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Research article

# Continuous production of lactic acid from glycerol in alkaline medium using supported copper catalysts

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ABSTRACT

With increasing demand for biodiesel, large quantity of crude glycerol has been produced both in Brazilian and world market, and this excess glycerol has become a problem that must be solved. Several studies have been performed with the objective to transform glycerol in value-added chemical products. Lactic acid has wide uses in chemical and food industries, and the hydrothermal transformation of glycerol to lactic acid is presented as an alternative to conventional production process. In this study, the production of lactic acid from glycerol under alkaline conditions, using copper (20 wt.% CuO) catalysts supported on $Al_2O_3$, ZnO and MgO in continuous flow reaction system was investigated. The catalysts were prepared by impregnation method and characterized by XRF, XRD, $N_2$ adsorption–desorption, TPR, and TPD-$CO_2$ and the dispersion of copper was determined by $N_2O$ oxidation. The reaction was carried out at 240 °C, 35 atm, with space velocity (WHSV) of 2 $h^{-1}$, 10 vol.% glycerol solution and NaOH/glycerol molar ratio of 0.5, 0.75 and 1.0. All catalysts showed high conversion of glycerol with yield and selectivity to lactic acid in the range of 80 and 90%, respectively, when the reactions are performed with NaOH/glycerol molar ratio of 1.0.



## 1. Introduction

Biomass has great potential to serve as a source of energy and sustainable carbon for our industrialized society. The production of fuels from biomass has potential to reduce emissions of greenhouse gases, compared to traditional fossil fuels. Furthermore, the $CO_2$ released is consumed during regeneration of the biomass. Thus, the development of renewable fuels and chemicals has become increasingly important over the last decade [1–7].

The biodiesel is typically produced by transesterification of vegetable oils or animal fats, and this process produces large amounts of glycerol as by-product. The production of a ton of biodiesel results in around 110 kg of crude glycerol, or 100 kg of pure glycerol [8]. In Brazil, according to National Agency of Petroleum, Natural Gas and Biofuels (ANP), the production of biodiesel (B100) in 2014 was approximately 3.45 million $m^3$, generating 345,000 $m^3$ of crude glycerol [9]. Biodiesel production is largely increasing in Brazil because of the compulsory addition of biodiesel to diesel: the addition of 2% biodiesel (B2) in diesel is mandatory since 2008, this amount increased to 5% (B5) in 2010 and after 1st of November of 2014, the percentage of biodiesel added to diesel reached 7% (B7). With the fast increase of glycerol supply in the world market the price of refined glycerol dropped from $1.20/kg in 2003 to $0.60/kg in 2006 [10], and in 2011 the price of crude glycerol in the United States reached the minimum value of $0.04–0.11/kg [11].

Glycerol is a very versatile raw material for producing various chemicals, polymers and fuels. Some of the processes described in the literature include polymerization; esterification to produce additives for fuels as octane; dehydration to produce acrolein, an important intermediate in the manufacture of polymers; selective oxidation to dihydroxyacetone, a versatile compound extensively used as a cosmetic ingredient, among others [12–14]. Furthermore, the catalytic conversion of glycerol with different metals under hydrogen or inert atmosphere can lead to a wide range of chemical products [15,16].

1,2-propanediol and lactic acid are two important chemicals that may be produced by catalytic conversion of glycerol. 1,2-propanediol is used in the food industry as antifreeze replacement of 1,2-ethanediol, being less toxic, and also used as a raw material in the production of films and polyester resins [17]. Lactic acid is widely used in cosmetic industry as moisturizing and in textile industry as a mordant (i.e. chemical that enhances the color durability of the tissue). Moreover, lactic acid is used in the dairy industry as a pH regulator, as a preservative or even as an inhibitor of bacterial spoilage. It is currently being used as a precursor of "green" solvents such as ethyl lactate, and also employed in the synthesis of poly lactic acid (PLA), which is increasingly used in the production of biodegradable packaging [18].

Currently commercial production of lactic acid is carried out by anaerobic fermentation of carbohydrates, such as glucose, sucrose

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