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Review

An overview of the role of ionic liquids in biodiesel reactions

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ABSTRACT

The concerns on the depleting petroleum resources and increasing environmental problems have driven the scientific community worldwide to develop large-scale non-petroleum-based alternative fuels, such as bioethanol and biodiesel. Biodiesel produced through the transesterification of vegetable oils or animal fats are highly attractive. On the other hand, ionic liquids which possess properties that are more environmental friendly have found significant applications as solvents and catalysts for reaction and separation. It is also beginning to find its way in many of the chemical process applications and has attracted significant attention including biodiesel production. This paper provides a brief overview on the feasibility of applying ionic liquids in biodiesel production for the purpose of powering diesel engines for transportation and utility generation. The potential of applying ionic liquids as catalyst and solvent for enzymatic production of biodiesel from feedstock is particularly highlighted.
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1. Introduction

The need for renewable energy sources is becoming increasingly more important as the exploitation of petroleum resources increases over the years while its reserve declining at an alarming rate worldwide. Biodiesel has been known as one of the potential fuel substitutes derived from relatively cheap renewable biological sources (vegetable oils or animal fats) which can be used widely for powering diesel engines and utility systems [1]. Besides that, other biological source such as oleaginous microbial biomass has also been considered [2]. Earlier, the transesterification of unrefined oils has been performed by various researchers using catalysts

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such as sulfuric acid, hydrochloric acid, phosphoric acid, and organic sulfonic acid [3,4] which are considered as hazardous and non-green material.

As the pressure on using greener and less hazardous material mounting up, several more environmental benign materials and processes have been investigated. Among them is the use of enzymes especially lipase for transesterification of vegetable oils which have been significantly studied over the past decade or so. However, the developed processes such as the lipase-assisted methanolysis of vegetable oils to produce fatty acid methyl esters yielded poor conversion due to the well-known effect of lipase deactivation by methanol [5].

Recently ionic liquids (ILs) have been found to be a very useful medium that could assist and promote better reaction and separation for various type and combination of enzymes used for the biodiesel synthesis. The ILs, which is a new class of material, are relatively non-volatile compared to the organic solvents and their development has evolved tremendously over the years to become increasingly more suitable media for many enzymatic reactions [6]. ILs are considered to be unconventional but eco-friendly media widely considered in many emerging research area particularly during recent times [7].

Besides being non-volatile, the ILs have excellent chemical and thermal solubility which is also tuneable based on the combination of cation and anion used. For the biological reactions such as the biodiesel synthesis, the ILs are capable of dissolving a wide array of substrates and more importantly, increasing their stability over a longer period during the reaction [7–10]. Moreover, some of these properties can be fine-tuned by changing the cation or anion of the ionic liquids which has led to the ILs being termed as 'designer solvent'. The potential of IL as green solvents for biochemical conversion has been well-known [7]. The ionic liquids (ILs) offer an excellent media for many lipase-catalyzed esterification/transesterification reactions compared to the organic solvents wherein an increased in the activity and specificity of the lipase enzyme was observed [11–15]. Many recent studies [1,16–39] proved the ILs as more environmental friendly solvents and catalysts for biodiesel reactions and separation.

This study aims at reviewing the roles of ionic liquid in biodiesel production reaction. The effect of varying the cation and anion combinations and the acidity/basicity of the ionic liquid used as well as the reaction conditions will be discussed. In addition, the synergistic effects of the enzyme-based catalysis in ionic liquid will also be considered.

2. Biodiesel fuel

The quickly growing demand for energy which has led to higher depletion rate of fossil fuels reserve, coupled with the increasing global warming threat due to increase in greenhouse gasses emission have drawn significant attention globally. This has led to the impeccable need of finding renewable energy sources to ensure future sustainability [1,2]. Biodiesel fuel i.e., fatty acid methyl esters (FAMEs), is a renewable and environmentally friendly fuel. There are different varieties of processes and feedstock's from which the biodiesel can be synthesized such as castor beans, palm, palm kernel, olive, sesame, corn, linseed, soybean, canola, sunflower, peanuts, coconut, oilseed radish, cotton, sunflower, babassu, algae, jatropha, sea mango, polanga, pongamia, animal fat (butter, lard, tallow, grease and fish oil, etc.) and waste cooking oil [6].

The current major challenge in making the biodiesel production economically viable is the high price of the vegetable oils compared to the fossil based diesel fuel. As a result, in some countries, non-edible oils such as jatropha or waste cooking oil have been used as a feedstock for biodiesel production [40]. Exploring ways to reduce the high cost of biodiesel is of much interest in recent biodiesel research, especially for methods focusing on minimizing the raw material cost. Comparing the prices of biodiesel from the three different sources, palm biodiesel shows the cheapest price; this indicates that palm biodiesel has better economic potential than the other indicated oils. Among the four leading vegetable oils traded on the world market, CPO is much cheaper than canola, rapeseed or soybean [35]. In October 2008, the price of CPO was approximately half (55%) of the price of crude soybean oil [16] (Fig. 1).

Zhang et al. [1], and Leung and Guo [26] reported that the cost of raw materials accounted approximately between 70 and 95% of the total cost of biodiesel production. Haas et al. [33] estimated the cost of feedstock to be 88% of total biodiesel production cost for soybean oil. Thus other feedstocks options are being evaluated by several researchers, instead of the highly refined oil. Among others include crude vegetable oil and recycled waste feedstock as the acceptable ways to lower the biodiesel production cost [28,34].

The use of waste cooking oil instead of the virgin oil to produce biodiesel is an option also considered for reducing the raw material cost in view of its extensive availability besides significantly alleviating the problems associated with its waste handlings. Although there were reports on some of the waste cooking oil being used for soap preparation and as additive oil for fodder making, but most of it end up in landfills and rivers causing significant environmental pollution [41]. This has led most of the developed countries to set stringent policies on the safe disposal of waste oil through the drainage system.

In 2002, the EU has enforced a ban on the utilization of all waste oils as domestic animal feed which was seen as one of the effective method of disposing waste cooking oil then. This is because during the frying process, there were many harmful compounds formed and feeding the waste cooking oil to the animal would eventually cause it to enter human system through the food chain. This is made worse especially if the waste cooking oil is reused several times due to economic reasons. Under normal frying conditions, the oil is boiled under atmospheric condition at temperature of 160–190 °C for a relatively long period of time. Under such condition, the waste oil will undergo various changes in its physical and chemical properties. Generally the changes observed in the oil comprised of the following; (i) increase in thickness and viscosity, (ii) increase in specific heat, (iii) increase in surface tension, and (iv) change toward a darker color. This could be attributed to the increased presence of higher longer chain saturated fats components in the oil as well as the other components. There are three types of reactions taking place during frying and they are mainly thermolytic, oxidative and hydrolytic. These three reactions will continuously cause the

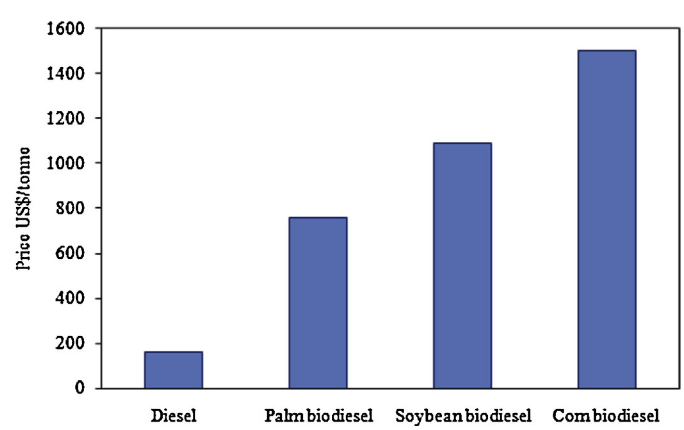

Fig. 1. Prices of diesel fuel and biodiesel from different sources [36].

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