



Simultaneous production of lactic acid and propylene glycol from glycerol using solid catalysts without external hydrogen



Lu Liu, X. Philip Ye*

Department of Biosystems Engineering and Soil Science, The University of Tennessee, 2506 E.J. Chapman Drive, Knoxville, TN 37996, USA

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ABSTRACT

Development of value-added chemicals from glycerol, the co-product with biodiesel, is imperative in sustaining the biodiesel industry. Combined usage of a solid base and a copper-based catalyst provided a catalytic pathway to convert glycerol to racemic lactic acid. A new pathway was found that during the glycerol-to-lactic acid conversion, hydrogen was formed, which could be used in situ to generate propylene glycol catalyzed by the copper-based catalyst. This new pathway was attested by results of systematically experimental study investigating the synergistic functions of a base catalyst (CaO, MgO, or SrO) and a copper-based dehydrogenation catalyst (Cu, CuO, Cu₂O, or Cu₂Cr₂O₅). Different combinations of catalysts and reaction conditions provided a tunable range for the yield of lactic acid and propylene glycol. Emphasis was put on the combined use of CuO and CaO due to their inexpensive availability and ease of recyclability; at optimal reaction conditions, the yield of lactic acid reached 52 mol% together with 31 mol% yield of propylene glycol.

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1. Introduction

Biodiesel production capacity worldwide is increasing with regulatory and socioeconomic motivations for renewable energy. One mole of glycerol is generated along with each mole of triglyceride converted to biodiesel. As a result of biodiesel growth, large amount of glycerol is produced and therefore available to the marketplace. Various sources [1,2] have reported that the price of glycerol has been lowered by its large availability, and even credits are given for selling the crude glycerol. Development of value-added chemicals from glycerol, the co-product with biodiesel, is necessary to help sustain the biodiesel industry. Glycerol is listed among the 12 top building block chemicals from renewable biomass by the U.S. Department of Energy (DOE) [3].

Lactic acid (LA) has been viewed as a “commodity chemical sleeping giant”, owing to its reactive functionalities that make it readily convertible to other important commodity chemicals, such as ethyl lactate and poly(lactic acid). Currently, LA was primarily produced via fermentation of carbohydrates, which suffers from low productivity and efficiency and may not be sufficient to meet the increasing demand of LA in the chemical industry [4]. In the past few years, researchers have made some progress in converting glycerol to lactic acid via chemical catalysis [5–10]. A couple of patent disclosures [11–13] also described the catalysis and processes converting glycerol to lactic acid. In these alkali

catalyzed glycerol-to-LA conversions, it is generally agreed on that reaction pathway of glycerol to lactic acid is through glycerolaldehydes, 2-hydroxypropenal, and pyruvaldehyde. In an aqueous alkaline condition, LA existed as lactate salt in the product. Such a mechanism was detailed in literature [5], suggesting that dehydrogenation of glycerol to glycerolaldehydes is the initial step, where one hydrogen molecule is released from one glycerol molecule.

Propylene glycol (PG, IUPAC name propane-1,2-diol) is another important chemical. It can be used as an industrial solvent and functional fluid (e.g. antifreeze, lubrication), or as an additive in foods, cosmetics and pharmaceutical products. It is also used for the production of unsaturated polyester resin. The large-scale commercial synthesis is through high pressure and high temperature hydrolysis of propylene oxide, which becomes unappealing from a sustainability point of view. On the contrary, glycerol-to-PG pathway provides an attractive alternative for PG production in this regard. Many studies have addressed the hydrogenolysis of glycerol to PG, and demonstrated that the glycerol-to-PG is a possible conversion route with pressurized hydrogen supply in the presence of metallic catalysts [14–35]. All of these studies require the supply of H₂, and most of them require highly pressurized conditions. Byproducts such as ethylene glycol, 1,3-propanediol, and butanediol were claimed by most of the studies. To the best of our knowledge, LA has never been claimed as a major co-product to PG.

To date, almost all reported glycerol-to-LA studies via chemical catalysis were conducted using homogeneous alkaline solutions; more specifically, good LA yields were achieved with homogeneous solution

* Corresponding author. Tel.: +1 865 974 7129; fax: +1 865 974 4514.
E-mail address: xye2@utk.edu (X.P. Ye).

of either NaOH or KOH. High corrosiveness caused by NaOH and KOH at hydrothermal conditions constrained the allowable concentration of alkaline, and consequently concentration of glycerol in the reactants. This limitation negatively influences the productivity of LA. Furthermore, there is no inexpensive separation process to remove NaOH/KOH from the products, hindering the promotion of industrialization of the technology. Meanwhile, most processes developed for glycerol-to-PG conversion require external supply of hydrogen, which is associated with additional purchase and handling costs. Depending on the hydrogen source, the developed PG process, which is supposed to be based on renewable resources, could become dependent on fossil fuels. It is important to point out that in the dehydrogenation of glycerol to LA, hydrogen gas is released, which could potentially allow in situ transformation of glycerol to PG.

Previously, glycerol-to-LA conversion was studied in our lab with the presence of only CaO as solid catalyst; an ~40% LA yield with an ~97% glycerol conversion was reported when 0.4 mol CaO was used per mole glycerol at an optimized reaction condition (290 °C for 150 min) [36]. One of the major advantages of the method is free of solvent, meaning overall higher productivity (compared to fermentation route) and less energy wasted in heating a solvent to the desired temperature. However, over 50% carbon loss was observed which might be due to polymerization (products lost in the solid phase) or decomposition (CO₂ lost in the gas phase). We reasoned that high temperature favored these undesirable reactions; therefore, we were seeking an additional catalytic ingredient to further decrease the activation barrier and to allow the formation of LA at a lower temperature. We accidentally found that significant yield of PG along with LA and improved carbon balance resulted from the addition of a copper-based catalytic ingredient.

Therefore, the objective of this study was to systematically investigate the potential of simultaneous and tunable production of LA and PG from glycerol, utilizing heterogeneous catalytic technology. The solid catalysts were to be developed, and the influences of different reaction conditions (e.g. reaction temperature and time) were to be studied.

2. Materials and methods

2.1. Overview

Base catalyst plays an important role in the formation of glyceroxide ion; benzilic acid rearrangement (formation from pyruvaldehyde to LA) usually occurs in a basic environment [5,7]. In addition, the base would

react with LA via acid–base neutralization to form lactate, which not only shifts the reaction equilibrium toward LA formation, but also helps protect LA from decomposition or polymerization. Therefore, base is an indispensable catalyst ingredient for glycerol-to-LA conversion.

As previously mentioned, dehydrogenation of glycerol to glyceraldehyde is the initial step, where one hydrogen molecule is released from one glycerol molecule. The addition of a dehydrogenation catalyst might assist the transition of glycerol to glyceraldehyde, and ultimately catalyze the glycerol-to-LA conversion. Therefore, we were to incorporate both a base ingredient and a dehydrogenation ingredient in our catalyst design. At first, we were to search for a good performer as the dehydrogenation ingredient. Copper-containing catalysts are common selections for catalyzing dehydrogenation reactions. Therefore, we conducted a comparison among several copper-containing catalysts, including copper metal (Cu), cuprous oxide (Cu₂O), copper oxide (CuO), copper chromite (Cu₂Cr₂O₅), and barium promoted copper chromite (Ba-Cu₂Cr₂O₅). While the dehydrogenation ingredient was a variable, the reaction condition and base ingredient remained the same, which were 60 min at 190 °C with CaO in a molar ratio of 0.4 mol/mol to glycerol. Previously, Roy et al. added 0.04 mol Cu₂O (per mol glycerol) to a NaOH-catalyzed reaction, which successfully lowered reaction temperature [37]. Such a molar ratio was adopted for the dosage of Cu₂O in our experiments. To draw a fair comparison, the ratio of the catalyst to glycerol was calculated based on the elemental Cu. Therefore, the ratio of 0.04 mol/mol of glycerol was used for Cu₂Cr₂O₅ and barium promoted Cu₂Cr₂O₅, but the ratio of 0.08 mol/mol of glycerol was used for Cu and CuO.

Importantly, our focus was on the base ingredient. Comparisons were conducted among different dosages of CaO (0, 0.1, 0.2, 0.3, 0.4, and 0.5 mol/mol of glycerol), and different solid bases (MgO, CaO, SrO). The reason that we paid great attention to CaO was that 1) CaO was inexpensive and readily available; 2) CaO has good basicity; and 3) it was based on our previous study using CaO [36]. While the base ingredient was the variable, the reaction condition and dehydrogenation ingredient remained the same, which were 60 min at 190 °C with Cu₂O in a molar ratio of 0.04 mol/mol to glycerol.

We then studied the effects of reaction temperature and time on glycerol conversion and product selectivity using the best combination of base ingredient and dehydrogenation ingredient (namely, CaO and Cu₂O; the details are to be presented in the [Results and discussion](#) section). We found an optimal condition for this combination of catalysts. However, we had difficulties with Cu₂O in our attempt to regenerate the spent catalysts because it is costly to control the Cu in its +1 active

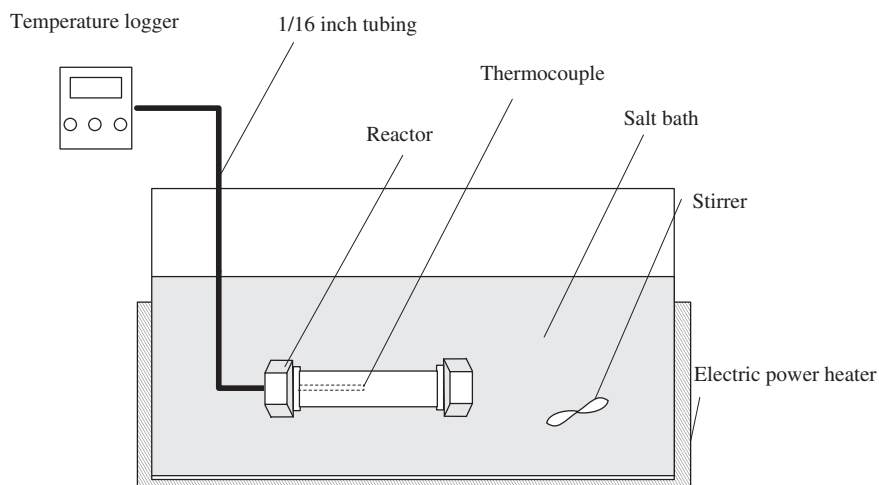


Fig. 1. Schematic of the reaction system.

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