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# A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production

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ABSTRACT

Biodiesel production is commonly carried out through the process of transesterification reaction. The reaction is expedited with a suitable catalyst either homogeneous or heterogeneous. The selection of an appropriate catalyst depends on the amount of free fatty acids in the oil. Recently, homogeneous catalysts are widely chosen for biodiesel production in large scale operation. However, they are toxic, highly flammable and corrosive in nature.

Furthermore, the use of homogeneous catalyst produced soaps as by-product and large amount of wastewater that required additional processing technologies and cost for proper disposal. On the contrary, heterogeneous catalysts are capable to overcome the problems faced by the former ones. However, they were mostly derived from non-renewable resources, highly expensive with low stability. Recently, heterogeneous catalysts derived from biological waste have gotten more attention. This type of catalysts offers several advantages, including renewable resources, non-toxic, reusable, high catalytic activity, stability in both acidic and basic conditions and high water tolerance properties, which depend on the amount and strengths of active acid or basic sites. Basic catalyst can be subdivided based on the type of metal oxides and their derivatives. Similarly, acidic catalyst can be subdivided depending upon their active acidic sites. In this article, efforts have been taken to review the bio-based heterogeneous catalyst utilized for sustainable biodiesel production and their suitability for industrial application. Catalyst generated from bio-waste and other biocatalysts, which are heterogeneous in nature and extensively reported in literature are also reviewed. The utilization of these biomass derived catalysts provides a greener synthesis route for biodiesel production.

## 1. Introduction

Nowadays, biofuel such as biodiesel and bioethanol has become a great interest to be the alternative source of energy as opposed to the conventional fossil fuel. The detrimental effect of global warming, rising numbers of environmental related problems, depletion of fossil fuel resources become the main factors that contribute to the global transformation in the development of biodiesel [1–4]. The used of biodiesel as a source of fuel offers several advantages, including renewable and sustainable resources, non-toxic, environmental friendly where it reduces the emission of $CO_2$, and hazardous compound namely arithmetic, sulfur, particulate matter and $NO_x$ [1–5]. The application of biodiesel showed a reduction in the net carbon dioxide emissions on a life cycle basis, carbon monoxide, particulate matter and unburned hydrocarbons by 78, 46.7, 66.7 and 45.2%, respectively [6]. Hence, the use of biodiesel will significantly reduce the effect of global warming. On top of that, biodiesel can be directly used in the engine or with little modification, blended with regular petroleum-based diesel at any ratio without losing the engine performance [2]. In addition, no sulfur content in biodiesel provides greater lubricity than conventional diesel fuel, thus improves the durability of the engine [7]. Generally, biodiesel displays good oil qualities, including higher cetane number, higher combustion efficiency, and less emission [8–10].

Biodiesel or chemically known as fatty acid methyl ester (FAME) can be derived from the chemical reaction of feedstock either vegetable oils or animal fats and alcohol with or without the presence of a catalyst. Several types of oil have been studied for the biodiesel

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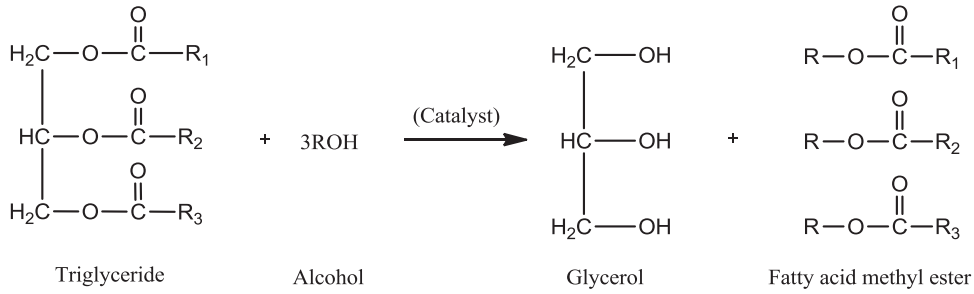


**Fig. 1.** General transesterification reaction scheme.

production, including the first generation fuels which can be categorized as edible oil including palm oil [11,12], sunflower oil [13,14] and soybean oil [15,16]. The second generation fuels component of the non-edible oil including Jatropha curcas seed oil [17,18], neem oil [19,20], castor oil [21] and waste cooking oil [22,23]. Lastly, the third generation fuel comprises of microalgae-based oil [24–26]. Apart from oil, biodiesel can also be derived from spending bleaching clay, a waste from an edible oil refinery process [27].

At the present time, there are several methods for producing biodiesel, including direct use and blending of raw oils, dilution, microemulsion, thermal cracking or pyrolysis and transesterification [28]. Among all, transesterification is the easiest and most cost effective approach to produce biodiesel [29–31]. Transesterification or alcoholysis can be defined as a reaction of fats or oils with an alcohol in the presence of a catalyst to form fatty acid methyl ester and glycerol [32–34]. The general transesterification routes for biodiesel production are as illustrated in Fig. 1. Several types of alcohol can be used, including methanol, ethanol, butanol and amyl alcohol. However, methanol is widely used since it is cheaper, short chain alcohol, quickly reacted and easily dissolved into the reaction medium.

The catalyst for transesterification reaction can be either alkali or acid or enzyme. Table 1 summarizes the advantages and disadvantages of each type of catalyst. The enzymatic transesterification is considered to be the most effective method for biodiesel production [35,36]. However, the cost catalyst is extremely high and the reaction rate is too slow, hence retards broader application [1,9]. Currently, homogeneous base catalysts have been widely chosen in industrial scale for biodiesel production [7]. A homogeneous base catalyst such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) offer several advantages, including high catalytic activities [37,38], shorter reaction time [39], modest operating conditions [1], raw materials are extremely cheap and abundantly available [31,32]. However, the homogeneous base catalyst reaction is highly sensitive to the presence of free fatty acids (FFA) and water. Moreover, the formation of soaps as a result of side reaction of neutralization and saponification will deter the separation and purification process, produced a large volume of wastewater and incur an additional cost of operation. This requirement makes this catalyst environmentally unfriendly [29,31,39].

On the contrary, a homogeneous acid catalyst such as sulphuric acid ($H_2SO_4$), hydrochloric acid (HCl) and phosphoric acid ($H_3PO_4$) are suitable for feedstock with high FFA content such as waste cooking oil, crude vegetable oils and animal fats. It significant advantages over the former one includes the insensitivity to the presence of FFA and water, ability to catalyze both transesterification and esterification reactions and no formation of soap by-products [6,29,31]. However, slow reaction time becomes the major factor that retards the wide application of this catalyst [32,39]. It has been reported that the conversion rate of acid-catalyzed transesterification is about 4000 times slower than that of base catalyst [6,31]. Apart from that, homogeneous acid catalysts are highly acidic and corrosives in nature [31,40]. Product separation and purification in homogeneous operation required a number of steps, produce a large amount of wastewater and contribute to the increase in the operational cost [41]. In addition, recovery and regeneration of homogeneous catalyst are difficult, not feasible, require more processing steps and extremely expensive [42].

The application of heterogeneous or solid catalyst has gained interest in the biodiesel production. The catalysts are neither consumed nor dissolved in the reaction mixture which made it easier to be separated from the product in the later [41]. On top of that, the recovered catalyst can be reused back in the reaction, hence reducing the catalyst consumption and cost associated [3]. The heterogeneous-based operation offers several benefits including noncorrosive, easy separation and longer catalyst life [31,32,39]. Numbers of catalysts are available in the market for basic-catalyzed reaction, which includes metal oxide, mixed oxide and hydrotalcite [43]. On the other hand, transition metal oxide, ion exchange resin, carbon-based catalyst, and zeolites are among the catalysts available for acidic operation [44]. However, the presence of three-phase system in a heterogeneous system will lead to diffusion problem that will inhibit the reaction [1]. Three phases of solid catalyst-alcohol-oil that is highly immiscible limit the mass transfer efficiency, thus lowering the rate of reaction [29,45]. Moreover, Sani et al. [42] stated that mass transfer efficiency is limited within a bulky molecule hence resulted in the poor conversion into biodiesel. Additional problems faced by solid catalyst are a low number of active sites, micro porosity, leaching, toxic, expensive, derived from non-renewable resources and environmentally unfriendly [40,46,47]. Hence, in order to produce an excellent solid acid catalyst, the catalyst must comprise of more specific surface area (hydrophobicity, external catalytic sites, etc.) and a large pore diameter [45].

Bio-based or 'green' catalyst is a term referring to a type of catalyst derived from natural sources such as biomass. The current trend shows that application of the natural biological source of calcium and carbon becomes a potential heterogeneous catalyst for transesterification of vegetable oil. This application is a promising method since it can produce a highly efficient bio-based heterogeneous catalyst. The solid catalysts prepared from biomass presents an environmental friendly solution since it is non-toxic, non-corrosive and eliminate the production of wastewater [40]. On top of that, it is mainly derived from biomass that is considered as a low-cost material and abundantly available [48]. Apart from that, there is no imminent disposal problem since the catalyst itself is biodegradable [49]. The present study reviews the development of heterogeneous base and an acid catalyst derived from biomass for biodiesel production. The source of catalyst, methods of preparation and performance of these catalysts is presented in this study. This paper aims to provide useful and informative knowledge on the current biomass-derived heterogeneous catalyst for future development in the field of biodiesel process and production.

## 2. Biomass-derived heterogeneous alkali/base catalyst

### 2.1. Sources of catalyst

#### 2.1.1. Waste shell

The application of solid base catalyst in biodiesel production is advantageous since it can be easily separated and further reused back in the process. However, the extremely high price of the available

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