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New horizons in the enzymatic production of biodiesel using neoteric solvents

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ABSTRACT

Globally, tougher legislation in greenhouse gases emissions is prompting the hunt for more sustainable and competitive strategies to synthesize biodiesel. Although enzyme-catalyzed processes are considered as a more environmentally-friendly option, there are still challenges to be approached like the replacement of traditional solvents due to their well-known disadvantages such as their volatility, toxicity or carcinogenic character. Thus, the emergence of neoteric solvents such as perfluorocarbons, liquid polymers, ionic liquids, deep eutectic solvents or supercritical fluids has opened up new opportunities to reach truly green processes. Nonetheless, literature analysis reveals the scarcity of research works, which are exclusively restricted to the last three types of solvents. One of the critical points to take into account refers to the performance of enzymes in this kind of milieu, as this environment may be deleterious in terms of protein structure, leading to enzyme deactivation. Therefore, the final purpose of this review paper is to identify the current trends of research in the field of neoteric solvents applied to enzyme-catalyzed synthesis of biodiesel and to shed light on the possible existing gaps.

1. Introduction

The recent world summit on climate change held in Paris negotiated a binding and universal agreement on greenhouse gases reduction. In this line, the EU is at the forefront in lowering these emissions, with a target of at least 40% in 2030, which parallels an increase in the use of renewable energy for electricity production from 22% to 45% in 2030 [1]. Similarly, EEUU is devising a plan to monitor and mitigate carbon footprint through the employment of renewable resources [2]. One of the most competitive alternatives is the utilization of biofuels, as they can be produced from renewable stocks like plants or animals, to the detriment of highly polluting fossil fuels. In this regard, the U.S. Renewable Fuel Standard Mandate aims at reaching 36 billion gallons of biofuels production in 2022 [3]. Among the existing alternatives, biodiesel displays different environmental advantages in relation to the conventional petroleum-derived diesel. Thus, although the NOx values are slightly higher, their combustion entails a great reduction of the levels of carcinogenic compounds (near to 85%), a higher biodegradability (4 times faster than petroleum-based diesel) and the mitigation of greenhouse gas emissions (more than 3 times lower than petrodiesel and gasolines) [4].

The production of biodiesel can be performed by pyrolysis or cracking, microemulsification and transesterification [5]. The last one is the most frequently referred, and consist in the reaction between triglycerides (e.g. vegetables oils, animal fats or lipids from algae) and alcohols such as butanol, propanol, amyl alcohols, ethanol or methanol, being these two latter the most common ones (Fig. 1).

Historically, this reaction has been carried out at elevated temperatures and in the presence of chemical catalysts. Both acid and alkaline catalysts have been proposed to yield high levels of fatty acid alkyl esters. For instance, sulfuric acid [6], chlorhydric acid [7] sulfonic acid [8], as acid catalysts, or NaOH [9], and KOH [10] as alkaline catalysis, are dissolved in methanol and added to the oil in a stirred tank reactor prior to phase segregation of an ester- and glycerol rich layers. Notwithstanding chemical transesterification has been traditionally proposed owing to economic and operational reasons (high yields of fatty acid esters, low cost and high process productivity), some hindrances such as soap formation, generation of acid or alkaline waste effluents, corrosive character of acids, and operation temperature, foster the investigation of more

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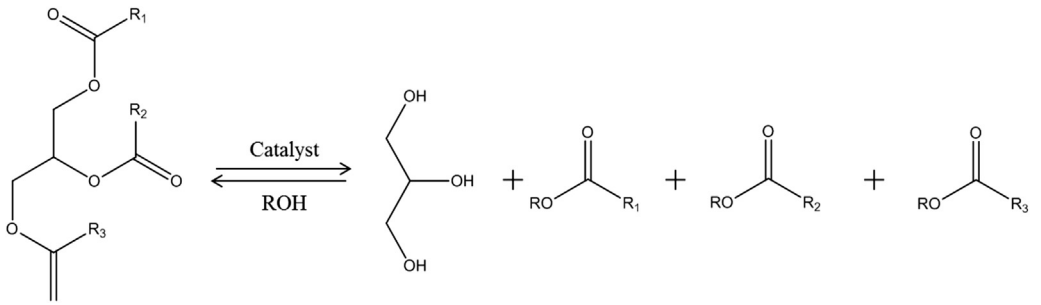

Fig. 1. Transesterification reaction for biodiesel synthesis from alcohols and triglycerides.

environmentally friendly opportunities [11]. Accordingly, the use of biological catalysts such as lipolytic enzymes has led the way in the production of this kind of biofuels on account of different advantages like the operation at mild temperatures, the existence of low treatment costs because of its easier downstream processing, the absence of soap generation and side reactions, the necessity of lower alcohol:oil ratios and the high selectivity and specificity towards substrates [4,12].

Lipases (triacylglycerol hydrolases, EC 3.1.1.3) have been identified in a large variety of bacterial, fungal, plant and animal sources, and their production at industrial scale has already been tackled [13]. Their kudos is founded on distinctive features such as their potential activity and stability in organic solvents and their high chemo-, enantio-, and regioselectivity [14,15]. In this sense, they display utmost importance in sectors ranging from food and pharmaceutical to waste management industries as a result of their versatility to act in mushrooming chemical reactions, such as hydrolysis, interesterification, esterification, alcoholysis, acidolysis and aminolysis [16]. Many of these reactions must be carried out in non-aqueous solutions, making lipase-catalyzed processes in organic solvents a matter of particular importance and practical significance to compete with the conventional chemical alternatives. Traditionally, organic solvents have been proposed as media for the transesterification due to different inherent advantages, like the shift of thermodynamic equilibrium to favor synthesis reactions, the increase the reactants solubility, the reduction of medium viscosity, the greater mass transfer favored by homogeneous media, the possibility of using non-polar substrates, the existence of an easier recovery of products, and the avoidance of many side reactions [17–19].

Despite these benefits, these solvents may negatively affect the enzyme performance, so initial biocompatibility tests are desirable. Apart from that, they often entail deleterious environmental and health effects, like their high vapor pressure or their toxicity. On account of this fact, the emergence of neoteric solvents has been pushed forward by both academicians and practitioners. Be that as it may, these solvents may affect the native enzyme structure even up to a complete deactivation. It is well known that an aqueous environment is required to maintain the biocatalytic function, and a minimum amount of water in the hydration shell equal to the mass of the protein must be retained [20]. Generally speaking, hydrophilic solvents tend to display a stronger deactivating character as they may compete for the water molecules hydrating the protein [21].

On the whole, the implementation of new competitive biocatalyzed-synthetic processes in neoteric solvents to obtain biodiesel is still in its infancy, and less than 80 papers dealing with this topic can be found. As can be visualized in Fig. 2, most of them are referred to a new class of molten salts, named ionic liquids, closely followed by supercritical fluids and deep eutectic solvents.

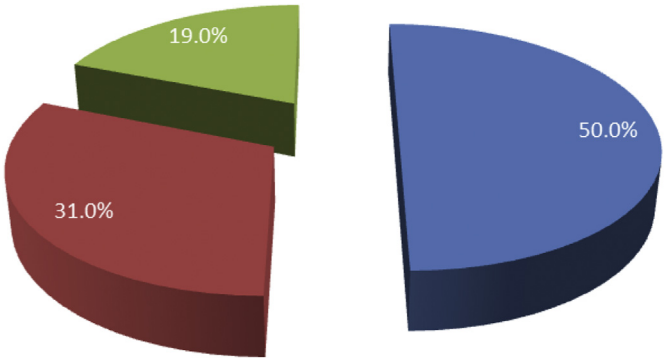

Fig. 2. Percentage of SCI articles focused in lipase-biocatalysed biodiesel production in neoteric solvents: (■) ionic liquids, (■) supercritical fluids, (■) deep eutectic solvents.

In this review, we will critically analyze the existing literature on the topic, identifying the main shortfalls and envisaging the future outlooks that must be addressed prior to these solvents cast the walls from research laboratories and cover the pathway to the industrial scale.

2. Lipase-catalyzed biodiesel production in ionic liquids

Over the last years, ionic liquids have posed a new inspiration for Green Chemistry as their low vapor pressure may reduce the air pollution with respect to the typical volatile organic solvents [22]. They exhibit remarkable properties such as thermal stability, null flammability and the possibility of combining an array of anions and cations that makes it possible the design of millions of task specific solvents [23]. These features have contributed to place them under the eye of the industry, and they are already manufactured by companies as paint additives (Degussa), in batteries (Pionics), in solar cells (G24i), in cellulose dissolution and aluminum plating (BASF), and in compressors for batteries (Linde). Thus, the annual production of some of the most common families, like those based on the imidazolium cation, has already surpassed the ton magnitude [24,25]. What is more, a recent breakthrough focused on the application of these molten salts in ultrafast-rechargeable aluminum batteries could act as spur to their widespread implementation [26].

Beside these applications, the potential of these molten salts in biocatalysis is also in the limelight. More specifically, ionic liquids have been proposed as inhibitors of protein aggregation, to increase the stability and enantioselectivity of enzymes, and as refolding and crystallization additives [27,28]. Nonetheless, the existence of millions of possible ionic liquids hinders drawing generalizations, and the interaction between them and the enzymes at an structural and functional level is still to be understood. This complex scenario