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Research review paper

Enzymatic reactors for biodiesel synthesis: Present status and future prospects

Jakeline Kathiele Poppe [a], Roberto Fernandez-Lafuente [b], Rafael C. Rodrigues [a,*], Marco Antônio Záchia Ayub [a,*]

[a] *Biotechnology, Bioprocess, and Biocatalysis Group, Food Science and Technology Institute, Federal University of Rio Grande do Sul, Av. Bento Gonçalves 9500, PO Box 15090, ZC 91501-970 Porto Alegre, RS, Brazil*
[b] *Departamento de Biocatalisis, ICP-CSIC, Campus UAM-CSIC, Cantoblanco, 28049 Madrid, Spain*

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A B S T R A C T

Lipases are being extensively researched for the production of biodiesel as a "silver bullet" in order to avoid the drawbacks of the traditional alkaline transesterification. In this review, we analyzed the main factors involved in the enzymatic synthesis of biodiesel, focusing in the choice of the immobilization protocol, and the parameters involved in the choice and configuration of the reactors. An extensive discussion is presented about the advantages and disadvantages of each type of reactor and their mode of operation. The current scenario of the market for enzymatic biodiesel and some future prospects and necessary developments are also briefly presented.

Contents

1. Introduction

The possibility of using agricultural-based fuels in diesel cycle engines is very attractive in the view of environmental aspects because these are renewable energy sources and can use several agricultural and agro-industrial residues for their synthesis. Biodiesel is defined by the National Biodiesel Board (USA) as a monoester of fatty acids derived

* Corresponding authors. Tel.: +55 51 3308 6685; fax: +55 51 3308 7048.
E-mail addresses: rafaelcrodrigues@ufrgs.br (R.C. Rodrigues), mazayub@ufrgs.br (M.A.Z. Ayub).
URL's: http://www.ufrgs.br/bbb (R.C. Rodrigues), http://www.ufrgs.br/bbb (M.A.Z. Ayub).

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from renewable sources of long chain, such as vegetable oils and animal fats (Knothe, 2006). Biodiesel is a renewable, carbon neutral biofuel, with neutral mass balance of CO_2 from emissions and absorption thereof by the plant (Yaakob et al., 2013).

Many oilseeds can be used to produce biodiesel, among them, the most important are soybean, sunflower, and palm oils, and the different alternatives depend upon the cultures in each region. On the other hand, given the large generation of waste oils by industrial and economical activities, it is becoming important to further explore alternative sources of oils, such as waste vegetable oils from cooking and various fats (Antczak et al., 2009).

Alkaline catalysis is still the most important technological route for the industrial production of biodiesel via transesterification reaction because of its shorter reaction time and high productivity. However, alkaline catalysis presents drawbacks related to the inevitable production of soaps caused by the saponification of free fatty acids, leading to losses of catalysts and difficult process of separation and purification of the formed glycerol, reducing the yields of the reaction (Leung et al., 2010).

The enzymatic synthesis of biodiesel, mediated through the use of lipases (EC 3.1.1.3, triacylglycerol hydrolases), presents important advantages over the chemical catalysts, such as the specificity, enantioselectivity, and regioselectivity of the reactions, therefore generating less side-products and wastes, and the reactions can be carried out at mild conditions of temperature and pressure (Ghaly et al., 2010). Enzymatic industrial processes are generally relatively simple, easy to control, and more efficient on energy input when compared to traditional chemical processes (Oliveira and Mantovani, 2009). Furthermore, in the case of lipase-based synthesis of biodiesel, the separation of glycerol generated as a by-product and the purification of the produced esters are easily performed (Fukuda et al., 2001).

The present market costs of lipases are still the main limitation that avoids their use in large-scale processes. Thus, many scientific groups are developing several studies aiming at reducing these costs. We can highlight, among strategies being investigated, the use of aqueous solutions of lipases, which are non miscible with oils and biodiesel (Cesarini et al., 2013; Pedersen et al., 2014); immobilized enzymes used in repeated operation cycles (Calero et al., 2014; Chen et al., 2011; Noureddini et al., 2005; Poppe et al., 2013; Shimada et al., 1999; Wang et al., 2008); the development and improvement of immobilization techniques (Rodrigues et al., 2013; Silva et al., 2014); the use of new materials for immobilization in substitution of expensive commercial supports (Miranda et al., 2014); and the improvement of reaction parameters in batch and continuous reactors (Hama et al., 2013; Kawakami et al., 2011; Lee et al., 2010).

The use of immobilized lipases may improve the development of commercial scale processes, favoring biotechnological processes based on their numerous advantages over the chemical process. In large-scale biodiesel production, selecting the most appropriate reactor depends on the characteristics of the reaction kinetics and conditions based on the biocatalyst, which, in turn, will define the operation mode and the flow characteristics (Castro et al., 2008).

In this context, this review will discuss some important aspects involving the use of reactors applied in the enzymatic process of biodiesel synthesis, showing the present status and the future prospects of their applications. Emphasis will be given to the interactions between the lipase and the immobilization support and the efficient use of the biocatalyst in the reactors; the operation mode and settings of the enzymatic reactors; and to the analysis of the main parameters involved in the transesterification reactions.

2. Technical aspects of biodiesel

The high demand for energy by the industrialized world and the recurrent environmental problems caused by the widespread use of fossil fuels are pushing the need for developments on renewable energy sources. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. One possible alternative to fossil fuel is the use of oils of plants or of algae origin, and animal fats for the synthesis of biodiesel (Meher et al., 2006). Biodiesel accounted for approximately 5% of the world biofuel production in 2000, and this value is continuously rising reaching, in 2011, about 20% of the total biofuel production (Geraldes et al., 2014). Several governmental policies worldwide are stimulating biofuel production by setting targets for blending quotas, and boosting the development of biofuels technologies by establishing financial and political support mechanisms (Geraldes et al., 2014).

Biodiesel is miscible with petroleum-based diesel in all proportions and can be used pure or blended with diesel. These blends are often coded such as B20, which indicates the blend of 20% of volume biodiesel and 80% of volume diesel (Issariyakul and Dalai, 2014).

Biodiesel is predominantly produced by transesterification reaction, which process is relatively simple and generates a fuel whose properties are similar to diesel (Dorado et al., 2003; Geris et al., 2007). The transesterification consists of a reaction between vegetable oil, or animal fat, and a primary alcohol in the presence of a catalyst, resulting in a mixture of alkyl esters of fatty acids (biodiesel) and glycerol (de Araújo et al., 2013). Excess alcohol in the reaction is necessary in order to increase the yield of esters and to promote the shifting of the reaction equilibrium towards products (Suarez et al., 2007).

Another biodiesel synthesis technology has been widely reported, known as hydroesterification (Cavalcanti-Oliveira et al., 2011; de Sousa et al., 2010; Soares et al., 2013). This process occurs in two consecutive steps: the first is the hydrolysis of all glycerides (mono-, di- and triglycerides) producing free fatty acids (FFAs) and glycerol; the second one is the esterification of the FFAs by a short chain alcohol to obtain esters (biodiesel) and water. Throughout this process, glycerol is separated in the first step, therefore not being mixed with the alcohol, thus being purer than glycerol obtained by transesterification (Aguieiras et al., 2014).

2.1. Raw materials for biodiesel production

The raw materials for biodiesel production are the lipid sources, mainly vegetable oils, animal fats, and, more recently, oils produced by algae (Nautiyal et al., 2014) and cyanobacteria (Karatay and Dönmez, 2011), and several types of alcohols.

The vegetable oils used as lipid feedstock for biodiesel production usually depend on regional production, for instance, as in rapeseed oil in the European countries and Canada, soybean oil in the United States and Brazil, and palm oil in tropical countries such as Indonesia and Malaysia. Coconut oil is another lipid feedstock used for synthesis of biodiesel in coastal areas (Issariyakul and Dalai, 2014).

Sources of oils such as soybean oil, palm oil, sunflower, rapeseed, coconut, and peanuts are considered as the first-generation biodiesel feedstock. However, their use leads to competition with the food industry, and may generate environmental problems such as serious destruction of vital soil resources, deforestation and the use of much of the available arable land (Atabani et al., 2012). Furthermore, the cost of raw materials accounts for 60–80% of the total cost of biodiesel production (in the alkaline rout), indicating that selecting the appropriate feedstock is of considerable importance for ensuring the economic viability of the process (Aarthy et al., 2014). The use of low-cost feedstock such as wastes of frying oil, non-edible oils such as colza, and oils extracted from other feedstocks such as yellow grease, lard, and animal fats, among others, are known as second generation biodiesel feedstock and are expected to reduce the production costs and environmental problems, making biodiesel production more commercially competitive with diesel (Christopher et al., 2014).

Many types of alcohols can be used to produce biodiesel, in some cases with the need to use organic solvents. Alcohols of higher chemical chains, such as propanol and butanol, posses better oil solubility and

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