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Advancement in Heterogeneous Catalysis of Triglycerides for Biodiesel Production

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Abstract

Heterogeneous catalyst of transesterification is gaining more support because of the friendly nature of the catalysts, easy separation from the products, their reusability and less process water require. This paper present the efficacy of some of the common solid catalysts for biodiesel production. Many researchers have developed different solid base/acid catalysts for transesterification of vegetable oil in order to replace the conventional homogeneous catalysts that have a lot of limitations. The performances of some of these heterogeneous catalysts with appropriate vegetable oils are reviewed in this paper. K/KOH/Υ.Al_2O_3 has yielded 84.5% biodiesel from rapeseed oil, X/Y/MgO/Υ. Al_2O_3 yielded 96.1% biodiesel from jatropha curcas oil, $SO_4/TiO_2.nH_2O$ and $SO_4/Zr(OH)_2$ yielded 90% biodiesel from cotton seed oil. CaO, SrO, $Ca(OCH_3)_2$ and $Ca(OCH_2CH_3)_2$ *yielded 95% biodiesel from soybean oil. ZnO,* $SO_4^{-2}/SnO_2/$, *and* SO_4^{-2}/ZrO_2 *have good yield of biodiesel with palm kernel oil and coco nut oil. Heterogeneous catalysis is a process intensification.*

Keywords: Heterogeneous catalysts, biodiesel, Transesterification, yield

Introduction

Transesterification of triglycerides with short chain mono-alcohols such as methanol and ethanol using homogeneous catalysts such as NaOH, KOH and MeONa is the conventional method of biodiesel production. The use of these catalysts has a lot of setbacks (Lotero et al, Retrieved, 2011) which include the following; high corrosiveness, intensive separation/ purification processes, Impossibility of catalyst reuse and inability of the homogeneous catalysts to catalyze high free fatty acid oils content.

The strong acids such as H_2SO_4, HCl and H_2PO_4 catalysts show tolerance for free fatty acid oil but they catalyze the transesterification reaction very slowly (Au and Dai, 2008). The acid catalysts can catalyze simultaneously both esterification and transesterification reaction. Acids homogeneous catalysts are not affected by the presence of free fatty acids and water, but the reaction rate is 4 000 times slower than in base catalysis (Au and Dai). To be economically viable and to compete commercially with petro-diesel, a continuous process for biodiesel production must be few in reaction steps and simple in separation processes, and obviously robust heterogeneous catalysts have to be employed.

Heterogeneous catalysts are categorized as solid acid and solid base. Solid base catalysts include a wide group of compounds in the category of alkaline earth metal oxides, hydrotalcites/layered double hydroxides, alumina loaded with various compounds, zeolites, and various other

compounds showing high basicity coupled with active basic sites, pore size, and other parameters. Solid base catalysts have been quite successful with high conversion and yield of biodiesel obtained (Sharma and Singh, 2011) and can be recycled several times without regeneration (Science-Article.com 2009). However, the solid base catalysts are sensitive to the presence of free fatty acids (Sharma and Singh, 2011).

The following alkaline earth metal oxides have been used as catalysts for transesterification of soybean oil; CaO, SrO, $Ca(OCH_3)_2$ and $Ca(OCH_2CH_3)_2$. The results indicated that at a reaction temperature of 65^0C, reaction time of 3 hours and mole ratio of 12:1 of methanol to oil, 95% biodiesel yield was obtained as reported by Science-Article.com (2009). The yield has little decrease after reused for 10-20 times. Among the four, Science-Article.com (2009) reported that, $Ca(OCH_3)_2$ has higher stability and better catalytic ability. A 95% yield of biodiesel at 65^0C over

With sulphated zirconia/alumina palm oil was transesterified to biodiesel at a temperature of 127^0C and reaction time of 3 hours and mole ratio of methanol to oil 8:1 (Fei and Teong, 2008). The yield was as high as 83.3% with 6% weight of catalyst. A 90.54% of biodiesel yield was produced from palm oil and methanol over a solid base KOH/Al_2O_3 catalyst (Isahak et al, 2010). The reaction was carried out in a batch reactor of a 3-neck flask, condenser and thermometer for 2

Palm Kernel Oil

Palm kernel oil was transesterified with methanol using the following solid acid and base catalysts; ZrO_2, ZnO, SO_4^{-2}/SnO_2/, SO_4^{-2}/ZrO_2,KNO_3/KL

Table 1: Yield of biodiesel from palm kernel oil with solid catalysts.

Solid acids have a preference over solid base catalysts for they can tolerate free fatty acids. The heterogeneous catalysts have the advantages of easy separation from the product without requirement of washing and reusability of the catalysts (Sharma and Singh, 2011)

Soybean Oil

CaO 8% wt has been achieved by the transesterification of soybean oil (Au and Dai, 2008).

According to Arefaat (2010), transesterification of soybean oil was carried out refluxing methanol in the presence of CaO, $Ca(OH)_2$ and $CaCO_3$ at 1 hour reaction time, a yield of fatty acid methyl ester (FAME) was 93% for with CaO, 12% with $Ca(OH)_2$ and 0% with $CaCO_3$. Hence, CaO and $Ca(OCH)_2$ are good catalysts for producing biodiesel from soybean.

Palm Oil

hours reaction time at 65^0C reaction temperature with 1% wt of catalyst.

These results indicate that, KOH/Al_2O_3 is a better catalyst for transesterification of palm oil compared to sulphated zirconia (SO_4^{-2}/ZrO_2), if the free fatty acid and water is low in the feedstock. Hence, base catalyst KOH/Al_2O_3 has better catalytic activity than acid catalyst for palm oil transesterification

zeolite and KNO_3/ZrO_2. The biodiesel yield by these catalysts were quite high ranging from 64% to 90.3% (Jitputi et al, 2004) as shown in Table 1 below.

No	Catalysts	Biodiesel yield (%)
1	ZrO_2	64.5
2	ZnO	86.1
3	SO_4^{-2}/SnO_2	90.3
4	SO_4^{-2}/ZrO_2	90.3
5	KNO_3/KL zeolite	71.4
6	KNO_3/ZrO_2	74.4

At a reaction time of 60 minutes and temperature of 200^0C, SO_4^{-2}/ZrO_2 and SO_4^{-2}/SnO_2 catalyzed palm kernel oil with methanol to 92.9% and 95% yield respectively (Hu and Dai, 2004).

The results in Table 1 when presented in bar chat as shown in figure 1 indicates that both sulphated tin oxide and zirconia are good catalysts for palm kernel oil transesterification. The base catalyst ZnO have lower yield compared to the two acid catalysts probably because of their tolerance to free fatty acids and water in the feedstocks

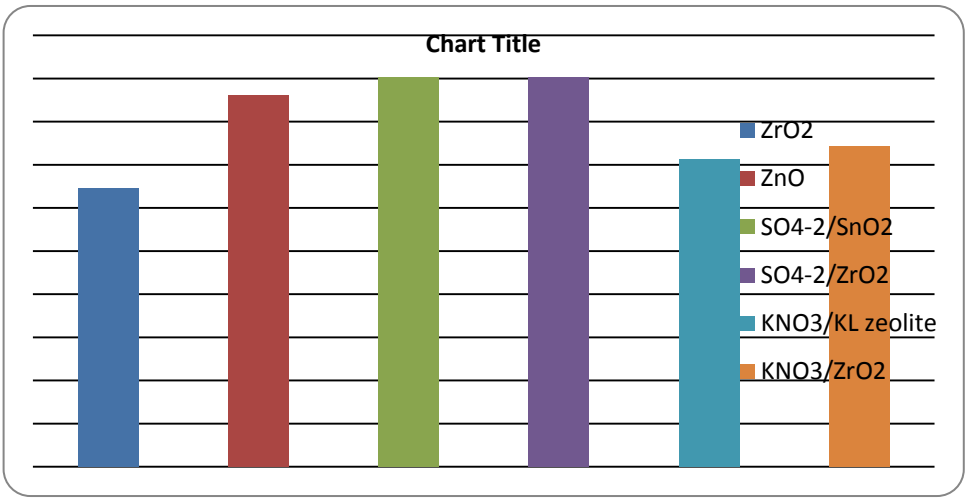

Figure 1: Yield of Biodiesel from Palm OIL

Coconut Oil

According to Jitputi et al (2004), ZrO_2, ZnO, SO_4^{-2}/SnO_2/, SO_4^{-2}/ZrO_2,KNO_3/KL zeolite and KNO_3/ZrO_2 catalyzed reaction of coconut oil with methanol produced remarkable yield, as shown inTable 2 below. The results in Table 2 is represented in bar chat as shown in Figure2 indicate that sulphated zirconia is the best catalyst among the listed catalysts for transesterification of cotton oil. The higher catalytic activity exhibited by acid catalysts may suggest that coco nut oil has high free fatty acids which base catalysts cannot handle effectively well.

Table 2: Yield of biodiesel from coco nut oil with solid catalysts.

No	Catalysts	Biodiesel yield (%)
1	ZrO_2	49.3
2	ZnO	77.5
3	SO_4^{-2} / SnO_2	80.6
4	SO_4^{-2} / ZrO_2	86.3
5	KNO_3/KL zeolite	77.2
6	KNO_3/ZrO_2	65.5

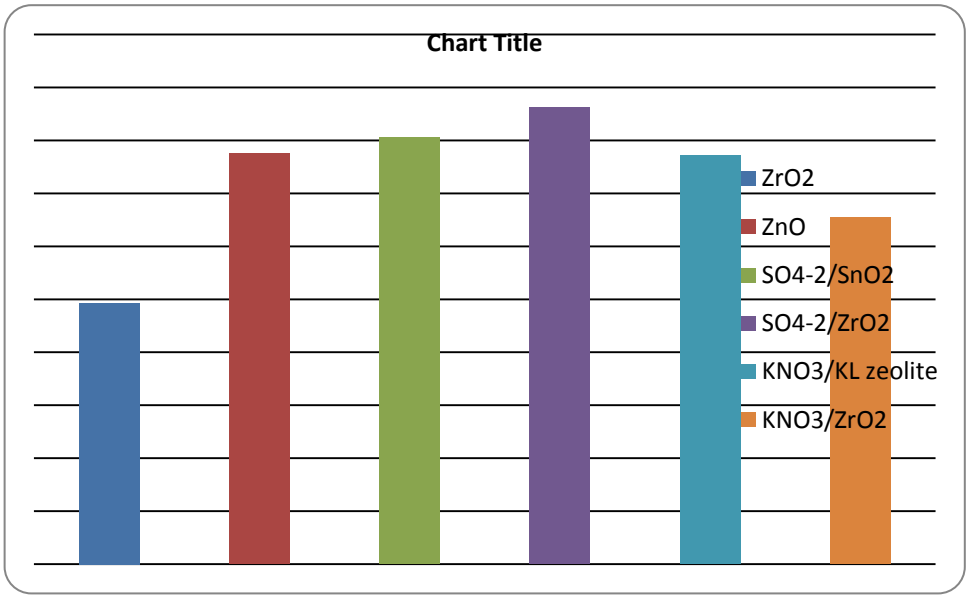

Figure 2: Yield of Biodiesel from Coco Nut Oil

Cotton Seed Oil

Methyl esters (biodiesel) were produced by the transesterification of cottonseed oil with methanol in the presence of solid acids, SO_4/TiO_2 and SO_4/ZrO_2, showed high activity (Chen et al, 2006). The yield of methyl esters was over 90% under the conditions of 230°C, methanol/oil mole ratio of 12:1, reaction time 8 h and catalyst amount (catalyst/oil) of 2% (w). The solid acid catalysts showed more better adaptability than solid base catalysts when the oil has high acidity. IR spectral analysis of absorbed pyridine on the samples showed that there were Lewis and Brønsted acid sites on the catalysts (Chen et al, 2006).

Rapeseed Oil

A transesterification reaction was carried out with rapeseed oil and methanol over $K_2O/\Upsilon.Al_2O_3$ catalyst at a molar ratio of 12:1 methanol to oil, reaction time of 3 hours and reaction temperature of 70^0C, biodiesel yield of 94% was obtained (Han and Guan, 2009). Report has also shown that transesterification of rapeseed oil with methanol, at molar ratio of 1:9, 60^0C reaction temperature, 1 hour reaction time and 4% catalyst weight, 84.52% biodiesel yield was obtained (Hongbin, et

al, 2008). Liu et al, (2010) obtained a conversion of 98.62% calcined K_2CO_3/γ-Al_2O_3 as solid catalyst

Jatopha Curcas Seed Oil

Transesterification of Jatropha curcas seed oil to biodiesel using CaO as a solid catalyst. This reaction was carried out using 12:1 mole ratio of methanol to oil at 70^0C for 3 hours 1.5% (cat.w/v oil) and 2% water content in the feed, a yield of 95% was obtained (Hawash, et al, 2011). Similar reaction was carried out by Highina et al, (2011), 98.00% yield was obtained using 1%wt ZnO as The biodiesel yield show little decrease after reused with base catalysts such as CaO, SrO, $Ca(OCH_3)_2$ and $Ca(OCH_2CH_3)_2$ for 10- 20 times. However, it is reported that, the recovered solid acid catalyst SO_4^{-2}/ZrO_2 used after filtration, yielded only 27.7% biodiesel (Jitputi et al, 2004). But when the spent catalyst was regenerated by

These two results indicate that the catalysts have good catalytic activity on rapeseed oil, with $K2O/\Upsilon.Al_2O_3$ upper hand, though at different reaction conditions. catalyst at 67^0C for 80minutes. With these yields, the FFA of Jatropha must have been reduced because; base catalysts cannot achieve this result if FFA is high. Jatropha oil is known to have high FFA above 10%.

Catalytic Strength of Spent Catalysts

immersion of the spent catalysts in 0.5M H_2SO_4 solution for 30 minutes, filtered and dried at 110^0C for 24 hours and calcined at 500^0C for 2 hours prior to use yielded 95.9% biodiesel. This indicates that regenerate catalyst has higher catalytic activity than the fresh catalyst (Jitputi et al, 2004).

Conclusion

This review has shown that very many solid catalysts are capable of replacing the conventional homogeneous catalysts currently in use for transesterification of vegetable oils. Hence, from this review, we can have a choice of catalysts for different feedstocks in the course of biodiesel production with regard to free fatty acid and water content;

Sulphated zirconia alumina and KOH/Al_2O_3 can be conveniently used to catalyze palm oil to biodiesel. Sulphated titanium oxide (SO_4/TiO_2) has high catalytic activity on palm oil and coco nut oil. Sulphated tin oxide and zirconia (SO_4/SnO_2 and SO_4/ZrO_2) have high catalytic activity for transesterification of cotton seed oil. Calcium oxide and calcium methoxide (CaO and $Ca(OCH_3)_2$) are good catalysts for soybean transesterification to biodiesel. CaO and ZnO are suitable for Jatropha oil.

Spent solid base catalysts require little or no regeneration before reuse. Regenerated spent solid acid catalysts show stronger catalytic activity.

Heterogeneous catalysts have the advantages of easy separation from the reaction medium and reusability. Heterogeneous catalysis can be considered to be a green process for biodiesel production, because, they are easy to separate from products, less corrosive and can be reused.

The purification steps of products in heterogeneous catalysis are much more simplified and high yields of fatty acid methyl ester (FAME) are obtained.

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