



Review Article

Solid Catalysts and Their Application in Biodiesel Production

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Abstract

The reduction of oil resources and increasing petroleum price has led to the search for alternative fuel from renewable resources such as biodiesel. Currently biodiesel is produced from vegetable oil using liquid catalysts. Replacement of liquid catalysts with solid catalysts would greatly solve the problems associated with expensive separation methods and corrosion problems, yielding to a cleaner product and greatly decreasing the cost of biodiesel production. In this paper, the development of solid catalysts and its catalytic activity are reviewed. Solid catalysts are able to perform transesterification and esterification reactions simultaneously and able to convert low quality oils with high amount of free fatty acids. The parameters that affect the production of biodiesel are discussed in this paper. © 2012 BCREC UNDIP. All rights reserved

Keywords: Biodiesel; Heterogeneous Catalyst; Solid Acid; Transesterification; Esterification

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1. Introduction

The world's crude oil reserve is fast declining due to demand in electricity generation and fuel oil in energy intensive sectors such as petrochemical and transportation. The consumption of transportation fuels is continuously increasing with large majority of it is derived from non-renewable fossil fuel. The drawback of using fossil fuels is well documented in various communications in media and scientific journals as a source of environmental problems particularly when dealing with the quality of the exhaust gases emitted from their respective combustion.

Such great concern is directed to the generation of the green-house gases such as CO_x, SO_x and NO_x. These pollutant gases are hazardous to human health and some are of carcinogenic in nature. Efforts are made by researchers, scientists and environmentalists to spearhead the use of alternative fuels which are non-pollutant, environmental friendly as well as renewable in nature. Biodiesel has been identified as one of the most promising sources of alternative fuels. Transesterification of triglycerides (TGs) with methanol has been known as the central reaction in the synthesis of biodiesel from oils and fats that

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produces chemical compounds known as fatty acid methyl ester (biodiesel).

Most of the commercial production of biodiesel worldwide uses homogeneous base catalysts, which are corrosive and non-reusable and produces waste that needs to be neutralized, hence, increasing the overall costs and leads to an environmental concerns. Homogeneous base catalyst (e.g., NaOH) is most commonly used process to produce biodiesel by transesterification of triglyceride and methanol.

Solid catalysts have found widespread application in the catalysis field and belong to the group of new catalytic material which has greatly developed in recent years. However, research activities using solid catalysts for biodiesel synthesis has been limited due to low expectations about reaction rates and probable undesired side reactions. Table 1 shows comparison of homogenous and heterogeneously catalyzed transesterification heterogeneous acid catalyst [1]. The advantage of using homogeneous catalyst especially base catalyst is cheaper catalyst cost. However, it requires refined oils containing not more than 0.5 % of free fatty acids (FFAs) and anhydrous conditions. Therefore, the production cost of biodiesel is higher if refined oil is used instead of low quality of feedstock. The main advantage of a heterogeneous catalyst is that the catalyst is easily separated from the reactants and products. Reduction of the biodiesel production cost can be achieved if heterogeneous catalyst is used. Heterogeneous catalyst offers easier production process, improve product quality and also reduce corrosion and toxicity problems. Furthermore, it

can be used for low quality feedstock, which contains high FFAs.

2. Current Technology in Biodiesel Production

Currently, most of the biodiesel produced worldwide comes from the transesterification of vegetable oil, animal fats, and recycled greases through the addition of methanol (or other alcohols) and a catalyst, giving glycerol as a co-product. These materials contain triglycerides, free fatty acids, and other contaminants depending on pretreatment process.

The most common catalysts in the production of biodiesel are homogeneous base catalysts such as sodium hydroxide and potassium hydroxide. The advantages of using homogeneous base catalyst is the reaction proceeds at a much higher rate and is less corrosive than the homogeneous acid (H_2SO_4) catalyst. Typical catalyst loadings range from 0.3 % to about 1.5 %. After the reaction, the catalyst must be neutralized and wash with a lot of water to remove the salt produced [2,3].

The reaction is carried out using a batch, stirred tank reactor with operating temperature is usually about 65 °C. Alcohol to triglyceride ratios from 4:1 to 20:1 (mole:mole) have been reported, with a 6:1 ratio most common. The main alcohol used in the production of biodiesel is methanol because of its low cost and availability [4].

Even though the homogeneous base catalyzed biodiesel production processes are relatively fast, and show high yield, they are still not very cost-competitive with petrodiesel ones because of the cost of raw material used and the catalyst cannot be recovered after the reaction. Choice of the fats or oils to be used in producing biodiesel depends on the process and raw material cost and impurities. Low quality oil contains high level of free fatty acid (FFA) and water. When FFA is present in the feedstock, it reacts with the homogeneous base catalysts and may deactivate the catalyst and form unwanted soap by-products. In addition, the present of water in the reaction mixture also leads to the deactivation of homogeneous catalysts. Ma and Hanna [2], reported that water should be kept below 0.06 % and FFA should be kept below 0.5 wt % to get the best conversions.

In order to reduce the production cost of biodiesel, some researchers conducted research by using solid catalyst and low quality oil such as residual oil from waste material [5]. Biodiesel production using solid catalysts has an economic benefit in terms of cheaper production costs because of reusable nature of the catalyst and the

Table 1. Comparison of homogenous and heterogeneously catalyzed transesterification [1]

Factors	Homogeneous Catalysis	Heterogeneous Catalysis
Reaction Rate	Fast and high conversion	Moderate conversion
After treatment	Catalyst cannot be recovered, must be neutralized leading to waste chemical production	Can be recovered
Processing methodology	Limited use of continuous methodology	Continuous fix bed operation is possible
Presence of water/free fatty acids	Sensitive	Not sensitive
Catalyst reuse	Not possible	Possible
Cost	Comparatively costly	Potentially cheaper

possibility to be use for low quality feedstock [6].

3. Solid Catalyst

A solid catalyst is a good alternative for homogeneous catalysts in the transesterification of vegetable oil for the production of biodiesel due to the fact that solid catalyst would not dissolve in the reactant mixture, thus eliminating the separation issues associated with the conventional homogeneous process. The removal of homogenous catalysts is technically difficult and large amount of wastewater is produced during the process and needs to be treated via neutralization process. Conventional homogeneous catalysts are expected to be replaced with solid catalyst due to economics and environmental reasons in the near future. Having said that, the research and development of solid bases catalyst in general has an upper hand than that of solid acids [7,8].

3.1. Solid bases catalyst for biodiesel production

The development of basic solid catalysts for biodiesel production has been widely mentioned in the scientific journals which include the use of carbonates and hydro-carbonates of alkaline metals; alkaline metal oxides; alkaline metal hydroxides; anionic resins and basic zeolites. Solid bases catalyze reactions by donating electrons. Table 2 shows typical solid base catalysts used in biodiesel production. Some of these catalysts have shown good catalytic activity similar to those of homogeneous base catalysts. However, solid base catalysts are still far from an industrial application, due to the lack of technical and scientific knowledge pertaining to its behavior and most of the studies are based on small scale stirred batch reactors.

The performance of solid bases such as cesium-exchanged sodium zeolites (NaCsX), hydrotalcites ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16.4}(\text{H}_2\text{O})$), Barium hydroxide ($\text{Ba}(\text{OH})_2$) and MgO have been investigated by Leclercq *et al.* [9]. They pointed out that strong basic properties are required to perform biodiesel synthesis reaction. Some of these solid catalysts such as alkali earth metal oxides (CaO , BaO) and alkali earth metal hydroxides ($\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$) are partially soluble in water and alcohol and present in the final biodiesel product. Results from Mazzochia *et al.* [10] confirmed that $\text{Ba}(\text{OH})_2$ is slightly soluble in the reaction mixture where the resulting biodiesel and glycerine contained 0.06 % and 0.25 % of barium, respectively.

Suppes *et al.* [11] carried out biodiesel production using zeolites namely NaX, NaY

faujasites, potassium-exchanged NaX (KX), cesium-exchanged NaX (CsX), and ETS-10 zeolite. The base strength of the metal ion exchanged zeolite increases with increasing electropositive nature of the cation. The occlusion of alkali metal oxide clusters in zeolite cages results in an increase in the basicity of these materials. Lotero *et al.* [12] reported that the use of ETS-10 zeolite has shown an 80% biodiesel conversion when conducted at 60 °C and after 24 hours of operation. They also reported leaching of ETS-10 into reaction mixture.

Helwani *et al.* [13] explained that alkaline earth oxides are potential solid bases for use in triglyceride transesterification. The origin of basic sites in alkaline earth oxides is generally believed to be generated by the presence of $\text{M}^{2+} - \text{O}^{2-}$ ion pairs in different coordination environments. The basic strength of the group II oxides and hydroxides increases by the following order; $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$. Ca-derived bases are the most promising as they are cheaper and exhibit low methanol solubility. Gryglewicz [14] tested the performance of CaO , MgO , $\text{Ca}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$ for biodiesel production at the reaction temperature of 65°C. Results showed that $\text{Ba}(\text{OH})_2$ exhibited good performance though it dissolved into methanol. It was also reported that CaO and $\text{Ca}(\text{OH})_2$ reacted with methanol to form calcium methoxide on the surface. These calcium methoxide ions catalysed the reaction similar to that of methoxide ions formed by NaOH , but with low catalytic activity. On the other hand, it was established that $\text{Ca}(\text{OH})_2$ was unable to catalyze the reaction whilst MgO was found to be an inactive catalyst. The performance of CaO was 3~4 times slower than that of NaOH , giving 90% conversion in 2.5 hours. It has been reported that even if CaO is reused for several runs without any significant deactivation, dissolution of CaO does occur [15]. The catalytic reaction is resulted from the contribution of both heterogeneous and homogeneous catalysis in the formation of leached active species.

The catalytic activity of materials generated by loading alumina with alkali metal salts has also been investigated. Kim *et al.* [16] used $\text{Na}/\text{NaOH}/\gamma\text{-Al}_2\text{O}_3$, a solid super-base, for the transesterification of vegetable oil to biodiesel. The catalyst was able to achieve equilibrium conversion of 94% in 2 hours. In spite of previously mentioned research efforts, there has been no successful commercial production of biodiesel using solid bases with main concerns are maintenance and reusability issues.

3.2. Solid Acids for biodiesel production

Sulfuric acid and alkyl sulfonic compounds are probably the most extended acid catalysts used for the biodiesel production. These liquid acids may cause corrosion problem and consequent environmental hazards posed by them. For this reason and many others, such as the impossibility to reuse liquid acids, solid acid catalysts are preferred over liquid acid. Solid acid catalysts can replace strong liquid acids. However, the usage of solid acid catalysts for biodiesel production is still limited due to lack of understanding of the factors that govern the reactivity of solid acid catalysts. A variety of solid catalysts has been examined for the transesterification reaction and new catalysts continue to be reported in the literature. Table 2 shows some of the solid acids used in the biodiesel production.

Solid acids catalyze reaction either by donating protons or abstracting electrons. Solid acids are so well-developed that numerous solid acids are even stronger than sulphuric acid. They are called solid superacids. A superacid is defined as an acid that exhibits an acid strength higher than the acid strength of 100 % sulphuric acid. Solid acids have been widely used in petroleum industry for applications like cracking and reforming. Table 3 shows some of the example of solid acid used in the study of biodiesel production. The solid acid-catalyzed process is clearly advantageous over liquid acid catalyst as it has the highest rate-of-return, and lowest capital investment, due to its simple process.

There are several considerations in the development of a strong solid acid; firstly, the catalyst should have higher stability of acid sites to avoid their leaching. Secondly is by enhancement of mass transfer to avoid diffusional limitations. In addition, it should be an inexpensive material that is readily available on the industrial scale. Considering these conditions, researchers searched for a strong Bronsted acid with an increased hydrophobicity and high thermal stability up to 250 °C. Hydrophobic catalyst surfaces are preferable in biodiesel production to avoid the covering of the solid acid surface with water [6,17].

Zeolites are among the different types of inorganic solids that have been employed as catalysts for the production of biodiesel. Since zeolites can be synthesized with variation of acidic and textural properties, it is possible to use zeolite catalyst in the biodiesel production. Recently mesoporous zeolites have shown promising results in biodiesel production using vegetable oil with high content of free fatty acids [18]. Noiroj *et al.* [19] reported the use of KOH/Na-Y zeolite catalysts to achieve a biodiesel yield of 91% conversion to

methyl esters in 8 hours at 66 °C. Microporous zeolites which have very small pore are not suitable for transesterification reaction of triglycerides because of the diffusion limitation of reactants inside micropores.

It appears that solid superacids are very useful catalyst in the biodiesel production. Sulfated zirconia and tungstated zirconia are typical examples of those superacids which show high catalytic performances. Furuta *et al.* [20] used tungstated zirconia-alumina, sulphated zirconia-alumina and sulphated tin oxide for their research on biodiesel conversion. The operation was conducted at 300 °C and the conversion yield was at 94 %, 77 % and 70 % for soybean transesterification using tungstated zirconia-alumina, sulphated zirconia-alumina and sulphated tin oxide respectively. They also reported the conversion of 94 %, 99 % and 100 % at operation temperature of 175 °C for the esterification of *n*-octanoic acid (a representation of FFA) by using tungstated zirconia-alumina, sulphated zirconia-alumina and sulphated tin oxide respectively.

It was mentioned by Furuta *et al.* [21] that the catalytic effect for the esterification reaction is important for the production of biodiesel fuel due to the existence of free fatty acid in the low quality oil. Thus, the esterification of *n*-octanoic acid with methanol to methyl *n*-octanoate was carried out in the same manner as that of the transesterification of soybean oil. Tungstated zirconia-alumina, sulfated tin oxide and sulfated zirconia-alumina have shown high catalytic activities at temperature over 175 °C with no by-product detected. Furuta *et al.* [21] also reported that tungstated zirconia-alumina is a promising catalyst for the production of biodiesel fuels due to its superior catalytic activity for both transesterification and esterification.

Another important group of strongly solid acid catalysts used in biodiesel production through transesterification of triglycerides is that formed by supported heteropolyacids. Kulkarni *et al.* [23] reported that high catalytic activity in the transesterification of canola oil containing 10% of FFA was achieved by using immobilization of Keggin-type heteropolyacids (HPA) on different supports such as hydrous zirconia, silica, alumina and activated carbon. Biodiesel was also produced through simultaneous esterification and transesterification of a mixture of vegetable oil and free fatty acid with ethanol using heteropolyacids supported on diverse oxides.

Katada *et al.* [24] reported that a heteropoly acid-derived solid acid catalyst has shown higher catalytic activities for transesterification between triolein and ethanol as compared to the activities of

conventional solid acid catalysts. The performance of the catalyst was sensitive to calcinations temperature and calcination temperature of about 500 °C provided a highly active catalyst.

4. Potential of the Solid Acid Catalyst

There are numerous publications on solid base-catalyzed transesterification with regards to their properties and catalytic activities. The solid base catalysts have shown high catalytic performance on high quality vegetable oils. On the contrary, poor catalytic performance is observed for low quality vegetable oils due to the presence of significant amounts of free fatty acids, which results in soap formation. An alternative way of processing these low quality vegetable oils is by using an acid catalyst. The drawback is that homogeneous acids such as hydrochloric acid and sulfuric acid need longer reaction time and may pose corrosion problem to the equipment. Table 3 lists some of research findings on biodiesel conversion using different solid acid catalyst. Findings show that acid-catalysed reaction needs high temperature and longer time for high yield of conversion.

Table 2. Typical solid acid and base catalysts employed for transesterification [31]

Solid acid catalysts	Solid base catalysts
Sulphonic ion exchanged resin	Hydrotalcites (Mg-Al)
Amberlyst -15	Cs-exchanged sepiolite
Nafion	Oxides like MgO, CaO, La ₂ O ₃ , ZnO
Unstated Zirconia-alumina	Quanidine anchored cellulose/polymer
Sulphated tin oxide	NN'N" tricyclohexyl guanidine
Sulphated zirconia/alumina	encapsulated in Y zeolite
Zeolites (H-Y) H-Beta, H-ZSM-5, ETS-4,10	MCM family
Heteropoly acids	Metal salts of amino acids
H ₃ PW ₁₂ O ₄₀ , H ₄ SiW ₁₂ O ₄₀	CaCO ₃ , Ba(OH) ₂
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	Cs exchanged faujasites
Zinc acetate on silica	Li-promoted CaO
Organosulphonic acid on mesoporous silica	KxX/Al ₂ O ₃ (X- halide ion or other mono/di-valent anion)
Mesoporous unstated zirconium phosphate	Zinc aluminates

5. Effect of Operating Conditions on the Biodiesel Production

5.1. Temperature of Reaction

The rate of reaction is strongly influenced by the reaction temperature. Generally, the reaction is conducted at 65 °C and at atmospheric pressure. Transesterification can occur at different temperatures, depending on the oil used. Marchetti *et al.* [32] studied the effect of varying operating temperature on product yield using solid catalyst. The chosen reaction temperature was at T = 30 °C, 45 °C and 55 °C. It was found that increasing the operating temperature resulted in a rise in final conversion. Higher reaction rate is obtained at

Table 3. Lists of research findings on biodiesel production with different solid acid catalysts

Solid Catalysts	Conversion (%)	Reaction Condition (°C)	Reaction Time (h)	Ref.
Sulfated tin oxide	100			
Sulfated zirconia-alumina	99	175 °C	20	[21]
Zirconia-alumina	94			
Zinc oxide (ZnO)	83			
Hβ – zeolite	59	120 °C	24	[22]
Montmorillonite K-10	47			
Sulfated zirconia	90.3			
Sulfated stannous oxide	90.2	200 °C	4	[25]
Zinc oxide	86.1			
KNO ₃ /ZrO ₂	74.4			
KNO ₃ /KL zeolite	71.4			
Zirconia oxide	64.5			
Fe-Co ⁻¹	32.8	170 °C	8	[26]
Fe-Zn ⁻¹	98.3			
Tungstated zirconia-alumina	90			
Titanium zirconia	83	250 °C	20	[27]
Aluminium zirconia	80			
NaX zeolite (Si/Al = 1.23), loaded with 10% KOH	85.6	65 °C	8	[28]
Sulfonated carbon	90	80 °C	12	[29]
Cesium exchanged tungstophosphoric acid	92	65 °C	3	[30]

higher temperature, but operating the reaction close to methanol's boiling point could potentially lead to the formation of bubbles which in turn preventing the reaction on the three-phase interface (solid catalyst – oil – alcohol). Liu *et al.* [33] claimed that the optimum reaction temperature was obtained at 65 °C when using CaO as a solid catalyst. Similar finding was reported by Encinar *et al.* [34] in their study of trans-esterification reaction of triglycerides with methanol using KNO₃/CaO catalyst.

5.2. Ratio of Alcohol to Oil

One of the most important variables affecting the yield biodiesel is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for the transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess alcohol is required to drive the reaction to the right. However, too high molar ratio of alcohol to vegetable oil causes an increase in the solubility of glycerol in methyl ester layer which makes the separation process difficult [35]. When glycerol remains in solution, it helps drive the equilibrium back to the left, lowering the yield of esters. Encinar *et al.* [34] conducted test runs based on different molar ratios of alcohol to vegetable oils using KNO₃/CaO catalyst, namely; with different methanol/oil molar ratio of 6:1, 9:1 and 12:1. Higher methanol/oil molar ratio requires longer time for conversion. They claimed that the optimum methanol/oil molar ratio for the reaction is 6:1.

5.3. Mixing Intensity

In the transesterification reaction, mixing is very important since the reactants initially are a three-phase system. The reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate of reaction. Once the three phases are mixed and the reaction has started, stirring is no longer needed since methyl ester acts as a mutual solvent for the reactants [36]. Similarly Encinar *et al.* [34] reported that once the methyl ester is formed, they act as a mutual solvent for the reactants and eventually forming a single-phase system. The mixing effect is significant during the slow reaction rate region and the increase in mixing rate improves the mass transfer in the surface of the solid catalyst. As the single phase is established, mixing becomes insignificant. The understanding of the mixing effect on the kinetics of the transesterification

process is important for the process scale-up design.

5.4. Reaction Time

The conversion of biodiesel increases with reaction time. Kim *et al.* [16] studied the biodiesel conversion yield using homogeneous catalyst (NaOH) and heterogeneous catalyst (Na/NaOH/ γ -Al₂O₃) with respect to their reaction time. The maximum biodiesel production was achieved within 1 hour of operation for both homogeneous and heterogeneous catalyst systems. However, the biodiesel yield for the homogeneous catalyst system was 20 % higher than that of the heterogeneous catalyst system. Xie and Li [28] studied the effect of reaction time on the product yield in the presence of 35 wt% KI/Al₂O₃ catalyst. The reaction time was varied from 1 to 10 hours. The experiment results showed that the conversion increased steadily at reaction time of 4 to 8 hours, and then remained nearly constant thereafter. The maximum conversion of 90 % of soybean oil was achieved after 8 hours [28].

5.5. Ratio of catalyst to oil

Biodiesel production can be affected by the amount of catalyst used in the reactions. For homogenous catalyst, biodiesel production is carried out using approximately 1 wt% catalyst. However, for heterogeneous catalyst the amount of catalyst used is depend on the type of solid catalyst. Liu *et al.* [37] studied the conversion of soybean oil to biodiesel using CaO as a solid catalyst. Biodiesel yield (95 %) was obtained when reaction was carried out for 3h using 8 wt% catalyst concentration. Garcia *et al.* [38] carried out a study using sulfated zirconia with catalyst concentration ranging from 2-5 wt%. They reported the highest conversion was achieved if 5wt% catalyst was used.

6. Conclusions

Several solid catalysts have been investigated for biodiesel synthesis but their uses have been limited to reasons associated with their reaction rates, unfavorable side reactions and leaching problem. Some solid catalyst has both acid and base property, thus enable to catalyze both esterification and transesterification reactions simultaneously. Further research and improvements are continuously being made for these catalysts in areas related to the stability of active sites, thermal stability and enhancement of mass transfer mechanisms. Studies are looking into improving the resistance to water impurities usually present in unrefined or low quality

feedstock. It is expected that homogeneous catalysts will be replaced by solid catalysts mainly due to environmental and economic reasons.

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