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Review on recent progress in catalytic carboxylation and acetylation of glycerol as a byproduct of biodiesel production

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A B S T R A C T

Biodiesel (BD) is an alternative energy source to conventional diesel derived from fossil materials, which are unsustainable and non-renewable and contribute to global warming. BD production via transesterification with methanol leads to the synthesis of glycerol; this process accounts for 10% (w/w) of the total BD produced worldwide. The increasing demand for environmentally harmless BD has created a glycerol glut, which must be utilized to increase BD profitability. Glycerol is a stable and multifunctional compound used as a building block in fine chemical synthesis. Acetylation and carboxylation pathways have been studied to utilize and/or upgrade glycerol into fine chemicals. The use of catalysts, especially heterogeneous catalysts, remains the green approach for tailoring carboxylation and acetylation routes to achieve the desired products, namely, glycerol carbonate and glycerol acetyl esters, respectively. However, side-product formation, poorly structured channels of some catalysts, and catalyst deactivation or reusability hinder the effective utilization of heterogeneous catalysts and must be further studied. Moreover, introduction of variations to optimize reaction-influencing parameters is a potential green method that must be explored.

Contents

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1. Introduction

In search for alternative sources of energy to fossil-derived fuel, researchers have focused on producing biodiesel (BD) fuel from biomass feedstock [1,2]. These feedstocks, including fatty acid-containing materials (triglycerides or fatty acid methyl esters (FAME) in free acid state or linked to other molecules), *Jatropha* seed, and algae, can be utilized to produce BD [3]. Fatty acid-containing materials comprise vegetable oils, animal fats, waste greases, and non-edible oils from seeds (e.g., *Jatropha* seed). The estimated global production of BD for 2015 is 3.1×10^{10} L and projected to increase by 11×10^{10} L by the year 2020 [4]. With increasing demand for BD, price increase in food-grade materials, such as vegetable oils, threatens the global food security [5]. As such, a low-cost alternative route, that is, using low-cost feedstock in BD production, has been proposed to reduce or avoid the utilization of food-grade materials [2]. These low-cost feedstocks can be sourced from non-edible oil sources, waste cooking oil, grease, *Jatropha* seed oil, and algae [1,6]. Nevertheless, the quality of feedstock utilized in BD production must be assessed for impurities, which may reduce the quality and affect the market value of the synthesized BD [7].

Triglyceride transesterification is a widely studied, applied, and industrially utilized synthesis pathway for BD production; this process involves three methanol molecules, a base or acid catalyst, and one- or two-phase reaction systems at ambient conditions or high temperatures and pressures to produce BD (FAME) and glycerol as byproducts [8]. The United States Department of Energy reported that in clean cities, the average cost per gallon of 100% BD is approximately USD 0.89 higher than that of fossil diesel fuel [9]. The high cost of BD could be due to high production cost, which is primarily driven by high energy requirement. Therefore, the price difference between BD and fossil diesel must be eliminated to make BD production attractive.

Glycerol (1,2,3-propanetriol) [10–15] is the major byproduct of BD production, that is, 10 kg of glycerol is produced for every 100 kg of BD [16–18]. As such, glycerol supply linearly increases with increasing BD demand. The global production of glycerol increased from 200,000 t in 2003 to 600,000 t in 2006; an additional amount of more than 2×10^6 t of glycerol was produced in 2011, and an increment of more than 2×10^6 t in glycerol supply, including the fractions obtained from the production of oleochemicals, was observed in 2012 [19]. Glycerol production is estimated to reach 4.2×10^9 L by 2020, provided that all market forces are constant [4]. The increasing global demand for BD has created a glycerol glut, which affects the glycerol market. For example, in 2007, the refined glycerol is as cheap as approximately USD 0.30/lb compared with the price (USD 0.7/lb) prior to the expansion of BD production in the United States. Accordingly, the price of crude glycerol sharply declined from about USD 0.25/lb to USD 0.05/lb [20]. In 2013, the cost of refined crude glycerol was approximately USD 900–965/t (depending on the raw material used in BD production), whereas that of crude or unrefined glycerol (approximately 80% purity) was nearly four times lower (approximately USD 240/t) in mid-2014. Therefore, the decreasing price of unrefined glycerol and the high cost of BD production require novel approaches of glycerol utilization to reduce the net energy requirement for BD production, compensate for the cost difference between BD and fossil diesel, and increase the market viability of BD. Meanwhile, the sustained low market value of glycerol may increase its potential for numerous applications.

Glycerol is a stable compound that consists of three hydroxyl functional groups, which render this compound with hydrophilic and hygroscopic properties. The molecular structure and physicochemical properties of glycerol confer the multi-functionality of this compound [11]. In an attempt to utilize glycerol, animal feed aggregates were produced using unmodified glycerol in the past [21]. However, the lack of understanding on impurity concentration levels and aggregate ratios of glycerol poses a barrier for effective utilization [21]. The upgrading of glycerol into value-added products has been recently studied. Table 1 summarizes the findings of several studies on purification techniques, upgrading routes, and applications of glycerol.

With continuous vast research on glycerol upgrading, recent studies have focused on the shift toward the production of glycerol-free BD. In this concept, glycerol derivatives, such as monoglycerides or glycerol carbonate (GC), are produced by utilizing lipids and various acyl acceptors, instead of methanol [30]. Studies indicated that triglyceride transesterification with ethyl acetate [31], methyl acetate [32], and dimethyl carbonate (DMC) [33] as acyl acceptors produces three molecules of fatty acid methyl or ethyl esters and one molecule of GC or glycerol triacetate (triacetin, TAG). These compounds exhibit the physicochemical properties of BD-like fuel and can be utilized in diesel engines without modification. Calero et al. [34] studied recent technologies to produce glycerol-free BD or glycerol-blended BD (Ecodiesel® and Gliperol®). In this study, the atom efficiency of these technologies is 100% because no byproduct or glycerol is generated

Table 1
Conducted studies on glycerol upgrading, purification steps and applications.

No	Conducted studies on glycerol	Ref.
1.	Conducted studies on several reaction pathways such as selective oxidation, selective hydrogenolysis, selective dehydration, pyrolysis, selective transesterification, carboxylation for glycerol upgrading to commodity chemicals.	[22]
2.	Recent challenges in optimizing glycerol steam reforming process to obtain hydrogen fuel with emphasis on thermodynamic behavior of the process, current catalytic application prospects and kinetics was reviewed with critical outlook.	[23]
3.	Studies on glycerol dehydration to acrolein in both petroleum and bio-based processes and textural properties of the applied solid catalysts for both liquid and gaseous phases, techniques employed in acrolein production and industrial cost feasibility of the process as factors that can affect acrolein selectivity and yield.	[10]
4.	Teng et al. elucidated various catalyst applications and methods utilized in synthesis of glycerol carbonate via catalytic transesterification reaction of glycerol and carbonate sources. Insights on catalysts performance, reaction influencing parameters and energy effectiveness of the underlying transesterification process were critically studied.	[14]
5.	Tan et al. conducted studies in details about various glycerol purification steps and technique with suggestions on industrial applications and challenges still facing some of the purification steps as a barrier for commercialization.	[24]
6.	Conducted separate reviews on glycerol oligomerization via etherification to produce hyper branched ether structures; they studied different production routes, application and catalysis of the process with a view of revealing pathways that are more environmentally benign to obtaining glycerol oligomers.	[25,26]
7.	Studied theoretical evaluation utilizing density functional theory calculation for acetylation via esterification of glycerol with acetic acid and acetic anhydride to produce glycerol acetates. They concluded that acetylation route using acetic acid is thermodynamically resisted while that of acetic anhydride is thermodynamically preferable as the reaction is exothermic. Unfortunately, the later has been documented as substance used for synthesis of narcotics and a contraband chemical.	[27]
8.	Conducted separate studies on carboxylation and acetylation with listed applications of fine chemicals obtained for glycerol upgrading via the two routes.	[28,29]