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An overview of ionic liquids as solvents in biodiesel synthesis

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ABSTRACT

Transesterification is the most common method for producing biodiesel. Known as a suitable substitute to diesel fuel, the synthesis involves renewable sources as feedstock. Application of both organic and inorganic solvents in biodiesel production has been widely established. However, as the properties of conventional solvents are perpetually hazardous to human and environment, utilization of greener alternative is a better option. Among the various types of solvents available, ionic liquid seems prevalent. An ionic liquid is a combination of cations and anions, has low or negligible vapor pressure, and exists as liquid at temperature below 100 °C. The prospect of ionic liquids as green solvents in chemical processes is increasing in recent years, especially in biodiesel synthesis. This paper highlighted the properties of ionic liquids that emphasized their versatility as solvents, and the use of switchable ionic liquids as green solvents is also presented. The roles of ionic liquids in biodiesel synthesis are discussed, focusing on their pertinent capability as solvents, particularly as catalysts for transesterification reaction. Since the cost of ionic liquid may be an issue, a brief discussion about the recyclability of ionic liquids is also included.

Contents

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1. Introduction

Energy crisis seems to be inevitable as the global demand for energy keeps rising as a consequence of industrial development and population growth worldwide [1]. Increased oil consumption in daily activities raised the alarm among consumers as we are dependent on crude oil and its derivatives. If the trend continues in coming years, there might be a possibility that in the future, there will be no more crude oil as there are finite amount of resources. This unfeasible situation can lead to shortage of crude oil as the energy demand escalates, and indirectly raised the price of crude oil [2]. Other than the possibility of diminishing fossil fuel reserves, the detrimental effect of exhaust gases from petroleum-based fuels on the environment is also worrying. Combustion of these fuels releases harmful and hazardous substances into the atmosphere. The biggest concern about the product from engine combustion is carbon dioxide, as it is one of the primary greenhouse gases in the Earth's atmosphere to contribute to global warming [3]. As more and more carbon dioxide is produced and confined in the atmosphere, the sun's heat is also trapped and increased the Earth's surface temperature, resulting in the rise of sea level due to the melting of ice sheets [4].

The limited crude oil reserves and environmental-threat exhaust gases have reiterated the importance of crude oil substitute. Biodiesel has potentials as an alternative to petroleum diesel. Biodiesel can be produced via chemical reaction between a feedstock; either vegetable oil or animal fat, to produce methyl esters [5]. Advantages of using biodiesel compared to diesel fuel are that biodiesel is renewable, emit fewer hazardous substances from exhaust gases, and its usage also reduces the dependency on petroleum-based fuel. Emission of carbon dioxide into the atmosphere can be reduced by substituting diesel fuel with biodiesel. A study by Sheehan et al. [6] stated that using 100% pure biodiesel (B100) reduced net carbon dioxide emissions by 78.45% compared to petroleum diesel. In addition, biodiesel is said to be carbon neutral as plants absorb carbon dioxide for photosynthesis process, thus reducing the amount of carbon dioxide in the atmosphere [7].

There are several methods available to obtain biodiesel from its feedstock. These include direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification [8]. Transesterification is defined as a process where esters of saturated and unsaturated carboxylic acid (also known as triglyceride) react with alcohol in the presence of catalyst to produce mixtures of fatty acid esters as the main product and glycerol as by-product [9]. The reaction between triglycerides and alcohol to produce fatty acid esters is shown in Fig. 1. This process is mainly carried out to reduce the viscosity of the feedstock, which can sometimes have high viscosity and not suitable for direct use in diesel engine. During the process, alcohol molecules replace the glycerol backbone, thus producing alkyl esters of fatty acids. Transesterification process can be influenced by various parameters, including free fatty acids and water content, molar ratio of alcohol to oil, catalysts type and loading, reaction temperature and stirring rate [10].

Organic and inorganic solvents are commonly utilized in biodiesel synthesis as catalyst [11–13], solvents for enzyme-catalyzed transesterification [14,15], and extraction agent for extracting lipid prior to conversion into biodiesel [16,17]. Although the solvents are widely available and can be obtained with reasonable price, issues regarding volatility, toxicity, physical hazards and possibility of environmental contamination can reduce the usage of conventional solvents in the future. As the awareness about the risk of using these solvents increased, the search for their alternatives becomes a priority. One alternative is found in ionic liquids (ILs). ILs are defined as salts that are usually liquid at room temperature due to its melting temperature of below 100 °C, and are solely composed of several cations and anions. ILs are eminent and green, suitable to replace conventional solvents in chemical synthesis. Among the unique characteristics of ILs are negligible vapor pressure, good solubility in both organic and inorganic materials, able to form multiple phase systems due to their miscibility, and highly tunable for specific tasks [18].

Ionic liquids are produced through different combinations of cations and anions. Physicochemical and thermal properties of ILs are influenced by the types of ions used. Manipulation of ILs functional groups can be applied to produce task-specific ionic liquids (TSILs) for different applications. The applications include substitution to solvents of higher volatility, purification of gases, homogeneous and heterogeneous catalysis, biological reaction media, and removal of metal ions [19]. ILs are also involved in biomass pretreatment and cellulose dissolution [20]. More recently, there is an increasing tendency of using ionic liquids in biodiesel synthesis of vegetable oils and animal fats, where ILs can be used as either catalysts or solvents [21]. The purpose of this review is to highlight the prospect of ionic liquids as green solvents in biodiesel synthesis. Their properties are presented to elucidate their advantages over conventional organic and inorganic solvents. In addition, recycling and reusability of ionic liquids are also discussed.

2. Ionic liquids properties

The utilization of ionic liquid (IL) in various industrial applications has progressed since its early discovery. Experiments and researches are conducted in order to obtain a deep understanding about the wide range of potentials that they can offer. Ionic liquids have been used and applied in a variety of processes, among them as homogeneous catalyst in hydrogenation and hydroformylation reactions, in removal of heavy metal traces and aromatic hydrocarbon, in protein extraction, and alkene/paraffin separation [22]. By definition, ionic liquids are organic salts that are solely composed of ions (cations and anions) with low melting temperatures, negligible vapor pressure, and exceptional thermal and chemical stability. They are liquid at room temperature and can be produced through different combinations of cations and anions. Fig. 2 represents cations and anions commonly used to prepare ionic liquids.

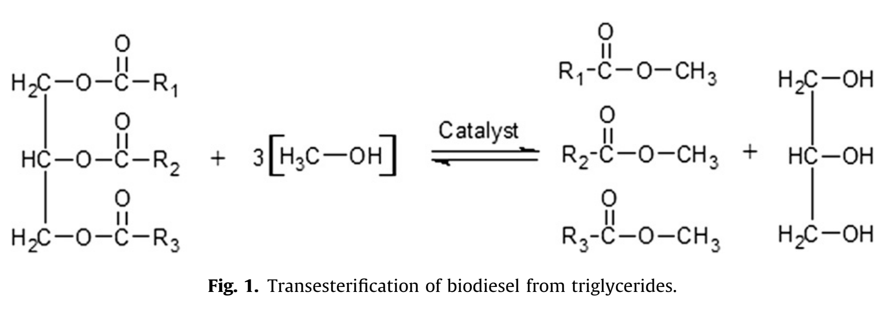

Fig. 1. Transesterification of biodiesel from triglycerides.