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# Current advances in catalysis toward sustainable biodiesel production

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ABSTRACT

Transesterification of vegetable oil/animal fat catalyzed by acid/base catalysts has been widely performed for biodiesel production and the utilization of catalysts directly affects the yield and quality of biodiesel. Based on the up-to-date literatures, the recent applications of various catalysts in biodiesel production processes are described in this work and the popular liquid acid/base catalysts used in biodiesel industry are discussed as well. However, the solid acid/base catalysts with advantages of easy separation and less waste are paid more attention on. Although the biodiesel production process carried out with heterogeneous catalysts is an alternative, the relatively low activity limits their applications in the industry compared to liquid catalysts. To better understand the formation of active sites and develop novel catalysts for the development of biorefinery, the structural properties of various solid catalysts are described since the catalytic properties of solid acid/base catalysts vary from their structures.



## 1. Introduction

Majority of the world transportation fuel requirements are supplied through petrochemical sources which are non-sustainable, depleting rapidly and causing environmental pollution. Moreover, energy requirements only for transportation are expected to increase by 2% every year. Therefore, it is estimated that the energy requirements in 2030 will be 80% higher than that of 2010 which will subsequently increase the greenhouse gas emission level [1]. Currently, sustainable energy management has attracted interest in both developed and developing countries. In such a situation, biofuels emerge as potential candidates to replace petroleum based fuels. Predictions indicate that by 2030, 7% of world transport fuels will come from renewable sources, like biofuels. Brazil has the highest penetration of biofuels (21% in 2010, rising to 39% by 2030), while the U.S. leads the Organization for Economic Co-operation and Development (OECD) in incentivizing biofuels (4% in 2010, rising to 15% by 2030). Biofuels will meet more than half of the incremental demand for alternative fuels in transportation in the future [2].

Four types of alternative fuels, such as pure vegetable oils, biodiesel, Fischer–Tropsch diesel, and dimethyl ether can be used in conventional compress ignition (CI) engines [3]. Since the beginning of 1900s, Rudolf Diesel tested the utilization of pure vegetable oil in his first compression type internal combustion engine [4]. However, the direct utilization of vegetable oil in diesel engines was problematic due to (a) high viscosity of oils, (b) high molecular weight of triacylglycerols resulted in incomplete combustion due to low volatility, (c) polymerization of unsaturated fatty acids, (d) formation of carbon deposits due to incomplete combustion [5]. To overcome these problems, several physical and chemical modifications, such as pyrolysis, microemulsification, dilution and transesterification, were investigated for vegetable oils. The later was found as more efficient in reducing the viscosity of vegetable oils and the resulting product of the reaction was termed as biodiesel [6].

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Biodiesel is a kind of renewable, biodegradable and sustainable fuel derived from vegetable oil or animal fats. It is usually produced through transesterification reaction by reacting long chain fatty acids with short chain alcohols (like methanol and ethanol) in the presence of catalysts resulting in a mixture of long chain alkyl esters and a byproduct glycerol, the reaction equation of which is shown in Fig. 1 [7].

Biodiesel has lower sulfur content and nearly neutral with respect to carbon dioxide emissions [8,9]. In addition, the utilization of biodiesel can reduce the emission of exhaust gases like carbon monoxide and unburned hydrocarbons compared with diesel fuel [10]. Furthermore, the production of biodiesel reduces dependence of a country on imported crude petroleum oil and thus helps to maintain the price of the fuel market. Due to the property of easily scaling up and growing market for renewable energy, the biodiesel production around the world has increased in the recent decades (shown in Fig. 2) [11]. In 2008, biodiesel production was increased so much that the share of biodiesel in diesel fuel was about 1.5% because of the rapid fluctuation of petroleum prices. European Union was the major producer of biodiesel, producing nearly 60% of the world biodiesel production [12].

In spite of all these benefits associated with biodiesel production in a commercial scale, the cost of biodiesel production is higher compared with petroleum based diesel. The major costs are due to feedstock used in the process (vegetable oil), alcohol (usually methanol), catalyst and operating costs [13]. Therefore, for making biodiesel more sustainable and economical, the major areas of research revolve around the (1) improvement in currently available feedstock resources, (2) development of advanced and efficient biodiesel technologies, (3) and socioeconomic benefits [14]. The major cost comes from the source of feedstock [15]. From this perspective, efforts have been made to improve the availability and quality of feedstock resources for biodiesel production [16,17]. There are a vast majority of feedstock resources for biodiesel production like vegetable oil (both edible and non-edible), animal fats (lard or beef tallow), trap grease (restaurant grease traps), etc. Majority of the biodiesel producers use edible vegetable oil resources which vary from country to country depending upon their economical and climatic conditions. Soybean, rape seed, canola and sunflower are used for biodiesel production in the USA, Germany, Canada, Argentina and Brazil. China is the major biodiesel producer from waste cooking oil, while India is producing biodiesel from non-edible Jatropha seed oil [18].

The biodiesel production process which always requires a high conversion rate and product selectivity is directly affected by the type and amount of catalysts utilized, and which further influences the cost of biodiesel production process [19]. Therefore, the catalysis process in biodiesel production has been extensively studied. A various range of homogeneous and heterogeneous catalysts, such as acid, base and biocatalysts have been studied for biodiesel production. Both of the catalyst types have their own advantages and disadvantages. Among many homogeneous reactions, liquid catalysts showed high activity in biodiesel production process. However, the separation of biodiesel products from reaction solutions results in a higher cost, which is a serious challenge. From the green chemical process perspective, more and more solid acid and base catalysts have been utilized in the biodiesel production process. A brief description for homogeneous catalysis and more details for heterogeneous catalysis processes were displayed in this review.

## 2. Homogeneous catalysts

Transesterification is one kind of acid or base catalyzed intermolecular reaction. Liquid mineral acid and base have been firstly used for the production of liquid biodiesel.

### 2.1. Homogeneous acid catalysts

The most widely accepted and applied theories of acid are Brønsted–Lowry theory [20] and Lewis theory [21]. According to Brønsted and Lowry [20,22,23], an acid is a molecule or ion that is able to lose, or "donate", a proton ($H^+$), while with respect to Lewis [21–23], an acid substance is one which can employ an electron lone pair from another molecule in completing the stable group of one of its own atoms.

Acid catalysts are more suitable for biodiesel production from waste vegetable oil due to the fact that the waste vegetable oil has a great number of free fatty acids. In transesterification reactions carried out with homogeneous acid catalysts, there are two reagents, like alcohol and a free acid (FFA), reacting to form an ester as the product of reaction. Therefore, acid catalysts were preferred in cases when FFA content of vegetable oil is greater than 1 wt% [24,25].

The most commonly used homogeneous acid catalysts in biodiesel production process include HCl, $BF_3$, $H_2SO_4$, $H_3PO_4$ and $FeSO_4$ [26–29]. According to Bhatti et al. [30], biodiesel production from the transesterification of animal fats (dairy cow and beef) was carried out with homogeneous acid catalysts under varying experimental conditions, such as different catalyst amount, catalyst nature, reaction time and temperature. The maximum biodiesel yields were 94.1 ± 2.43 and 98.4 ± 2.3% for dairy cow and beef tallow, respectively. The optimum conditions for biodiesel production with homogeneous acid catalysts were: 2.5 g of concentrated (conc.) $H_2SO_4$, 24 h of reaction time and 50 °C for dairy cow fat and 2.5 g of conc. $H_2SO_4$, 6 h of reaction time and 60 °C for beef fat. Based on the research work of Chongkhong et al. [27], production of fatty acid methyl ester (FAME) from palm fatty acid distillate (PFAD) which contains high free fatty acids (FFA) was investigated. Batch esterifications of PFAD were carried out to study the influence of reaction variables including reaction temperatures of

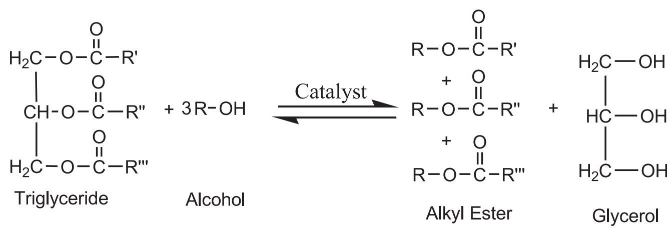


**Fig. 1.** Transesterification reaction.
Adapted from Puna et al. [7].