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Review

Value-added processing of crude glycerol into chemicals and polymers

Xiaolan Luo [1], Xumeng Ge [1], Shaoqing Cui, Yebo Li *

Department of Food, Agricultural and Biological Engineering, The Ohio State University/Ohio Agricultural Research and Development Center, 1680 Madison Ave., Wooster, OH 44691-4096, USA

HIGHLIGHTS

- Crude glycerol components vary with the feedstock and biodiesel production methods.
- Routes for direct conversion of crude glycerol to high-value products are reviewed.
- Low product yield and productivity and impacts of impurities are major issues.
- Low production issues may be addressed by techniques developed with pure glycerol.
- Strategies for addressing the impurity issues are discussed.

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ABSTRACT

Crude glycerol is a low-value byproduct which is primarily obtained from the biodiesel production process. Its composition is significantly different from that of pure glycerol. Crude glycerol usually contains various impurities, such as water, methanol, soap, fatty acids, and fatty acid methyl esters. Considerable efforts have been devoted to finding applications for converting crude glycerol into high-value products, such as biofuels, chemicals, polymers, and animal feed, to improve the economic viability of the biodiesel industry and overcome environmental challenges associated with crude glycerol disposal. This article reviews recent advances of biological and chemical technologies for value-added processing of crude glycerol into chemicals and polymers, and provides strategies for addressing production challenges.

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* Corresponding author.
E-mail address: li.851@osu.edu (Y. Li).
[1] Both authors contributed equally to this work.

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1. Introduction

Crude glycerol, also referred to as crude glycerin, is commonly generated during the production of biodiesel. Crude glycerol is traditionally refined to pure glycerol, a useful raw material for industries, such as foods and beverages, pharmaceuticals, cosmetics, tobacco, and textiles. In 2014, over 67% of the pure glycerol globally produced is from biodiesel-derived crude glycerol (Radiant Insight Inc., 2015).

Biodiesel production in the United States grew rapidly from 250 million gallons in 2006 to 1.8 billion gallons in 2013 (National Biodiesel Board, 2014). With approximately 1 kg of crude glycerol generated for every 10 kg of biodiesel produced, the large quantities of crude glycerol produced each year have impacted the glycerol market, resulting in low prices of refined glycerol and crude glycerol. Crude glycerol has been a financial and environmental liability of the biodiesel industry. Thus, it is imperative to convert crude glycerol into higher-value products in order to improve the economic sustainability of the biodiesel industry and reduce environmental impacts of crude glycerol waste disposal.

One route for value-added processing of crude glycerol is to produce pure glycerol, *via* refining processes, e.g. the "Universal Recovery Strategy" that has been developed for recovery of valuable compounds from food by-products (Galanakis, 2012). Purified glycerol can be converted into various value-added products, which has been well reviewed previously (Clomburg and Gonzalez, 2013; Tan et al., 2013). However, this route may not be economically feasible for small- or medium-sized biodiesel producers due to the high cost of refining processes. Shipping crude glycerol to a glycerol refinery is only viable when a group of biodiesel plants are located within a limited area. Another route is to directly convert crude glycerol into value-added products, which can be achieved via either biological or chemical pathways. In recent years, there has been an increase in research on direct utilization of crude glycerol for the production of value-added products, such as butanol, 1,3-propanediol, 2,3-butanediol, citric acid, lipid, poly(hydroxyalkanoates), acrolein, monoglycerides, maleated glycerides, polyglycerol, solketal, polyols, and bio-oils. These chemicals and polymers have extensive applications as biofuels, fuel additives, detergents, polymeric materials, and other uses. There are a number of articles that have reviewed conversion of crude glycerol to value added products (Almeida et al., 2012; Clomburg and Gonzalez, 2013; Dobson et al., 2012; Rahmat et al., 2010; Tan et al., 2013; Yang et al., 2012). However, some value-added products, such as 2,3-butanediol, polyglycerol, and polyols have generally been overlooked in these reviews. Besides, strategies for specific issues in conversion of crude glycerol to value added products have not been well discussed in previous reviews. In addition, most of the reviews focus on only one approach, either biological or chemical conversion (Almeida et al., 2012; Clomburg and Gonzalez, 2013; Dobson et al., 2012; Rahmat et al., 2010).

This paper reviews the chemical composition of crude glycerol from different biodiesel production processes, as well as routes for value-added conversion of crude glycerol, with a focus on direct utilization of crude glycerol to produce chemicals and polymers, including 1,3-propanediol, butanol, 2,3-butanediol, citric acid, lipid, poly(hydroxyalkanoates), acrolein, monoglycerides, maleated glycerides, polyglycerol, polyols, and others. Both biological and chemical pathways are discussed. Strategies for addressing challenges to value-added processing of crude glycerol into chemicals and polymers are also provided.

2. Characteristics of crude glycerol

Biodiesel is produced by the transesterification reaction of triglycerides (including vegetable oils, animal fats, waste cooking oils, and algae oil) with an alcohol, mostly methanol, in the presence of a catalyst. In general, the transesterification reaction can be carried out using either acid or base catalysts. Acid catalysts such as sulfuric acid, hydrochloric acid, and solid acids, are suitable for the transesterification of low-grade oils containing water and free fatty acids, while base catalysts are commonly used for the transesterification of triglyceride feedstocks with low free fatty acids contents (Tan et al., 2013). Base catalysis also has advantages of high reaction rates and low methanol to triglyceride molar ratios. The base catalysts include alkaline metal alkoxides and hydroxides and heterogeneous solid metal-oxide catalysts. Among these, sodium hydroxide and potassium hydroxide are the most widely used base catalysts. Besides acids and bases, enzymes have also been developed to catalyze transesterification.

During the biodiesel production process, two phases usually form, with biodiesel located in the upper phase and crude glycerol in the lower phase, due to differences in densities and polarities. Crude glycerol is a mixture consisting of glycerol and some impurities, such as water, methanol, soap, and matter organic non-glycerol (MONG). Depending on the feedstock, the process used for biodiesel production, and the post-treatment methods used, the crude glycerol components vary. When seed oils such as Ida Gold Mustard, Pacific Gold mustard, rapeseed, canola, crambe, and soybean, and waste cooking oils were used as feedstocks, crude glycerol contained 62.5–76.6% (w/w) glycerol (Tan et al., 2013). During the base catalyzed processes for biodiesel production, soap is usually formed and included in the crude glycerol. In a biodiesel production process that used canola oil as a feedstock and sodium hydroxide as a catalyst, about 15.3% (w/w) soap was detected in the crude glycerol stream (Pyle et al., 2008). In another process for the production of biodiesel from soybean oil using potassium hydroxide as a catalyst, crude glycerol with approximately 25.2% (w/w) soap was obtained (Pyle et al., 2008). Compared to heterogeneous base catalysts, homogeneous alkali catalysts resulted in relatively high salt contents (5.0–7.0% based on weight) of crude glycerol (Yang et al., 2012). Additionally, crude glycerol with higher purity of glycerol were obtained by enzymatic