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Review on enzymatic synthesis of value added products of glycerol, a by-product derived from biodiesel production

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Abstract

Crude glycerol is produced as a by-product from biodiesel production via trans-esterification with methanol and this process accounts for 10% (w/w) of the total biodiesel produced worldwide. The glycerol glut created can be utilized to increase biodiesel profitability since disposal can pose a threat to the environment. The need is to transform this surplus crude glycerol into added-value products. Biological based conversions are efficient in providing products that are drop-in replacements for petro-chemicals and offer functionality advantage, commanding higher price with the potential to increase bio-refinery revenue. Glycerol is a stable and multifunctional compound used as a building block in fine chemical synthesis like bio-polymers, polyunsaturated fatty acids, ethanol, hydrogen, *n*-butanol, glycerol carbonate, glycerol acetyl esters etc. Bio-catalysts add higher value to bio based products by catalyzing not only their selective modification, but also their synthesis under controlled and mild conditions. This article focuses on different bioconversion technologies of crude-glycerol to value added industrial products – obtained as waste from current bio-diesel production. We abridge the recent relevant approach for the production of various platform chemicals from bio-glycerol over enzyme and chemical catalysts.

Keywords: Enzyme catalysis; Bio-glycerol; Renewable chemicals; Green processes; Bio-refinery

1. Introduction

Petroleum derivatives are fuels that allow existence of fast, efficient ways of transportation and industrialization [1–3]. However it is likely that they will not last longer than few decades due to their finite reserves, energy security and environmental concerns [4–7]. Researchers are now focusing on bio-energy and value added chemicals that are derived from biomass of renewable sources which emit less greenhouse gases than fossil fuels. Studies show edible plants, ligno-cellulosic biomass, microalgae, animal/vegetable oil etc. being commonly used for biodiesel production by transesterification in the recent past and glycerol, a by-product, amounts to 10% of bio-diesel production (Fig. 1) [8–10]. The EU is still the world's largest biodiesel producer with production capacity of 24.9 billion liters in 2016 and is expected to increase to 25.5 billion liters by 2017 [11]. Some of the major biodiesel producing countries include the US, Brazil, Germany, France, Argentina, Netherlands and Indonesia. India ranked 13th with the production of 0.1 billion liters in the year 2015 [12]. Though the production of bio-diesel globally is still in its nascent stages, the market price of glycerol has dropped rapidly and is available in excess [13–16]. The classical use of glycerol has been in pharmaceutical, food and cosmetic industries [17,18]. However, crude glycerol from biodiesel industry needs further purification in order to be industrially applicable since it contains various impurities. Application of different downstream steps and the costing make its utilization economically un-viable [19–22]. Thus, the valorization of glycerol can potentially improve the profitability of biodiesel in a broader bio-refinery scenario [23]. With biochemical research, we may be in a position to mitigate environmental impact of fossil fuel based products within the realms of technological innovations that can enhance production of bio-based monomers from renewable carbon, on an

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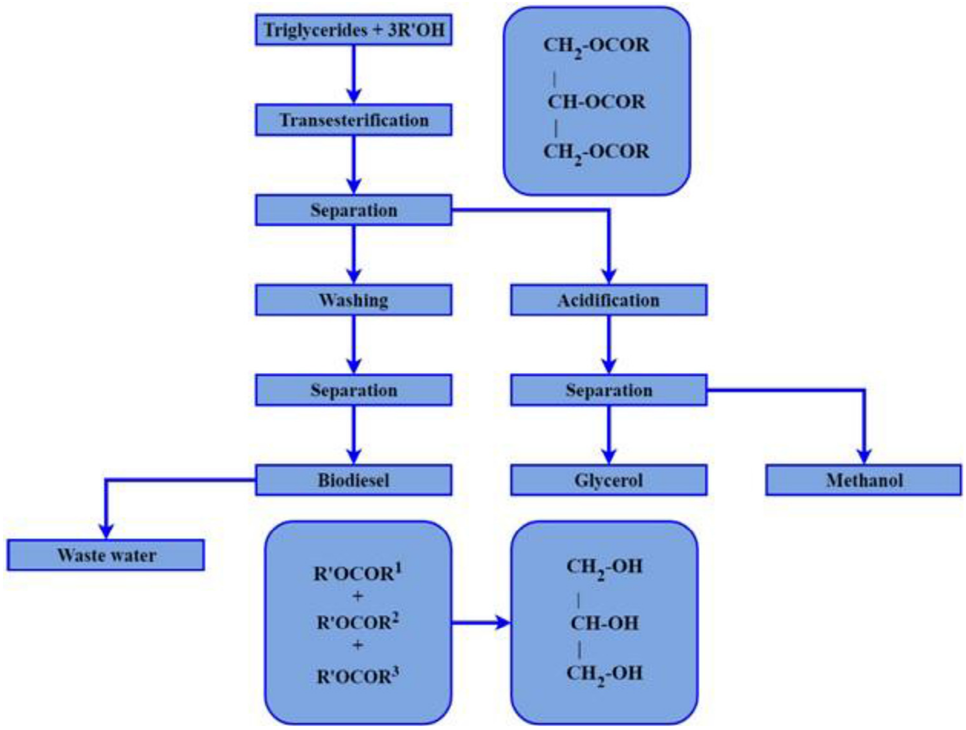

Fig. 1. Schematic representation of general transesterification process; R[1], R[2] and R[3] are alkyl chains.

industrial scale [24–27]. These next generation bio-based chemicals may not only address their sustainability, but also compete in terms of superior technological and functional properties [28]. Bio-catalysis goes a step further by accentuating the production of structured, functionalized and biodegradable products through highly selective and novel synthetic processes. Also, biocatalysts enable targeted hydrolyses and modification that are not possible with conventional strategies. In this review, gist of some recent developments in conversion of bio-glycerol to added-value products is provided [29,30]. The examples mentioned below demonstrate various alternatives that promise conversion of abundantly available crude glycerol toward betterment of bio-refinery.

2. Glycerol

Glycerol (1.2.3-propanetriol), $C_3H_8O_3$ [31–33], is a highly hygroscopic polyalcohol with clear and colorless texture, odorless, highly viscous, hygroscopic, sweet to taste and non toxic to both human and environment. The boiling point, flash point and melting point are 290 °C, 177 °C and 18 °C respectively with negligible vapor. Glycerol has a molecular weight of 92.09 g mol^{-1}, viscosity of 1.5 Pa-s and density of 1.261 g cm^{-3} under normal atmospheric pressure [34–38]. It is a stable compound that consists of three hydroxyl functional groups, which render this compound with hydrophilic and hygroscopic properties. Its molecular structure and physiochemical properties make it a highly functional and versatile compound that can be readily esterified, reduced, halogenated, oxidized, etherified etc. to obtain alternative green chemicals [39–42]. Pure glycerol finds application in industries such as food, cosmetics, textile, pharmaceuticals, feedstock etc. In contrast, usage of crude glycerol from biodiesel industry is very limited because of its composition, which includes spent catalysts, residual methanol, heavy metals, free fatty acids etc. Its disposal is also difficult as the methanol content deems it as hazardous waste. The purity of glycerol is a major concern [43–51] and hence conversion of (crude) glycerol to various highly valuable products by the means of chemical and/or microbial technology is of great importance. As far as enzyme technology is concerned, in the recent years, only limited editions of scientific papers on valorization of crude glycerol are published. Several technologies for synthesis of alternatives have been reported in the literature and a significant number of platform molecules have been synthesized and are found to be highly potential in replacing petroleum based products [52–54]. Fig. 2 summarizes the findings of several studies on upgrading routes and their products.

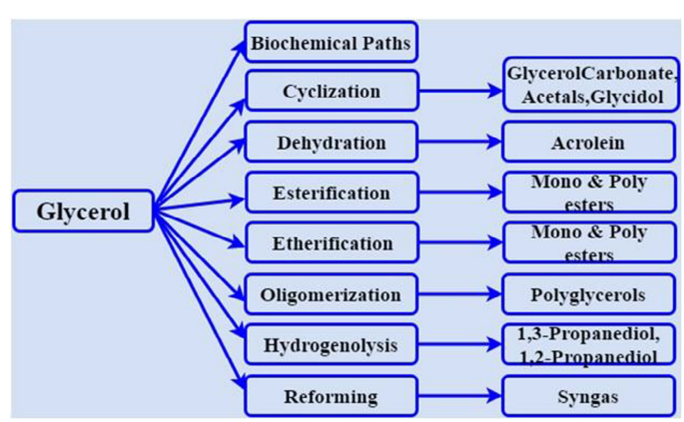

Fig. 2. Different pathways for possible glycerol derivatives.

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