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# Catalytic conversion of biodiesel derived raw glycerol to value added products

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ABSTRACT

The huge amount of glycerol obtained during the production of biofuels has led to the search of alternatives for the use of this by-product. New applications for this polyol as a low-cost raw material need to be developed and existing ones need to be expanded. To address this problem, production of value-added molecules from crude glycerol is an effective alternative method for its disposal by incineration. Thus, the ready bioavailability, renewability and unique structure of glycerol make it a particularly attractive starting point for the production of a large number of specialty chemicals. The main purpose of this review is to focus on the catalytic reactivity of different kinds of catalysts in oxidation, dehydration, acetylation, etherification, esterification, acetalization, and ammoxidation process of glycerol conversion. Typical products are citric acid, lactic acid, 1,3-dihydroxyacetone, 1,3-propanediol, dichloro-2-propanol, acrolein, hydrogen, and ethanol. Recent studies on the catalysts, reaction conditions and possible pathways are primarily discussed.



**Contents**



## 1. Introduction

The traditional applications of glycerol are as additives in food, tobacco, and pharmaceuticals. Alkidic resins and polyurethanes are vital towards the application of glycerol, as they are all utilized as feedstock for the production added-value compounds, such as bio-plastic, platform chemicals, and fuels (Table 1). However, for glycerol to be incorporated into consumer products, it must be refined and purified. The main approach of green chemistry is the provision of simplified refinering and catalyst, while removing the need for purification through extraction [1]. Catalysts are tailored by controlling the size, spatial distribution, surface composition, thermal/chemical stability, shape, and electronic structure to reach the maximum selectivity on the glycerol conversion process (Fig. 1). Metal, metal oxides, and metal sulfides are the first batch of catalysts developed for hydrocarbon-based conversion that included partial oxidation and combustion reactions (Table 2). The development of highly porous, large surface area, heavily hydroxylated, functionalized, and pore

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**Table 1**
List of glycerol applications based on its natural characteristics.

| Applications | Glycerol characteristics |
|---|---|
| **Food industries**<br>● Humectant<br>● Solvent<br>● Antioxidant<br>● Sweetener<br>● Preserve Food<br>● Filler<br>● Thickening agent<br>● Sugar substitute | i. It does not feed the bacteria that form plaques and cause dental cavities<br>ii. Recognized as safe by the Federal Drug Administration and the U.S. food (FDA)<br>iii. Considered as carbohydrate<br>iv. Transesterified with alcohol to produce methyl (alkyl) ester |
| **Medical, pharmaceutical and personal care**<br>● Allergen immunotherapies<br>● Cough sirups<br>● Toothpaste<br>● Mouthwashers<br>● Skin care<br>● Expectorants and elixirs<br>● Products<br>● Hair care<br>● Table holding agents<br>● Fiber softener | i. Smoothness<br>ii. Provide lubricant<br>iii. Moisturizing properties<br>iv. Allowed as feed additive<br>v. Can cause a rapid, temporary decrease in the internal pressure<br>vi. Hydrolyzed or saponified to produce fatty acids<br>vii. Saponification with olive oil produces a sweet tasting substance |
| **Botanical extracts**<br>● Tannins prevention<br>● Alcohol free alternatives<br>● Removal of numerous constituents and complex compounds<br>● Preserving agent<br>● Cryoprotective agent for microorganisms | i. Low glycemic load<br>ii. Slowly absorbed by the body<br>iii. High degree of extractive versatility<br>iv. Good intrinsic property<br>v. High extractive power assumes<br>vi. Does not allow an inverting/reduction–oxidation of a finished extract's constituent<br>vii. Bacteriostatic in its action |
| **Antifreeze**<br>● Automotive applications<br>● Enzymatic reagents<br>● Acryoprotectant (for bacteria, nematodes, mammalian embryos) | i. Nonionic kosmotrope<br>ii. Able to form strong hydrogen bonds with $H_2O$ molecules<br>iii. Able to disrupt the crystal lattice formation of ice<br>iv. Freezing point $= -37.8$ °C (70% glycerol in water)<br>v. Non-toxic<br>vi. Formation of ice-crystals in the cell<br>vii. Maintaining stability and vitality of the cell wall during the freezing process |
| **Chemical intermediates**<br>● Nitroglycerin (ingredient of various explosives)<br>● Soap making (glycerin)<br>● Synthesis of resin and ester<br>● Sub-lingual tablets<br>● Ally iodide (blocks polymer, preservatives, organometallic, catalysts and Pharmecuticals) | i. Ethylene glycol functional groups<br>ii. Non-toxic |
| **Waste water treatment**<br>● Denitrification | i. Abundant carbon content<br>ii. Porosity<br>iii. Absorption ability |

diameters ranging from microporous-to-macroporous supported catalyst is intended to reduce the costs of large-scale applications [1].

## 2. Catalytic oxidation of glycerol

Green technology, entailing hydrothermal electrolytic decomposition of glycerol using continuous flow reactor and equipped with metallic catalysts, has been developed. This overcomes the technical barrier brought about by the oxidation of glycerol, which is the selective catalytic oxidation engineering that operates on a polyfunctional molecule and a simple oxidant [2]. The derived oxygenated products from glycerol include dihydroxyacetone, hydroxypyruvic acid, glyceric acid, tartaric acid, oxalic acid, mesoxalic acid, and intermediates (e.g.: glyoxylic acid, glyceraldehyde and glycolic acid) (Fig. 2 and Table 3). The most studied metallic catalysts are Pd, Pt, and Au, although the main disadvantage of Pt and Pd is their deactivation at high reaction times [3]. To overcome this probl;em, support materials are incorporated into the metal catalysts to produce a hybrid system. A major product of glycerol oxidation within Pt/C or Pd/C catalyst is glyceric acid, with a selectivity of up to 70% (Table 4).

The selectivity on the oxidation process of the secondary OH group of glycerol was significantly improved by combining Pt with other metals, such as Bi, resulting in a yield of 30% hydroxyacetone at a 60% conversion rate. Pt/C combined with Bi has been