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A review on glycerol valorization to acrolein over solid acid catalysts

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ABSTRACT

The projected rise in global biodiesel production and demands inevitably implied a linear rise in glycerol production. The paper therefore critically tailored recent literature on the progress made regarding the glycerol to acrolein process. Emphasis was given to the role of catalysts such as oxides, heteropoly acids, zeolites and silicoalumino phosphates (SAPOs) and their associated activity and stability properties. Concise details on the reaction mechanisms and the strategies being employed to ensure optimal catalytic performance, hinder deactivation and improve product yields were also appropriately captured and analyzed. An outlook was simultaneously tailored to identify new paths for future research.

1. Introduction

The unsustainability and environmental challenges associated with fossil fuels production and utilization have in the recent years triggered interest for a shift to renewable feedstocks, as alternative sources of energy and petrochemicals. Burning of fossil fuels emits large quantities of CO_2 and other greenhouse gases with strong potentials to pollute the global environment [1-5]. Biofuels are therefore currently considered as key prospective alternatives that could help in addressing these difficulties. Among the biofuels, biodiesel is widely accepted as an important fuel that can be used directly or as a blend without compromising engine specifications [6-11]. Its production had been on the rise in many areas around the world. For example, according to the recent statistics, biodiesel production in the United States was 20 million gallons in 2003 but increased to 700 million gallons in 2008. In the year 2011, the production hits 1.1 billion gallons and later 1.8 billion gallons in 2013 [12]. By the year 2000, the total global biodiesel production was 0.8 billion gallons but increased to 4 and 16 billion gallons in 2005 and 2010, respectively, with continuous increase predicted for the future up to 2050 [13]. Biodiesel is mainly produced from the process of transesterification via which fats and/or oils of plants and animals react with short chain alcohol like methanol under either homogeneous or heterogeneous conditions. The reaction products are the methyl esters (*i.e.* biodiesel) and glycerol [14]. While the methyl esters are employed as fuels, the glycerol is employed as raw-material for the petrochemical industries. The projected rise in biodiesel production inevitably sends a signal on the simultaneous rise in associated glycerol production. According to statistics, in 2008, the world production of biodiesel reached 11.1 million metric tons with 32.6 million metric tons capacity. There are projections that by 2016, biodiesel market will hit 37 billion gallons, given rise to an average growth rate of 42% per annum. According to these statistics glycerol production can hit 6 billion gallons by that period [15]. Among the key players, countries in the Asia, USA and the Western Europe stand for 75% of the net global glycerol consumption in 2011 [16]. The Asian region consumed 36% of the whole world consumption in that year. China alone accounted for 18%, with predictions that the consumption will further grow due to advances in the epichlorohydrin manufacture from glycerol. In 2016, the persistent rise in glycerol-to-pharmaceuticals in China will shift the consumption to 27% with overall growth of 45% focused for the whole Asia [16]. Countries in the Western Europe consumed about 26% in 2011 with projections of 8% growth annually. In other parts of Europe and Africa, the consumption had been projected to rise by 7% and 9%, respectively [16]. Therefore, devising more industrial options for its valorization would be very beneficial for the industries [17-19]. Glycerol had been successfully converted into a range of fuels and petrochemicals including diesel, light naphtha, succinic acid, synthesis gas, olefins and polyesters [14,20–28]. There are recent reports that diesel and gasoline range hydrocarbons could be generated from glycerol [29]. Figure 1 illustrates some of these species that can be obtained from glyc-

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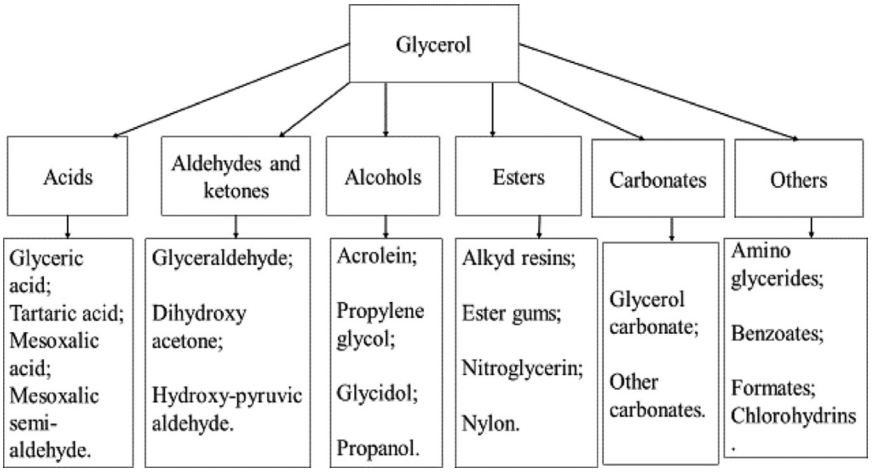

Fig. 1. A range of some compounds that could be derived from glycerol.

erol [30]. An important derivable industrial raw-material that is gaining attention in the recent years is the acrolein. It is commonly employed as good candidate for the synthesis of compounds like amino acids, polymers, herbicides and many other classified products. The vast applications have thus triggered research on sustainable production routes, especially in relation to catalysts and reaction conditions [31-35]. This paper therefore critically reviewed the recent progress on the conversion of glycerol to acrolein. Issues related to catalysts explored and their associated activity/stability properties were carefully and appropriately captured and examined.

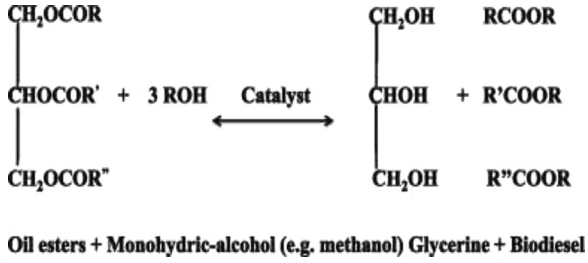

Fig. 2. Chemical equation for glycerol/biodiesel production from oils/fats. Adapted from Ref. [14].

2. Green glycerol production

Since from the 1940's, various options have been investigated for commercial glycerol production. Production from propene based intermediates such as allyl alcohol, epichlohydrin and propene oxide was among these early options [36,37]. With allyl chloride, oxidation into dichlorohydrin is first achieved using hypochlorite. Hydroxide of calcium or sodium is then employed as catalyst to convert the dichlorohydrin into epichlohydrin. Glycerol is subsequently synthesized by the process of hydrolysis. During the process, aqueous NaOH or Na_2CO_3 is utilized at temperatures closer to 200 °C and 1 atm to achieve high yield (up to 98%) of glycerol. Alternatively, propene can be transformed into propene oxide by the process of epoxidation, followed by subsequent isomerization to produce allyl alcohol, which is subsequently epoxidised to yield glycidol using peracetic acid. Glycerol could finally be obtained by hydrolysis of the glycidol in basic media. The major problems with propene-intermediates-glycerol routes are; (1) dependence on propene, which is mainly derived from fossil fuels, as primary feedstock and (2) homogeneous nature of the reactions. These make the process unsustainable and environmentally challenging.

The two key biomass-based options (green routes) to glycerol production are the hydrogenation of carbohydrates and the transesterification for biodiesel synthesis. Green routes to fuels and petrochemicals syntheses always target processes that ensure environmental sustainability without comprising quality and efficiency [38,39]. In the former case (*i.e.* carbohydrate hydrogenation), transition metals based oxides usually of Ni, Cu and W, are employed as catalysts to hydrogenate biomass-based polyalcohols like starch and sugars [40,41]. The reaction yields a mixture of glycols that could be separated via distillation process. A considerable difficulty here is that, glycerol derived through this method is of very low quality and therefore special expensive refining operations are necessary. These escalate the process cost and render the overall process less-attractive. Glycerol production via the transesterification route is also not without challenges, but is the commercial option gaining much interests in the recent times, particularly due to the rapid growth in the production and demands of biodiesel as fuel. The transesterification process (Fig. 2) proceeds by the reaction of triglyceride esters in fats/oils with short chain alcohol (usually methanol) to produce mono-alkyl esters (*i.e.* biodiesel) and glycerol as the only reaction products [42,43]. The reaction can be achieved using both homogeneous and heterogeneous catalyst systems [44,45]. Among the homogeneous catalysts, strong bases (*e.g.* hydroxides of sodium and potassium), their derived methoxides and common acids like hydrochloric and sulphuric acids are very popular [46,47].

Homogeneous transesterification produces low purity glycerol because the catalyst systems are themselves soluble in both the biodiesel and glycerol [48]. This factor implies that, high-degree purification is necessary to achieve good quality product and consequently escalated process cost. Another important issue to be considered is the corrosive nature of the hydroxides and acids, as well as their environmental disposal problems. These therefore attributed for a shift to the exploitation of a range of heterogeneous catalysts. Solid basic or acidic catalysts yield slower reaction rates compared to the homogeneous catalysts but they can produce equivalent yields of both biodiesel and glycerol. They can easily be separated by simple methods and are subject to recycle and reuse given optimal performance. Catalysts in this category include metal oxides and carbonates, zeolites, heteropoly acids, et cetera [49–52]. Transesterification is normally conducted employing reaction temperatures closer to the boiling point of the monohydric-alcohol (*e.g.* 50–65 °C for methanol), using stoichiometric oil/alcohol ratio (*i.e.* 1:3). However, the process being equilibrium dependent

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