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Review

Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review

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ABSTRACT

The conventional fossil fuel reserves are continually declining worldwide and therefore posing greater challenges to the future of the energy sources. Biofuel alternatives were found promising to replace the diminishing fossil fuels. However, conversion of edible vegetable oils to biodiesel using homogeneous acids and base catalysts is now considered as indefensible for the future particularly due to food versus fuel competition and other environmental problems related to catalyst system and feedstock. This review has discussed the progression in research and growth related to heterogeneous catalysts used for biodiesel production for low grade feedstocks. The heterogeneous base catalysts have revealed effective way to produce biodiesel, but it has the limitation of being sensitive to high free fatty acid (FFA) or low grade feedstocks. Alternatively, solid acid catalysts are capable of converting the low grade feedstocks to biodiesel in the presence of active acid sites. The paper presents a comprehensive review towards the investigation of solid acid catalyst performance on low grade feedstock, their category, properties, advantages, limitations and possible remedy to their drawbacks for biodiesel production.

Contents

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1. Introduction

Rapid population growth in developing countries worldwide, depletion of fossil fuel reserves and concern over environmental issues such as global warming, high energy demand globally for human activities such as transportation, production of goods and services as well as health problems associated with fossil fuel exhaust fronted the search for renewable energy sources alternatives to popular conventional fossil fuels [1]. The global economy is currently dependent on the transportation of goods and services [2,3] which depends entirely on petroleum source of energy. Apart from coal, nuclear power, natural gas and hydroelectricity, transportation sector is more than 90% dependent on fossil fuels with more than 60% annual worldwide fuel consumption [4,5].

Biofuels are generally alternative renewable sources of energy which are environmentally friendly due to its biodegradability and low emission of carbon monoxide, free sulfur and non-toxic nature [1,2,6,7]. Biodiesel was found promising alternative to popular fossil fuels, as it possesses all the properties of the conventional diesel such as high flash point and improved cetane number [6–9]. Although the global demand for biodiesel has been estimated to either double or triple globally by 2020 and beyond, relevant researches fully verified a number of factors that have not yet been critically addressed. Conversion of the triglycerides (major components of vegetable oil) to mono alkyl esters (biodiesel) requires a reaction of the former with monohydric alcohol. Various researchers have recommended lower monohydric alcohols (i.e. methanol to propanol), with no clear justification of which provides the best viscosity requirements in line with specifications by American Society of Testing and Materials (ASTM) or related international agencies [10–12]. Secondly, biodiesel is not yet considered as a popular alternative fuel worldwide due to its higher cost of production when compared with conventional petroleum diesel; hence, the central policy for biodiesel is not yet achieved [12,13]. The major problem in the commercialization of biodiesel is mainly due to the non-availability of raw materials, cost of production and most importantly viable solid acid catalysts that can perform simultaneous esterification and transesterification especially for low grade feedstocks. However, cheap low grade feedstock such as waste cooking oil, palm fatty acid distillate (PFAD) and animal fat, often contains large amount of high free fatty acid (FFA) [14,15]. The interaction of FFA with water in the alkali-catalysed process for producing biodiesel has limited the use of that recycled, inexpensive, low grade feedstock, or whatever may significantly reduce the costs of biodiesel.

According to West et al. [16] solid acid-catalysed process for biodiesel production is more efficient than homogeneous acid and alkali catalysis and supercritical processes. The study also emphasized it as having the least capital investment with the highest return on investment, through a technically simple process. Hence, numerous solid acid catalysts were developed to overcome the drawbacks of homogeneous catalysts currently used in the industries. The numerous problems identified with regard to catalytic biodiesel production stimulated researches at both the industry and academia to explore better options with greater emphasis on better catalyst system and flexible feedstocks.

2. Problems of currently used catalysts for biodiesel

Biodiesel was meant to alleviate the problems of high vehicular and other poisonous emissions such as green house gas (GHG) that causes both human health and environmental problems such as asthma and global warming respectively, high cost and imminent depletion of conventional fossil fuels [1,2,17]. Presently, biodiesel production focused on edible vegetable feedstock such as palm oil, rape seed oil, cotton oil, sun flower oil, and soybean oil. However, the high cost of feedstocks accounts for about 88% of total production cost of biodiesel. Moreover it is predicted that hike in the prices of edible vegetable oils coupled with hunger threats an soil degradation has forced many agencies, particularly food and agricultural organizations to consider the vegetable oil as non-reliable feedstock [3,18]. Non-edible based vegetable oils such as Jatropha oil, waste cooking oil and animal fats and micro algae oil that are affordable and readily available can serve as means of reducing biodiesel cost and are now considered as reliable feedstock for biodiesel production [7,19,20]. Generally edible vegetable oils (high grade) are easier to be converted into biodiesel due to its purity and low FFA content. The available edible vegetable oils that are used as feedstock for biodiesel production are sunflower oil, soybean oil, cotton oil, palm oil, etc. These oils contain less water content and FFA content <1% which is suitable for homogeneous catalysts [21].

Biodiesel can be produced by either esterification of FFA or transesterification of triglycerides (TGs) with short chain alcohol (usually methanol) as shown in Figs. 1 and 2, respectively [6,15,20,22].

Fatty acid methyl ester (FAME) is generally produced at industrial scale by using homogeneous catalysts such as NaOH, KOH and H_2SO_4. However, the process has many limitations, a considerable amount of energy is required for the purification of products and catalyst removal and furthermore these catalysts are not reusable [23,24]. Besides, the use of homogeneous acid and base catalysts will lead to unavoidable reactor corrosion and soap formation respectively when low grade oil containing water and high FFA is used. The water present in the feedstock will hydrolyse the TGs into new fatty acids and diglycerides [25]. This leads to the formation of stable emulsions and saponification and hence decreases the biodiesel yield [19]. Heterogeneous catalysts have significant advantages in catalytic transesterification of vegetable oils to produce biodiesel over homogeneous catalysts. Many different solid heterogeneous basic catalysts have been recently tested for biodiesel production showing promising results with recommendable biodiesel yields [20,26–29]. The activity of these catalysts is usually attributed to the presence of alkali or alkaline earth metals such as Ca, Na, Mg, and K, providing them with basic characteristics that enhance the active sites for these catalysts. Moreover, these catalysts are usually prepared in the form of millimetric spherical particles and nanostructured materials (nanocrystals or nanotubes) in order to increase their surface area as well as the catalytically active sites [30]. However, the major drawbacks of the aforementioned catalysts are soap formation, leaching of catalytic active sites in reaction medium during reaction, and high sensitivity to moisture and FFA (>1%). Low stability during storage in the presence of water and CO_2 is another disadvantage [1]. In order to use high FFA feedstocks in a single run process, there is

$$\underset{\text{(Fatty Acid)}}{RCOOH} + \underset{\text{(Methanol)}}{CH_3OH} \xrightleftharpoons{\text{Acid Catalyst}} \underset{\text{(Methyl Ester)}}{RCOOH_3} + \underset{\text{(Water)}}{H_2O}$$

Fig. 1. Esterification of fatty acid with methanol.

$$\underset{\text{(Triglyceride)}}{\begin{array}{l} CH_2\text{-}OOC\text{-}R' \\ | \\ CH\text{-}OOC\text{-}R'' \\ | \\ CH_2\text{-}OOC\text{-}R''' \end{array}} + \underset{\text{(Methanol)}}{3CH_3OH} \xrightleftharpoons{\text{Base Catalyst}} \underset{\text{(Methyl Ester)}}{\begin{array}{l} R'\text{-}COOCH_3 \\ | \\ R''\text{-}COOCH_3 \\ | \\ R'''\text{-}COOCH_3 \end{array}} + \underset{\text{(Glycerol)}}{\begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}}$$

Fig. 2. Transesterification of triglycerides with methanol.

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