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Modern heterogeneous catalysts for biodiesel production: A comprehensive review

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ABSTRACT

Steep hikes of petroleum prices and rising demand of petroleum products compels the scientific society to think for the renewable alternative fuels like biodiesel. Biodiesel production is generally carried out through the process of transesterification reaction. The reaction is facilitated with a suitable catalyst either homogeneous or heterogeneous. The selection of appropriate catalyst depends on the amount of free fatty acids in the oil. Heterogeneous catalyst provides high activity, high selectivity, high water tolerance properties and these properties 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. New varieties of mixed catalyst are also available in literatures. Catalyst generated from bio-waste and other biocatalysts which are heterogeneous in nature and extensively reported in literature are also reviewed. This review focused about the recent invention and use of the heterogeneous acid, base and biocatalysts for biodiesel production and their suitability for industrial application.

Contents

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1. Introduction

At present the focus of the human society is to produce energy from low carbon sources and introduction of eco-friendly Green Technology. Biodiesel, the alternative renewable liquid fuel, derived from triglycerides holds promise to compensate the increase demand of petroleum diesel [1]. The process of transesterification of triglyceride with methanol, ethanol or any other suitable alcohol produces biodiesel [2–4].

Transesterification, also called alcoholysis, is the reaction of an oil or fat with an alcohol to form esters and glycerol. The basic reaction is depicted in Fig. 1. Transesterification consists of three consecutive reversible reactions viz.; conversion of triglyceride to diglyceride, diglyceride to mono glyceride and monoglyceride to fatty ester and glycerol [5]. The reaction is facilitated with a suitable catalyst [6]. If the catalyst remains in the same (liquid) phase to that of the reactants during transesterification, it is homogeneous catalytic transesterification. On the other hand, if the catalyst remains in different phase (i.e. solid, immiscible liquid or gaseous) to that of the reactants the process is called heterogeneous catalytic transesterification [7,8]. The heterogeneous catalytic transesterification is included under Green Technology due to the following attributes: (1) the catalyst can be recycled (reused), (2) there is no or very less amount of waste water produced during the process and (3) separation of biodiesel from glycerol is much easier [9,10]. During homogeneous catalytic transesterification the glycerol produced is of low quality and requires lengthy process and distillation for purification [11–14]. All these processing increases the cost of the end products: biodiesel and glycerin. Moreover, the homogeneous base catalyzed transesterification process encountered problems to handle multiple feed stocks. On the other hand, heterogeneous catalytic transesterification process overcomes these problems because methanol or ethanol does not mix with solid heterogeneous catalyst. After the transesterification reaction it is relatively easy to separate the catalyst from biodiesel and glycerol.

Oils (non-edible) with higher fatty acid content lead to the formation of soap, consequent loss of oil and problems of product separation during homogeneous catalytic transesterification [15,16]. The major drawback of the homogeneous catalyst (NaOH, KOH) is found for its hygroscopic nature, hazardous for the environment as compared to heterogeneous catalyst. The use of enzyme catalytic production of biodiesel has attracted much attention in recent years because enzymes tolerate free fatty acid and water contents, facilitating easy purification of biodiesel and glycerol. However, enzymatic transesterification could not be commercialized for production of biodiesel due to long residence time and high cost [17–19]. Heterogeneous catalyst converts triglycerides into biodiesel slowly but produced biodiesel in a very feasible economic way due to the reusability of catalyst for both the processes, e.g. batch and continuous [20–22].

Dossin et al. [23] demonstrated the first heterogeneous catalytic transesterification pilot plant using MgO as catalyst, triolin and methanol as feedstock with a production capacity 1,00,000 tonnes per year. An ideal solid catalyst (heterogeneous catalyst) favors the following steps such as large pore size to minimize diffusion problems [24,25]. High concentrations of acid sites, high catalytic stability against leaching and poisoning effects and the possibilities to tune the hydrophobicity of the surface to promote the preferential adsorption of substrates and repulsion of highly polar compounds which could cause deactivation [26]. On the basis of the reported literature catalysts can be generally classified into homogeneous, heterogeneous and biocatalyst [1,7–9,27–36] which are listed under in the flow chart (Fig. 2), including their subclassification. Table 1 presented below summarizes the reported work in the last 5-year and their brief inclusions in the review articles [1,7–10,29–31,33,35,37,38].

A large numbers of heterogeneous catalysts such as alkali metal oxides and derivatives [39–43], alkaline earth metal oxides and derivatives [42,44–51], transition metal oxides and derivatives [52–55], mixed metal oxides and derivatives [3,57–68], ion exchange resins type acid heterogeneous catalyst [21,69–73], sulfated oxides as a acid heterogeneous catalyst [22,70–84], carbon based heterogeneous catalysts [85–87], boron group base heterogeneous catalyst [3,57,58,60–65,67,68] waste material based heterogeneous catalysts [88–92], enzyme based heterogeneous catalyst [93–95] are found in literatures in the recent years and their uses in laboratory scale biodiesel production. All the efforts have been made to include recent literature so as to select suitable catalyst for industrial applications. The authors emphasize the catalytic activity, selectivity, catalyst loading, catalyst reusability and the summary for future prospects through classical and graphical representations.

2. Base heterogeneous catalyst

A general divalent metal oxide catalyst having substantial amount of covalent character facilitates the transesterification reaction as depicted in Fig. 3.

Some of the commonly used heterogeneous base catalyst are K/γ-Al_2O_3 catalyst [96], $HTiO_2$ hydrotalcite catalyst [97], Ca and Zn mixed oxide [98], Al_2O_3 supported CaO and MgO catalysts [3], alkaline earth metal oxides [47], KF/Ca–Al [99], basic zeolites, alkali metal loaded alumina [100]. A process flow diagram for biodiesel production using heterogeneous base catalyst has been depicted in Fig. 4.

2.1. Biodiesel production with alkaline earth metal oxides and derivatives

2.1.1. MgO as a base heterogeneous catalyst

Alkaline earth metals such as Be, Mg, Ca, Sr, Ba and Ra, their oxides and derivatives are used by different researchers. MgO and SrO are widely used among the other alkaline earth metals, which are having good heterogeneous nature as catalyst [8,23,42,44–51].

Lopez et al. [44] used MgO as a catalyst with calcinations temperature 600 °C and found 18% conversion of the feedstock, triacetin after 8 h of reaction time; the reason is attributed to the low surface area of the catalyst. Very recently, MgO has shown to possess catalytic activity for synthesis of biodiesel. Di Serio et al. [46,101] observed 92% biodiesel yield with MgO catalyst, using 12:1 methanol to oil molar ratio with 5.0 wt.% of the catalyst in 1 h. Dossin et al. [23] studied that MgO worked efficiently in batch reactor at ambient temperature during the transesterification reaction with a production capacity 500 tonnes of biodiesel. Biodiesel production cost is reduced in batch reactor due to the use of ambient temperature. Tateno and Sasaki [45] and Di Serio et al. [46] investigated that MgO worked well in supercritical condithions during transesterification at 300 °C in a high methanol to oil molar ratio of 39.6:1, and reported 91% of FAME yield.

2.1.2. CaO as a base heterogeneous catalyst

Among the alkaline earth metal oxides CaO is most widely used as catalyst for transesterification and report says as high as 98% FAME yield is possible during the first cycle of reaction [102]. The reactivity of such CaO is further determined by its calcinations temperature. However, reusability of catalyst for subsequent steps prevail big question mark. Modification of CaO to organo metallic nature, e.g. $Ca(OCH_3)$, $Ca(C_3H_7O_3)_2$, however, found very effective with respect to reusability. The reported literature shows the biodiesel yield as high as ~93% even after 20 cycles of reactions. $Ca(C_3H_7O_3)_2/CaCO_3$ is also observed as an efficient heterogeneous catalyst with a reusability for 5 cycles and FAME yield as high as