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Catalytic conversion of glycerol to value-added chemicals in alcohol

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A B S T R A C T

With the aim to directly use the mixture of glycerol and methanol from the biodiesel production for value-added chemical production, catalytic conversion of refined glycerol to lactic acid (LA) and propylene glycol (PG) using mixed solid catalysts of CaO and CuO in methanol medium was first investigated. At the optimum condition, the yields of LA and PG achieved were 46 mol% and 35 mol%, respectively. For recycling the catalysts, a combined process of glycerol conversion to alkyl lactate was further investigated. Using this integrated process, 45 mol% methyl lactate yield and 28 mol% PG yield were achieved in methanol medium, and 45 mol% ethyl lactate and 18 mol% PG yield were achieved in ethanol medium. The test for crude glycerol conversion showed that the impurities had slightly negative effects on glycerol conversion and product yield in methanol medium but no obvious effect in ethanol medium. Similar glycerol conversion and product yield were obtained when the mixture of glycerol, methanol, and CaO from biodiesel production were directly used as starting material. This result suggests that the mixture from biodiesel production can be directly used to produce valued-added chemicals such as methyl lactate and PG.

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1. Introduction

With the increasing concern on greenhouse gas emission, global biodiesel production has greatly increased in the last ten years. In the U.S., biodiesel production also increased dramatically and is predicted to grow to approximately 912 million gallons in 2015 [1]. Glycerol, principal by-product in biodiesel production, has been overproduced because of this fast increase of biodiesel production, and today's market of glycerol has been saturated and the supply of glycerol is independent its demands [2]. Therefore, converting glycerol to value-added chemicals will open new markets for glycerol application and improve the sustainability of biodiesel production.

Lactic acid (LA) and its derivatives such as alkyl lactate are being used in food, chemical and pharmaceutical industries [3,4]. With the increase in environmental concerns, LA and alkyl lactates has drawn great interest for being used as green solvents and building block for biodegradable plastics.

Glycerol as starting material for LA production via chemical synthesis route has been intensively investigated in the past few years [5–9]. Kishida et al. reported 90% LA yield obtained in glycerol conversion with 1.25 M NaOH at 300 °C for 90 min [5]. Shen et al. studied the effects of different alkali-metal hydroxides and alkaline-earth hydroxides on the glycerol conversion and LA production; they found that KOH and NaOH were more effective catalysts than others and LA could be yielded to 90% in hydrothermal conversion of glycerol at 300 °C with KOH or NaOH as a catalyst [6]. To improve LA productivity, Ramirez-Lopez et al. investigated the conversion of high concentration (2.5–3.5 M) of glycerol using NaOH as catalyst and achieved 84.5% LA yield when using a 2.5 M glycerol concentration at the reaction condition of 280 °C and 90 min with a 1.1 NaOH/glycerol molar ratio [10]. However, strong alkali catalysts used in the previous reports resulted in high corrosiveness to reactors and problematic downstream separations. To reduce the negative effects of high alkalinity, Chen et al. developed a fed-batch process to convert glycerol to LA with NaOH and observed lowered corrosiveness to stainless steel reactors [11]. Although high glycerol conversion and LA yield were achieved in previous studies, it is worth noting that LA produced in the process was of low purity and existed in the form of lactate salt. Tedious processes such as esterification, hydrolyzation, and distillation to such produced LA will be required and gypsum will be produced to obtain high purity LA [12–15]. Therefore, from both an economic and environmental viewpoints, directly producing methyl lactate or ethyl lactate is preferred.

Propylene glycol (PG) is also an important chemical served as functional fluid in antifreeze and lubricants, additive in foods, cosmetics and pharmaceutical product, and intermediate chemical in the production unsaturated polyester resins. Catalytic hydrogenolysis of glycerol to PG using metallic catalysts with pressurized hydrogen supply has been intensively investigated and progress has been made [16–21]. However, one major issue associated with this process is that an external hydrogen source is required. Several efforts have been made seeking an in situ hydrogen supply instead of an ex-situ hydrogen source, but the selectivity and yield of PG were low [22,23].

Calcium oxide (CaO) as a solid catalyst in biodiesel production has been reported [24–28]. In our previous study, CaO as a solid catalyst for LA production has been investigated and 40.8 mol% LA yield with a

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glycerol conversion of 97.8 mol% was achieved at optimal conditions [29,30]. Copper-based catalysts in PG production from glycerol has also been reported [31–33]. However, water was usually used as solvent to dilute the glycerol in previous studies for LA and PG production. However, in the biodiesel production, considerable amount of methanol remains with crude glycerol after separating the biodiesel. The separation of methanol, catalyst, and the purification of crude glycerol are costly. Directly using the mixture of glycerol, methanol, and catalyst from biodiesel production for value-added chemical production is desirable. Therefore, catalytic conversion of glycerol in alcohols should be evaluated.

The major objective of this study was to investigate catalytic conversion of glycerol to value-added chemicals in methanol or ethanol solvent using mixed solid catalysts of CaO and CuO. Process conditions such as reaction time, catalyst and methanol loading amount were optimized. Integrated conversion of glycerol in alcohol media to alkyl lactate was also investigated. Direct use of industrial crude glycerol was further investigated in order to evaluate the effects of impurities on the glycerol conversion and product yield. Calcium oxide catalyst for both soybean oil transesterification with methanol to biodiesel and the subsequent crude glycerol conversion to methyl lactate were also investigated.

2. Materials and methods

2.1. Materials

Refined glycerol (99.5%) used as the starting material was first investigated in this study. CaO and CuO were used as solid catalysts. Before use, CaO was calcined at 910 °C in a muffle furnace for 3 h to remove $Ca(OH)_2$ and $CaCO_3$ formed during the storage. Anhydrous methanol (99.99%) and ethanol (99.99%) were used as solvents and reactants in the conversion of glycerol. LA (90%), methyl lactate (>96%), ethyl lactate (>96%), and PG (>99.5%) were used as standard chemicals. All these chemicals, refined glycerol, and catalysts were purchased from Thermo Fisher Scientific, Inc. (Waltham, MA). Carbon dioxide in the form of dry ice (> 99%) used in this study was purchased from a local supplier (Airgas, Knoxville, TN).

2.2. Reaction procedure

The reactions were performed in batch tube reactors made of stainless steel (SS316). The volume of the tuber reactor is 2.72 mL with the outside diameter (OD) of 9.53 mm, the inside diameter (ID) of 7.04 mm, and the length of 70.00 mm. The process of glycerol conversion was carried out in a heated oil bath. Glycerol, catalysts, and alcohol with a pre-calculated molar ratio based on experimental design were well mixed and placed into the reactor. Before sealing the cap, the reactor was degassed by purging with nitrogen. Then the sealed reactor was immersed into the preheated oil bath for designated time lengths. After the reaction, the reactor was quenched in an ice-water bath immediately, and the product sample was collected for analyses.

2.3. Glycerol conversion to LA and PG using CaO and CuO in methanol

The process conditions of glycerol conversion to LA and PG using solid catalysts in methanol were first investigated. According to our previous study, the optimum reaction temperature for glycerol conversion to LA (product existed in the form of calcium lactate) using CaO and CuO was 230 °C without alcohol solvents [30,34]. Therefore, in this study, we fixed the reaction temperature at 230 °C, and reaction time ranged from 60 to 300 min was studied. To determine the effects of catalyst loading on the glycerol conversion and product production, different CaO loading (molar ratios of CaO to glycerol at 0.4, 0.6, 0.8, and 1) and CuO loading (molar ratios of CuO to glycerol at 0.05, 0.1, 0.15, and 0.2) were investigated. The molar ratios of methanol to glycerol ranged from 3 to 6 were tested to evaluate the effects of methanol in glycerol conversion.

2.4. Alkyl lactate production from refined and crude glycerol

Because LA exists in the form of calcium lactate in the conversion of glycerol using CaO catalyst with methanol solvent, the tedious recovery of LA is still required, and gypsum ($CaSO_4$) will be produced. To recover the LA and avoid the gypsum production, an integrated process for alkyl lactate production, which includes the glycerol conversion to calcium lactate and PG in methanol/ethanol solvent and calcium lactate transesterification with methanol/ethanol and carbon dioxide, was studied. The refined glycerol and two types of crude glycerol (Table 1) obtained from biodiesel industry were used as starting materials. The conversion of glycerol in methanol/ethanol solvent to calcium lactate and PG was conducted at the optimum condition obtained in Section 2.3 (230 °C, 240 min, CaO/glycerol = 0.8, CuO/glycerol = 0.2, and methanol/glycerol = 5). The subsequent calcium lactate conversion to methyl or ethyl lactate was conducted at 180 °C/240 min or 220 °C/240 min, respectively, based on our previous study [34]. To reach the optimum condition, additional methanol or ethanol (molar ratio of methanol/ethanol to glycerol at 10) were added to the reactor before the transesterification of calcium lactate. In this study, dry ice was as the carbon dioxide source and the amount of dry ice added in the process was about 0.2 g. The autogenous pressure of the process reached about 10 MPa at the final reaction temperature.

2.5. Biodiesel and methyl lactate production

Biodiesel production from soybean oil with methanol and subsequent glycerol conversion to methyl lactate were investigated. The reaction of biodiesel production was carried out at 65 °C for 3 h, with a molar ratio of methanol to oil at 12:1, 8 wt.% CaO powder as catalyst based on oil weight, and 2.03 wt.% water (based on methanol), which is the same as the method reported by Liu et al. [28]. After biodiesel production, the sample was centrifuged and the top layer containing biodiesel and a small amount of methanol was separated and collected. The remaining mixture consisting of methanol, glycerol, and CaO was collected for methyl lactate production. To determine the biodiesel yield, the methanol in the collected top layer was distilled off under vacuum, and the biodiesel was weighted.

2.6. Sample analysis

The sample after reaction was washed out with deionized water (DI water), then centrifuged at relative centrifugal force (RCF) of 4070 g for 5 min. Clear liquid at the upper layer was collected, and pH value was adjusted to around 3 using 0.025 M H_2SO_4 in order to convert the unconverted calcium lactate to LA. Then the sample was fed through an ion-exchange column packed with DOWEX 50WX8-400 resin (Sigma Aldrich) to remove metal ions. The samples after ion-exchange were analyzed on an HPLC equipped with a Shodex SH 1011 column (300 × 8 mm), a refractive index (RI) detector (waters 410), and an Ultraviolet (UV) detector. The column temperature was set at 60 °C, and the mobile phase used was 0.5 mmol H_2SO_4 in DI water with a flow rate of 0.6 mL/min. The LA, glycerol, and PG were well identified by the RI detector, and the methyl/ethyl lactate was well identified by

Table 1
Compositions of crude glycerol.

ID no.	Glycerol (wt.%)	Water (wt.%)	Soap content (wt.%)	Methanol (wt.%)	Sodium (wt%)
CG1	85.4 ± 1.39	7.4 ± 1.54	2.8 ± 0.60	2.6 ± 0.40	4.1 ± 0.09
CG2	83.4 ± 1.59	13.0 ± 1.21	BDL[a]	0.5 ± 0.09	4.7 ± 0.15

[a] Below the detection limit.