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Review on latest developments in biodiesel production using carbon-based catalysts

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ABSTRACT

Catalyst plays an important role in biodiesel production. Owing to the advantages of heterogeneous catalysts in terms of separation and reusability over the traditionally used homogeneous catalyst, the research has now been focused on these heterogeneous catalysts in recent years. In order to make the process fully "green", researchers are trying to prepare catalysts from renewable sources such as biomass. Within this concept the carbon based catalysts have been introduced. Carbon based materials are considered as ideal catalysts due to desirable features such as low material cost, high surface area and thermal stability. They are easily prepared by functionalizing carbon surface with acids or bases; in other cases carbon material was reported to be used as a support. Additionally, the carbon could be produced from most of the waste generated in different industrial processes. Therefore, its utilization as catalyst makes the biodiesel production a "greener" one. Under optimal conditions biodiesel (FAME) yields up to 90–98.3% were reported over various carbon based catalysts.

Contents

1. Introduction

Due to the continuous decline of limited petroleum reserves and the growing environmental concerns, the use of biodiesel in recent years as a fuel in the existing diesel engines has gained much importance [1]. Current generation biodiesel production usually utilizes homogeneous transesterification of vegetable oils with strong alkali (NaOH, KOH) as catalysts [2]. The process has many limitations, a considerable amount of energy is required for the purification of products and catalyst separation, and furthermore these catalysts are not reusable. This results in substantial energy wastage and the production of large amounts of chemical waste. Strong acids such as H_2SO_4, HCl can also catalyze this reaction but at a much slower rate limiting their industrial applicability [3]. Enzymes such as lipase can also do the same but the process is not economically viable [4]. In order to overcome these issues researchers have utilized different heterogeneous catalysts (both acidic and basic) for transesterification.

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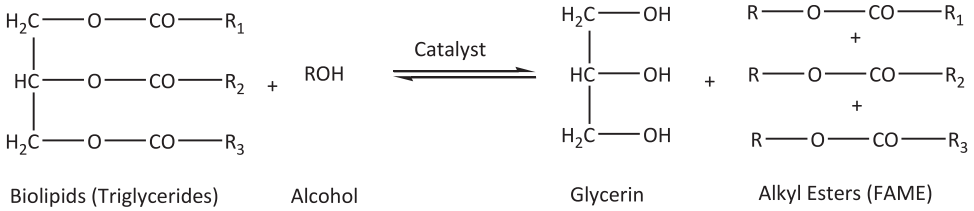
These catalysts can be readily separated from the products at the end of the reaction and reused for the next reaction cycle [5,6]. This has been demonstrated by different catalysts reported such as supported alkali metal catalysts [7], alkali and alkaline earth oxides, mixed metal oxides [5,8], dolomites perovskite-type catalysts and zeolites [9], heteropolyacids [10], Amberlyst-15 [11], $H_3PW_{12}O_{40} \cdot 6H_2O$ [12], WO_3/ZrO_2 [13], hydrotalcite and so on [14]. Ionic liquids have also been explored as catalysts in transesterification [15]. However, most of the ionic liquid catalysts reported so far utilized complex and expensive synthesis routes, demonstrated poor reusability and were non-biodegradable. Moreover, none of the catalysts were capable of showing activity comparable to alkali metal hydroxides. To address these issues, catalyst research for the production of cost effective biodiesel has been focused towards low cost renewable "green catalyst". Such a novel catalyst could be prepared either from biomass or from waste generated from it in the households. Recently renewable heterogeneous catalysts such as metal oxides catalysts derived from oyster shells [16], shrimp shell [17,18], eggshells [19,20] and carbon-based catalysts [21–23] have gained much importance owing to their low material costs which could significantly bring down the biodiesel production cost. Many review papers regarding biodiesel feedstocks, properties, characterization and the development of heterogeneous catalysts in biodiesel production have been published in recent years. In some of the review papers the reviewers have divided the heterogeneous catalysts into different categories such as oxides, mixed metal oxides, and zeolites. However, review on the carbon based catalyst has rarely been mentioned in most of the review papers. The focus of this review paper is to present the latest research on carbon based catalysts, specific outcome and its importance in environmentally benign biodiesel production.

1.1. Overview of biodiesel production by transesterification

Conventional biodiesel production is based on the transesterification of triglycerides and alcohols (Scheme 1). Transesterification is the general term used to describe the important class of organic reactions where one ester is transformed into another ester through interchange of the alkoxy moiety.

Transesterification is the easiest and the most cost effective way to produce biodiesel. The reaction can be catalyzed by an acid or a base, in principle transesterification proceeds most efficiently on base catalysts. The overall economy of biodiesel production depends mainly on two crucial factors: (i) feedstock and (ii) catalyst (determines the no of steps and synthesis route). Nearly all the biodiesel plants are currently using refined vegetable oils such as soybean, rapeseed, and cottonseed as main feedstock and contribute nearly 80% of the overall biodiesel production cost [24]. In order to overcome these limitations and ensure economic



Scheme 1. Biodiesel production by transesterification.

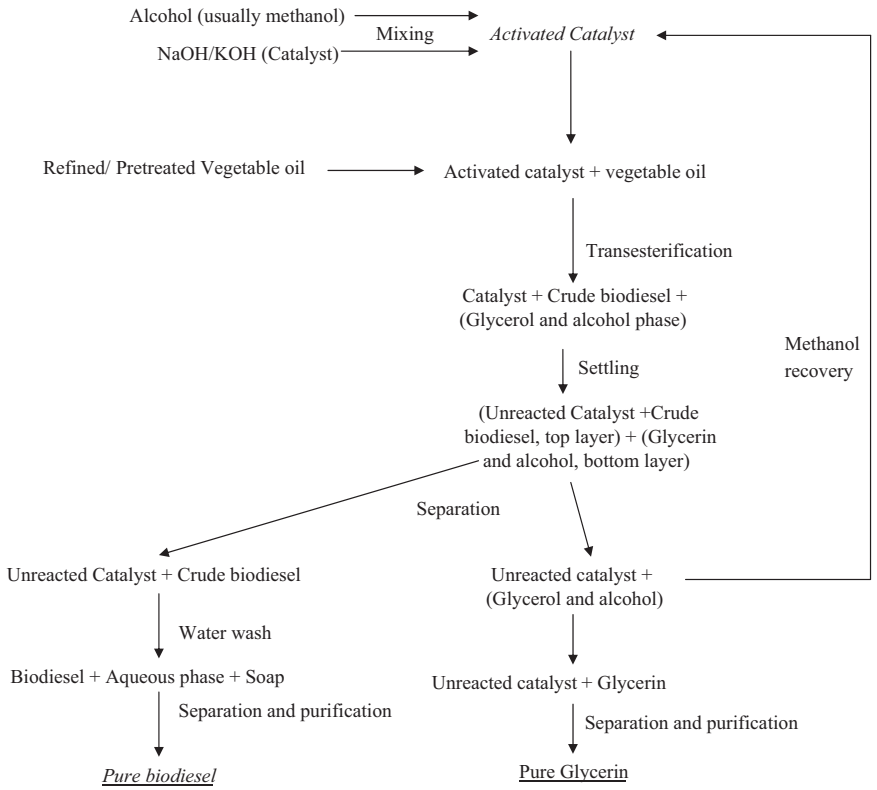


Fig. 1. Schematic block diagram of homogeneous biodiesel production.