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A review of the enzymatic hydroesterification process for biodiesel production

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ABSTRACT

Enzymatic hydroesterification has recently attracted research interest because of the high-value products created during biodiesel production. The use of this process overcomes problems related to conventional methods for biodiesel production, such as slow reaction rate and soap formation. The method comprises two basic processes to produce fatty acid alkyl esters from triacylglycerols, namely, enzymatic hydrolysis and enzymatic esterification. Although enzymatic hydroesterification for biodiesel production has many advantages, such as lower energy consumption and converting low-quality feedstock, it has not been used on an industrial scale mainly because of some impediments, including enzyme cost and conversion efficiency. This review presents a comprehensive evaluation of recent investigations on enzymatic hydrolysis and enzymatic esterification to lower process costs and increase yields.

Contents

1. Introduction

Issues of impending supply crisis, mounting carcinogenic emission problems, and global warming are associated with the use of petroleum-based products and are the main reasons for the development of renewable biofuel sources [1–3]. Under current conditions, biodiesel (fatty acid alkyl ester), an alternative clean-burning fuel for diesel engines, has gained the most attention among biofuels because of its similarity with conventional diesel in energy content and chemical structure [3,4]. Moreover, biodiesel reduces carcinogenic compound emissions by approximately 85% compared with diesel fuel and is essentially free of sulfur, metals, and polycyclic aromatic hydrocarbons [5].

Global worriment about the use of edible oils as substrates in biodiesel production because of the potential competition with

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food consumption and high cost of edible oil [6] (60–75% of the total cost of biodiesel production) has encouraged researchers to examine low-cost raw materials for this process [7,8]. Second-generation biodiesel feedstocks, such as nonedible oils, waste edible oils, and animal fats, can remarkably reduce biodiesel production costs and ensure the economic feasibility of the process [9]. However, substrates containing high levels of free fatty acids (FFAs) are undesirable in common methods of biodiesel synthesis (alkali-catalyzed alcoholysis) [10].

Transesterification of triacylglycerol (TAG) using methanol in the presence of alkaline catalyst-like sodium hydroxide, potassium hydroxide, or methoxide process is most commonly employed in industrial-scale biodiesel production [11]. The major drawback of this alkaline process is its sensitivity to FFAs in oils ($>2.5\%$), which results in soap formation, thereby reducing the yield and complicating the separation process [8,12,13]. Acid catalyst processes can be applied to substrates with high FFAs, but they have a lower reaction rate and can cause technical problems with glycerol byproducts and the purification and separation of biodiesel from the catalyst [12,14,15]. Subcritical and supercritical reactions, as non-catalytic processes, can produce a high rate of conversion over a short period of time. Nonetheless, the operating temperatures and pressures are quite high (200–400 °C and 10–25 MPa respectively) and not economical for biodiesel production [16].

The aforementioned problems have led to the development of an enzyme-catalyzed route for biodiesel production that is characterized by certain environmental and economical advantages over conventional chemical methods [17]. The enzyme catalyst process diminishes inherent problems associated with the use of an alkali/acid for producing fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE) from substrates with either low or high FFAs. Lipase is the most prevalent enzyme used in this process [18]. The advantages of enzymatic biodiesel production include (1) no soap formation, (2) higher purity of glycerol byproducts, (3) simplified production process, (4) low-energy consumption, (5) easy enzyme recycling, and (6) easy separation of lipase from the products [19,20]. However, low reaction rate, high cost of lipase, and inhibition of enzyme activity by using organic solvents, such as n-hexane, are drawbacks of applying enzymes as catalysts for biodiesel production [5]. As a result, most current investigations in this field focus on eliminating the drawbacks of enzymatic biodiesel production, such as developing an enzymatic route with a higher reaction rate, lowering enzyme cost, and creating a more environmentally friendly process [21].

This review examines state-of-the-art process technologies for enzymatic biodiesel production, with emphasis on the two-step hydroesterification method. Recent investigations and developments on enzymatic hydrolysis and esterification of various feedstocks have also been reviewed in depth. This review also aims to present the advantages and disadvantages of using enzymes in biodiesel production from different substrates, as well as the factors influencing enzymatic biodiesel production. The results of this work may provide a reliable reference for future enzymatic hydrolysis operations and clarify the enzymatic esterification mechanism for screening proper enzymes, reactants, and operating conditions in further investigations.

2. Enzymatic biodiesel production

Enzymatic biodiesel production using lipase (TAG acylhydrolase) has long been considered an environmentally friendly and energy-efficient consumption route for the production of FAAE from vegetable oils [22,23]. Owing to several drawbacks in this process, it has not been used on a large scale despite its advantages, such as converting low-quality (high FFA) feedstock, lower energy consumption, and food-grade glycerol production [24]. The main hurdles impeding the industrial application of enzymes for biodiesel production are enzyme cost and conversion efficiency [25–27]. Reducing enzyme (lipase) cost and improving overall process economics for large-scale enzymatic biodiesel production have been the major challenges of recent research investigations [28].

Enzymatic biodiesel production can be performed through three reaction mechanisms: transesterification, interesterification, and esterification [5,29]. According to lipid chemistry, transesterification is the catalytic route of replacing the alkoxy group of an ester with an acyl acceptor (methanol, ethanol) that converts TAG in oils to glycerol and FAAE. The advantages of biodiesel production through enzyme-catalyzed transesterification include little or no byproduct generation, mild reaction conditions, reuse of the catalyst, and insensitivity to high-FFA oils [30–33].

Ester production can be achieved through synthesis with FFAs and alcohols in a process called esterification [34,35]. Esterification reactions catalyzed with lipase are among the most important, industrially relevant biochemical and chemical processes [36–38]. In enzymatic esterification of oils with high FFAs, biodiesel is directly produced through the reaction of FFAs with alcohol in the presence of an enzyme, which results in FAAE and water as byproducts [39].

The use of short-chain alcohols such as methanol in biodiesel production has drawbacks, including the inhibition of lipase activity and the undesirable combination of water and FFAs. As a result of fast deactivation and the short lifespan of enzymes during repeated experiments, a considerable amount of enzymes are required for biodiesel production, ultimately increasing the cost of biodiesel production [40]. To prevent problems with the use of short-chain alcohols and increase efficiency, enzymatic interesterification (using alternative acyl acceptors such as methyl acetate, dimethyl carbonate, and ethyl acetate) can be used in biodiesel production. Enzymatic interesterification is the transformation of TAG to biodiesel in the presence of both an acyl acceptor (like methyl acetate) and an enzyme, which results in the formation of another TAG, rather than glycerol, as the byproduct [41].

Previously mentioned biodiesel production processes have not yet been implemented on an industrial scale because of several constraints, such as slow reaction rate, alcohol inhibition, exhaustion of enzymatic activity, and high cost of enzymes [33]. Nonetheless, considerable efforts have been made by researchers to increase reaction efficiency and high-quality biodiesel production to meet the stringent quality requirements of international standards, such as ASTM 6751-03 [42–44]. Recent investigations on biodiesel production systems can be categorized into the following approaches: co-solvent systems, two-step methods, lipase combinations, value-added byproducts, ionic liquid technology, microwave usage, and ultrasonic technology [28,45,46]. Table 1 illustrates the latest developments for each system mentioned above.

Among the mentioned developments for enzymatic biodiesel production, the two-step process has attracted considerable attention in the production of second-generation biodiesel given its application in a wide range of FFAs and water in feedstocks, high reaction rate, high quality of byproducts, and minimized deactivation of lipases by an acyl acceptor (such as methanol). In Section 3, hydroesterification, a two-step process for biodiesel production, is reviewed in depth. All examined conditions for oil hydrolysis and fatty acid esterification are collected to create a complementary reference aimed at lowering enzymatic hydroesterification costs and increasing efficiency at each step of the biodiesel production process.

2.1. Key factors on enzymatic biodiesel production

Crucial factors affecting economic viability, yield, and conversion efficiency of enzymatic biodiesel production processes include enzymes (type and preparation method), substrates, acyl acceptors, and bioreactor design [61,62].