively low even the reaction is performed at high temperature (200°C) and long reaction time (4 hours). 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 rate of the transesterification of crude palm kernel oil.

Table 2 Crude palm kernel oil transesterification by solidcatalysts



No.	Catalyst	M.E. Content (wt%)	M.E. Yield (wt%)
1	-	32.3	30.4
2	ZrO_2	69.0	64.5
3	ZnO	98.9	86.1
4	SO_4^{2-}/SnO_2	95.4	90.3
5	SO_4^{2-}/ZrO_2	95.8	90.3
6	KNO_3/KL zeolite	77.8	71.4
7	KNO_3/ZrO_2	78.3	74.4

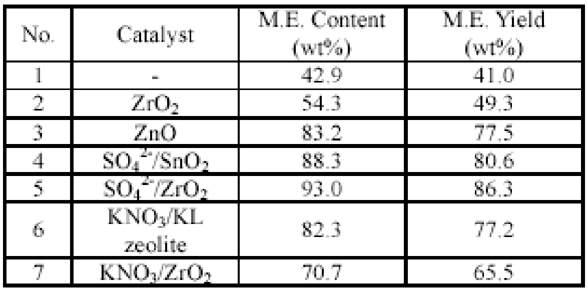
Among the investigated catalysts, SO_4^{2-}/SnO_2 and so_4^{2-}/ZrO_2 super-acid solid catalysts render the highest yield of methyl esters at 90.3 wt% based on crude palm kernel oil. Moreover, the purities of methyl esters (or esters content) from these two catalysts are relatively high as well (95.4 wt% and 95.8 wt% for SO_4^{2-}/SnO_2 and SO_4^{2-}/ZrO_2 respectively). However, the esters content if uses ZnO is the highest (98.9 wt%). For the solid super-base catalysts (KNO_3/ZrO_2, KNO_3/KL zeolite), they are moderately active. The methyl esters content of 78.3 wt% is obtained if KNO_3/ZrO_2 is used as the catalyst, whereas methyl esters content of 77.8 wt% is obtained when KNO_3/KLzeolite is used. Both of them give the 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 of investigated catalysts have shown potential to be used as heterogeneous catalysts for the transesterification with methanol. Moreover, soap formation was not observed when the solid catalysts were used. In addition, from the methyl esters yield, the order of solid catalysts which provide the amount of esters from highest to lowest is: SO_4^{2-}/ZrO_2 and SO_4^{2-}/SnO_2 > ZnO > KNO_3/ZrO > KNO_3/KL-zeolite > ZrO_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.

Table 3 Crude coconut oil transesterification by solid catalysts



No.	Catalyst	M.E. Content (wt%)	M.E. Yield (wt%)
1	-	42.9	41.0
2	ZrO_2	54.3	49.3
3	ZnO	83.2	77.5
4	SO_4^{2-}/SnO_2	88.3	80.6
5	SO_4^{2-}/ZrO_2	93.0	86.3
6	KNO_3/KL zeolite	82.3	77.2
7	KNO_3/ZrO_2	70.7	65.5

Zirconia (ZrO_2) catalyst possesses both acidic and basic properties. It has been used in several chemical reactions, such as hydrogenation, esterification, and etc. In this study, ZrO_2 exhibits the lowest catalytic activity because it gives the lowest methyl esters content and yield when compare to the other studied catalysts. It can catalyze the transesterification of crude palm kernel oil and crude coconut oil to yield only 64.5 wt% and 49.3 wt% of methyl esters, 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. patented ZnO and mixture of ZnO 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 can give high methyl esters content up to 98.9 wt% and methyl esters yield of 86.1%. When compare with the SO_4^{2-}/SnO_2 and SO_4^{2-}/ZrO_2, ZnO give higher methyl ester content, but lower methyl ester yield. However, for crude coconut oil transesterification, ZnO also give the methyl esters content and yield of 83.2% and 77.5% respectively, which are lower than the case of using SO_4^{2-}/SnO_2 and SO^{42-}/ZrO_2.

Both sulfated stannous oxide (SO_4^{2-}/SnO_2) and Sulfated Zirconia (SO_4^{2-}/ZrO_2) can be considered as super-acid solids, which have high acid strength. They can be prepared from methods described in other studies [5-6]. As expected, both of them 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 amount 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 to be used as a heterogeneous catalyst for the transesterification since it gives high methyl esters content and yield. When compare to the transesterification of crude palm kernel oil and crude coconut oil catalyzed by ZrO_2, the methyl esters produced from SO_4^{2-}/ZrO_2 is much higher than that from unsulfated ZrO_2.

Sulfated stannous oxide is another solid super-acid which can be used as catalyst for transesterification. It was applied to catalyze the crude palm kernel oil and crude coconut oil transesterification. From the results, SO_4^{2-}/SnO_2 shows relatively high activity. Methyl esters content and yield of about 95.4 wt% and 90.3 wt% are obtained in case of crude palm kernel oil and 88.3 wt% and 80.6 wt% are received in case of crude coconut oil, respectively. These demonstrate that SO_4^{2-}/SnO_2 is also a promising heterogeneous catalyst to be used in crude palm kernel oil and crude coconut oil transesterification.

KNO_3/KL zeolite used in the experiments was prepared by impregnating 21 wt% (based on weight of KL zeolite) of KNO_3 onto KL zeolite, which was reported to exhibit very high basic strength [7]. As expected, the KNO_3/KL zeolite can catalyze the transesterification reaction and gives moderate methyl esters content and yield for both crude palm kernel oil and crude coconut oil as shown in table 2 and 3.

KNO_3/ZrO_2 is another catalyst which has high basic strength [8]. From table 2 and 3, it can fairly catalyze the transesterification of both crude palm kernel oil and crude coconut oil.

Many of the investigated solid catalysts show high potential to be used as the heterogeneous catalysts for the transesterification. Among them, SO_4^{2-}/ZrO_2 and SO_4^{2-}/SnO_2 exhibit the highest catalytic activity to catalyze the crude coconut oil transesterification. High methyl esters content and yield can be obtained when SO_4^{2-}/ZrO_2 and SO_4^{2-}/SnO_2 are used as the heterogeneous catalysts. Therefore, it is interesting to further investigate the parameters affecting the transesterification catalyzed by SO_4^{2-}/ZrO_2 and SO_4^{2-}/SnO_2. Since SO_4^{2-}/ZrO_2 shows better catalytic activity than SO_4^{2-}/SnO_2, therefore, SO_4^{2-}/ZrO_2 is selected for further investigation.

Transesterification Catalyzed by SO_4^{2-}/SnO_2

Sulfated zirconia (SO_4^{2-}/ZrO_2) is then selected for further study of crude palm kernel oil and crude coconut oil transesterification. First, the reaction time is varied in order to find the optimized reaction time for transesterification. Second, the amount of SO_4^{2-}/ZrO_2 is varied to find the optimum amount of solid catalysts. Finally, the preliminary study of re-used catalysts is then reported in this section. The results of catalytic and non-catalytic crude palm kernel oil transesterification are shown in Figure 1. The methanol to oil molar ratio is kept constant at 6 to 1. Initially, the mixture of reactants and the sulfated zirconia solid catalyst was at room temperature and it was then heated to desired reaction temperature at 200°C. The heating period was 15 minutes. Interestingly, 84.1 wt% of methyl esters is already observed after heating the mixture from room temperature to 200°C in the test that contains SO_4^{2-}/ZrO_2. However, for the blank run, only 3.7 wt% of methyl estersis observed. These results indicate that the presence of the SO_4^{2-}/ZrO_2 catalyst significantly increases the rate of the transesterification. After the reactor's temperature reaches the desired temperature, the methyl esters content increases slowly with increasing reaction time for both catalytic and non-catalytic reaction. At 60 min, 95.0 wt% of methyl esters is 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 seems to be constant at around 95 wt%. This may be explained by the fact that the reaction has reached the equilibrium or the catalyst has deactivated. Another possible reason is that the rate constants for the conversion of di- and monoglycerides to monoglycerides and glycerol is very low when compare to the rate constants for conversion of triglycerides to diglycerides [11]. Therefore, further investigation is needed to examine the reason for that phenomenon. In case of non-catalytic reaction, however, methyl esters content still increases slowly with increasing reaction time.

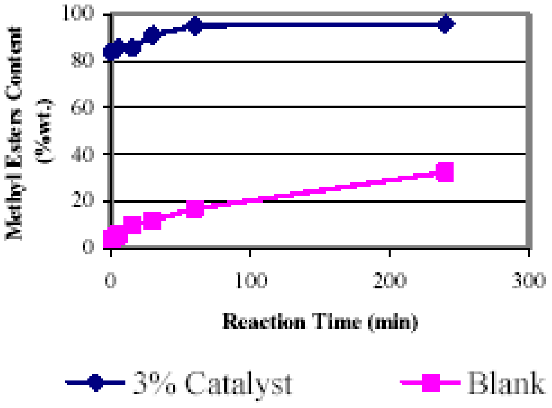


Fig. 1 Catalytic and non-catalytic transesterification of crude palm kernel oil at various reaction times.

The crude coconut oil transesterification catalyzed by SO_4^{2-}/ZrO_2 was also performed to study the effect of the reaction time on the methyl esters content. The results are reaction time on the methyl esters content. The results are reported in Figure 2.

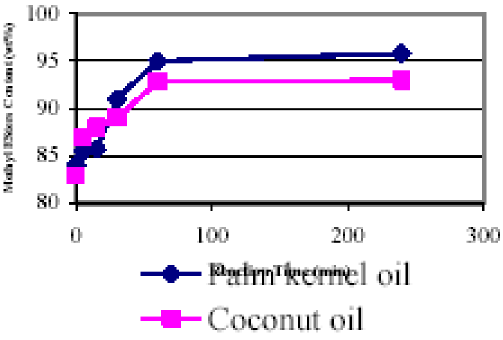


Fig. 2 Catalytic and non-catalytic transesterification of crude palm kernel oil and crude coconut oil at various reaction times.

As shown in Figure 2, the transesterification of crude coconut oil catalyzed by SO_4^{2-}/ZrO_2 shows the similar trend as in case of crude palm kernel oil transesterification. After the temperature reaches 200°C, up to 82.9 wt% of methyl esters is achieved when SO_4^{2-}/ZrO_2 is used as the catalyst.This indicates that high amount of coconut methyl esters is also produced during the heating period, which is absolutely due to the high activity for transesterification of SO_4^{2-}/ZrO_2. The methyl esters content reaches 92.8 wt% at reaction time 60 minutes and the methyl esters content is relatively constant after this reaction period. This may be explained by the fact that the reaction has reached the equilibrium or the catalyst has deactivated. However, the methyl esters produced from crude palm kernel oil was slightly higher than that from crude coconut oil. This is probably due to the higher amount of free fatty acid and water content in the crude coconut oil which may have an effect on the reaction.

For 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]. Therefore, the effect of the amount of SO_4^{2-}/ZrO_2 on transesterification of crude palm kernel oil and crude coconut oil is studied. The reaction was carried out with a methanol: oil molar ratio of 6:1, under nitrogen atmosphere at pressure of 50 bars, at temperature 200°C and the stirrer speed of 350 rpm. The effect of the amount of SO_4^{2-}/ZrO_2 on the methyl esters esters content. deactivated. The spent SO_4 content are shown Table 6 and plotted in Figure 3.

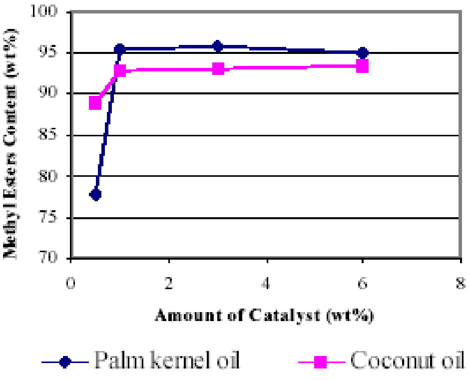


Fig. 3 Effect of the added amount of SO42-/ ZrO2 on methyl esters content.

In case of crude palm kernel oil, after 4 hours, 77.8 wt% of methyl esters are obtained when only 0.5 wt% of SO_4^{2-}/ZrO_2 is used. However, when 1 wt% of SO_4^{2-}/ZrO_2 is added, much higher methyl esters content (95.5 wt%) can be obtained. Moreover, the methyl esters content produced by 3 wt% and 6 wt% of SO_4^{2-}/ZrO_2 are 95.8 wt% and 95.0 wt%, respectively. The amount of ester is significantly increased when the amount of catalysts is increased from 0.5 wt% to 1 wt%. However, if the amount of SO_4^{2-}/ZrO_2 is added beyond 1 wt%, the methyl esters content is relatively constant.

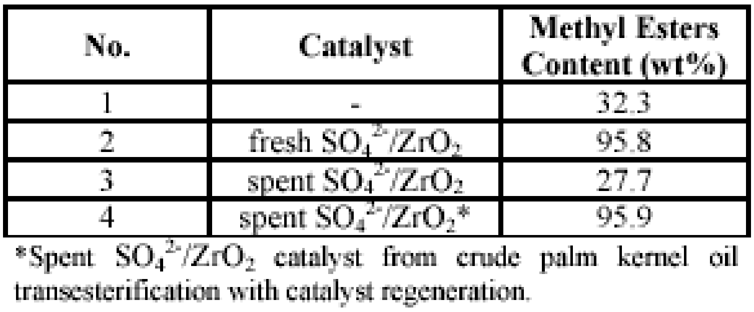
For the crude coconut oil, the results are strikingly similar as in the case of crude palm kernel oil. The amount of methyl esters (88.8 wt%) is obtained when 0.5 wt% of catalyst is added. When 1 wt% of catalysts is used, the methyl esters content is increased to 92.8 %, and when 3 wt% and 5 wt% of SO_4^{2-}/ZrO_2 are added, the methyl esters respectively are 93.0% and 93.5%.

It can be concluded that 1 wt% of SO_4^{2-}/ZrO_2 (based on weight of vegetable oil) is 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_4^{2-}/ZrO_2 is used, the maximum methyl ester content is probably limited by the equilibrium of transesterification, since the amount of ester is relatively constant after more than 1 wt% of SO_4^{2-}/ZrO_2 is added. The spent SO_4^{2-}/ZrO_2 catalyst obtained from transesterification of crude palm kernel oil with 3 wt% catalyst and 4 hours reaction time is fruther tested to determine whether the one-time used SO_4^{2-}/ZrO_2 catalyst is fully deactivated.

The spent SO_4^{2-}/ ZrO_2 catalyst is recovered by filtering the product mixture with nylon membrane filter. The recovered catalyst is then dried at 100°C and directly added to the reactor to test for crude palm kernel oil transesterification.

As shown in Table 4, the reaction catalyzed by spent $SO_4{}^{2-}/ZrO_2$ yields only 27.7 wt% of methyl esters content, which is close to methyl esters content produced by non-catalytic reaction, and of course, is much lower than oil. methyl esters produced by fresh SO_4^{2-}/ZrO_2. This indicates that the spent SO_4^{2-}/ZrO_2 is fully deactivated and cannot be directly reused for transesterification without further treatment.

Table 4 Comparison between fresh catalyst and spent catalyst for the crude palm kernel oil transesterification



No.	Catalyst	Methyl Esters Content (wt%)
1	-	32.3
2	fresh SO_4^{2-}/ZrO_2	95.8
3	spent SO_4^{2-}/ZrO_2	27.7
4	spent SO_4^{2-}/ZrO_2*	95.9

*Spent SO_4^{2-}/ZrO_2 catalyst from crude palm kernel oil transesterification with catalyst regeneration.

However, if the spent SO_4^{2-}/ZrO_2 is regenerated by immersion the spent catalyst in a 0.5 M H_2SO_4 solution for 30 min, filtered, and dried at 110°C for 24 hours to form the sulfated sample (SO_4^{2-}/ZrO_2) again. The regenerated catalyst is calcined at 500°C for 2 hours prior to use. As expected, the regenerated SO_4^{2-}/ZrO_2 give high amount of methyl esters content (95.9 wt%) as in the case of freshly prepared SO_4^{2-}/ZrO_2 catalyst (95.9 wt%). This shows that the spent $SO_4^{2-}/ZrO2$ from transesterification can be easily regenerated and results in the same activity as in fresh catalyst.

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 their potential to be used as the heterogeneous catalysts for the transesterification of crude palm kernel oil and crude coconut oil. Based on methyl esters yield, S SO_4^{2-}/ZrO_2 super-acid solid catalyst provides the highest yield of methyl esters when compare with the studied solid catalysts. The order of activity of 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 case of crude coconut oil, the solid catalysts' activity can be shown from highest to lowest as following: 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 can yield up to 90.3 wt% of esters from crude palm kernel oil and 86.3 wt% from crude coconut oil.

The SO_4^{2-}/ZrO_2 is then selected for further study as a solid catalyst for transesterification of crude palm kernel oil and crude coconut oil since it shows the highest activity for transesterification of both types of oils. It can be concluded that 1 hour reaction time is sufficient for the amount of methyl esters to reach maximum. In addition, only 1 wt% of SO_4^{2-}/ZrO_2, based on weight of vegetable oil is adequate to catalyze the transesterification of crude palm kernel oil and crude coconut oil. 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, it was found that the spent SO_4^{2-}/ZrO_2 can be easily regenerated and results in the same activity as in fresh catalyst.

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