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State of the art and prospective of lipase-catalyzed transesterification reaction for biodiesel production

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ABSTRACT

The world demand for fuel as energy sources have arisen the need for generating alternatives such as biofuel. Biodiesel is a renewable fuel used particularly in diesel engines. Currently, biodiesel is mainly produced through transesterification reactions catalyzed by chemical catalysts, which produces higher fatty acid alkyl esters in shorter reaction time. Although extensive investigations on enzymatic transesterification by downstream processing were carried out, enzymatic transesterification has yet to be used in scale-up since commercial lipases are chiefly limited to the cost as well as long reaction time. While numerous lipases were studied and proven to have the high catalytic capacity, still enzymatic reaction requires more investigation. To fill this gap, finding optimal conditions for the reaction such as alcohol and oil choice, water content, reaction time and temperature through proper reaction modelling and simulations as well as the appropriate design and use of reactors for large scale production are crucial issues that need to be accurately addressed. Furthermore, lipase concentration, alternative lipase resources through whole cell technology and genetic engineering, recent immobilizing materials including nanoparticles, and the capacity of enzyme to be reused are important criteria to be neatly investigated. The present work reviews the current biodiesel feedstock, catalysis, general and novel immobilizing materials, bioreactors for enzymatic transesterification, potential lipase resources, intensification technics, and process modelling for enzymatic transesterification.

1. Introduction

World is facing serious issue of limited supply of fossil energy leading to exploration into alternative renewable energy. Currently, harvesting electricity from renewable energy sources such as solar, wind and biomass have been proposed as the alternative technologies and commercially well-established in the latest years [1]. Rapid depletion of fossil energy and the limited resources as well as un-sustainability of fossil energy are among major world concerns in modern life, especially in terms of transportation. In addition, the deteriorated atmospheric greenhouse effect and global warming due to burning fossil fuels becomes a huge obstacle of environmental sustainability [2,3]. The depletion of petroleum energy sources will affect numerous aspects of the consumer life and economy, and hence concentrating on renewable alternative is now more substantial.

Generally, biofuels are renewable fuels produced from biomass and are categorized as biodiesel, bioethanol, biogas and biohydrogen which are currently studied extensively as renewable energy resources. To date, biodiesel has been accepted as a promising fuel because of being highly biodegradable and containing low toxicity to be replaced by diesel fuel in devices like boilers and internal combustion engines with a low decrease in performances and no huge alteration [4]. Biodiesel can also be blended with the conventional petroleum diesel fuel in order to reduce CO_2 emissions problems. Furthermore, biodiesel is estimated to be 66% more efficient as a lubricant in diesel engines compared with petro-diesel [4]. Biodiesel contains properties like diesel fuel leading to make it a suitable alternative to diesel fuel [5]. The overall strategy of generation of hydrocarbon fuels from renewable resources is to decrease the oxygen content of the feedstock to energy density and to create C—C bonds between biomass-derived intermediates, and to increase the molecular weight of the produced hydrocarbons [6]. Hence, the physicochemical properties and qualities of biodiesel produced from any resource and through any chemical reaction must follow international specification standards such as European

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Union Standards for Biodiesel (EN 14214) and the American Standards for Testing Materials (ASTM 6751-3).

Technically, biodiesel is described as fatty acids monoesters derived from long chain renewable sources including vegetable oils and animal fats. It consists of a mixture of esters chiefly produced through transesterification reaction of triglycerides by short chain alcohols such as methanol and ethanol while the main by-product is glycerol [7]. Vegetable oils are not used directly as fuels in diesel engines, particularly due to their high viscosity, Fatty Acid (FA) composition and free fatty acids (FFAs) content. To overcome this issue, conversion of FA and FFA to their respective Fatty Acid Alkyl Esters (FAAE) is widely investigated. Transesterification of vegetable oils has been broadly known and applied since the 19th century [8]. This reaction is a simple, prominent method which proceeds well in the presence of a catalyst. The reaction is carried or by either catalytic or non-catalytic or methods. In supercritical conditions, alcohol is both a reactant and an acid catalyst [9,10]. For non-catalytic reactions it is very rapid by supercritical fluids compared with the conventional catalytic biodiesel production [11].

In the production of biodiesel, any triglyceride of the feedstock is transesterified where the feedstocks are mainly bearing crops, animal fats, and algal lipids and the alcohol is methanol or ethanol [12]. The choice of catalyst is critical in order to design an efficient process capable of maximizing the value of starting materials while minimizing waste generation and energy [13]. So far, a broad range of catalysts has been used to catalyze biodiesel production reactions including acids and bases, sugars, ion exchange resins, zeolites, enzymes (lipases) and other materials [14]. Three types of most applied and common catalysts are homogenous chemical catalysts, heterogeneous solid catalysts and biocatalysts. NaOH and KOH, carbonates, and the corresponding sodium and potassium alkoxides are the major chemical catalysts used in the reaction [15]. In general, transesterification via chemical catalysts results in shorter reaction times with higher yield production [16]. However, there are some drawbacks to the use of homogeneous catalysts in the biodiesel production. Currently, there is a favourable trend of the use of heterogeneous catalysts, especially biocatalysts to reduce problems associated with chemical homogeneous catalyzed reaction. Lipases are isolated from several biological resources which usually go through immobilization process prior to the application. The use of microorganism as lipase resources is advantageous since most of them are capable of producing enzyme at high production rate and relatively low cost. Currently, Novozym 435, which is isolated and purified from fungal resources of *Candida Antarctica and Rhizopus oryzae*, is the most common lipase currently employed to catalyze enzymatic transesterification with really high efficiency (above 90%). However, commercial lipases are limited to their cost. Moreover, compared to chemical catalysis, lipase requires longer reaction time for transesterification. It may also get inactivated by methanol and glycerol during transesterification [17]. A large number of researches focused on the use of whole cell lipases from the wild-type microorganisms containing lipase or genetically modified microorganisms with high lipase activity to reduce the cost. It must be economically feasible and several aspects of lipase catalyzed biodiesel production needs to be neatly and wisely studied to address the limitation for industry used in the future scale-up. In this case, the correct catalyst, feedstock and acyl acceptor, adoption of feasible methods, proper design of bioreactors and the reaction modelling are of importance.

The study reviews the current state of lipase-catalyzed production of biodiesel through transesterification of plant oils from various resources and short chain alcohols. The aim of this study was to consider the relevant aspects of the potentiality of enzymatic biodiesel production for the prospect scale-up process. The review discusses mechanism of lipase-catalyzed transesterification, efficiency of Novozym 435, methods and novel materials for lipase immobilizations and the capability of the bioreactors. Besides, modelling of the enzymatic reaction by advanced tools as well as intensification technics including supercritical fluids, microwave and ultrasound irradiation assisted are considered. The potential lipase resources and development of lipase catalysis through whole cell and recombinant technologies are studied as well. Furthermore, the importance of non-edible, low-cost feedstock and their influence on reduction of total cost of the system is presented.

2. Biodiesel feedstock and raw material

The feedstocks used for biofuel are categorized into edible and non-edible plant oils, animal fats, algal oils, waste oils and oils from oleaginous microorganisms. The composition of feedstocks varies significantly depending on the oil source and the degree of refining. Distinctive compositions of oils and fats that are exploited for biodiesel production are triglycerides, diglycerides, monoglycerides, and FFA [18]. Consumption of oils for biodiesel production depends on the availability of the oil source in origin lands. For instance, palm oil in Asian countries such as Malaysia, Indonesia, Thailand, and the Philippines are used as a major feedstock in those countries [19]; however, there is a gap between production and demand in the case of edible oils arising food versus fuel debate. Biodiesel production from low cost non-edible vegetable oil is an important way to handle the issues associated with energy crisis and environmental concerns as well as total cost reduction of the system [20]. Apart from using non-edible feedstock, it is also desirable if the non-edible feedstock is a no or low-cost waste material to have double benefits to the environment; reduce waste pollution and produce environmental friendly fuel.

Researchers have been investigating on the exploitation of non-edible plant oils sources over last decade such as *Jatropha curcas* [21,22], *Calophyllum inophyllum* [23,24], tobacco [25,26], rubber [27,28], mahua [29], cotton [30,31], keranja [32], and castor [33]. Furthermore, as raw material is the major responsible for the total biodiesel production cost, using such oils will result in considerable overall system cost reduction. It has been suggested that oil factory wastes and some industrial by-products are efficient fatty acid resources such as palm oil sludge [34] and waste cooking or oils [35–38]. Recently, algae, microalgae and bacteria have been extensively studied and proven to be potential oil resources [39–41,43] for being fatty acid-rich and non-edible. However, biofuel production from algal lipids has yet to enter industry as it is 2.5 times as energy intensive as petroleum diesel and almost equivalent to the high fuel cycle energy consumption of oil shale diesel [42].

Methanol and ethanol, which are short chain alcohols, are the most applied alcohols as acyl acceptors used in transesterification. In terms of production from biomass and low toxicity, ethanol is a better alcohol used in diesel engines [44]. However, transesterification by ethanol gives lower yield and ethanol has a higher price than methanol which does not seem economically feasible for biodiesel large scale production.

The efficiency of transesterification may decline due to the presence of free fatty acids (FFAs) in the oil, resulting soap formation [45,46]. Presence of high level of FFA is a serious drawback of major non-edible, low-cost and waste oils. Thus, for crude oil with high FFA, it is critical to perform a pre-treatment process called degumming to reduce FFA level by using acid esterification followed by transesterification reaction in a so-called two-step process [47]. Several studies show the efficiency of degumming for low-cost, waste and non-edible oils as listed in Table 1, and the initial and reduced FFA level before and after acid esterification are stated.