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Catalytic Pathways for the Conversion of Glycerol to Industrial Chemicals

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Abstract

Glycerol valorization is of strategic importance. Key platform chemicals, like lactic acid, a precursor to polylactic acid, and another prominent monomer of the polymer industry, namely acrolein, can be produced from this molecule with three hydroxy groups. Glycerol is one of the 12 platform chemicals identified by the US Department of Energy, serving as a building block for various other molecules of relevance to the polymer industry owing to its high degree of oxygen functionality. Recent research published between 2021 and 2026 demonstrates significant advance in the application of advanced heterogeneous catalysts for the catalytic conversion of glycerol into value-added chemicals. The compiled results clearly show the effectiveness of solid acid catalysts, solid base catalysts, and metal-supported catalysts in directing glycerol transformation through dehydration, oxidation, reforming, and hydrogenolysis pathways under a wide range of reaction conditions. High glycerol conversions, in several cases in the range of 90–99%, have been achieved depending on catalyst composition, metal loading, support characteristics, and operating parameters such as temperature, pressure, and reaction time. Solid acid catalysts, particularly vanadium- and niobium-based oxide systems, exhibit outstanding activity for glycerol dehydration, producing acrolein as the primary product with selectivities above 70% at elevated temperatures. The near-complete glycerol conversion observed over these catalysts confirms the crucial role of surface acidity in promoting selective dehydration reactions. In contrast, solid base catalysts and base-assisted metal catalysts demonstrate excellent performance for lactic acid production, achieving glycerol conversions greater than 90% with lactic acid selectivities reaching up to 90% under optimized reaction conditions. Furthermore, metal-supported catalysts, such as Au, Pt, Pd, and Cu, supported on oxide or carbon materials enable selective oxidation and reforming reactions, yielding products including dihydroxyacetone, glyceric acid, hydrogen, and propanediols. Thus, the current insightful review provides the latest developments in the field in a nutshell with recommendations of the best catalytic pathways for producing the desired target molecules like acrolein, lactic acid, and dihydroxyacetone.

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INTRODUCTION

Research on the valorization of feedstock derived from biomass has intensified due to the growing demand for sustainable chemical processes. For example, biocatalysts, like yeast, were successfully used for the conversion of glycerol to 1,3-propanediol [1]. Glycerol has drawn a lot of attention as a versatile platform molecule. Large amounts of glycerol are produced as a byproduct of the production of biodiesel via transesterification [2–5] and bioethanol via fermentation of carbohydrates [6–15], and this excess has led to problems for the environment and the economy. Catalytic conversion of glycerol into high-value industrial chemicals is a useful tactic to increase biorefineries' overall profitability and also to achieve the UN Sustainable Development Goals.

Lactic acid and acrolein are two of the many value-added chemicals that can be made from glycerol that are crucial to industry. Acrolein is a crucial intermediary to produce acrylic acid, polymers, and specialized compounds. It is primarily synthesized via catalytic dehydration of glycerol. Solid acid catalysts, such as metal oxides, zeolites, and heteropoly acids, are primarily responsible for this transformation. They offer benefits in catalyst recovery and environmental compatibility, as well as the acidic sites required for selective dehydration. However, issues including limited selectivity and catalytic deactivation from coke production continue to push research toward better catalyst design.

On the other hand, base-catalyzed processes including dehydration, rearrangement, and hydration reactions are usually involved in the conversion of glycerol to lactic acid. Under mild circumstances, solid base catalysts, such as hydrotalcite-derived materials and alkaline earth metal oxides, have shown encouraging activity and selectivity for the generation of lactic acid. Compared to homogeneous base systems, the use of solid base catalysts has advantages, such as decreased corrosion, simpler separation, and improved process sustainability.

Understanding the role of solid acid and solid base catalysts in directing glycerol conversion toward specific products, such as acrolein and lactic acid, is crucial for developing efficient and scalable processes. This study focuses on elucidating the catalytic pathways involved in glycerol transformation and evaluating catalyst performance in terms of activity, selectivity, and stability. Advances in this area will contribute significantly to the development of greener catalytic technologies and the sustainable production of industrial chemicals from renewable resources.

BIOCATALYSIS AS THE GREEN PATHWAY FOR GLYCEROL VALORIZATION

Pulidindi et al. (2014) proved that baker's yeast is an ideal biocatalyst for the conversion of glycerol to 1,3-propanediol (1,3-PDO). The fermentation was carried out under strictly anaerobic, semi-aerobic, and aerobic conditions as shown in Figure 1. Among various conditions tested, the optimal yield of 1,3-PDO was 42.3% at a glycerol conversion of 93.6% under anaerobic conditions at 25°C as shown in Figure 2.

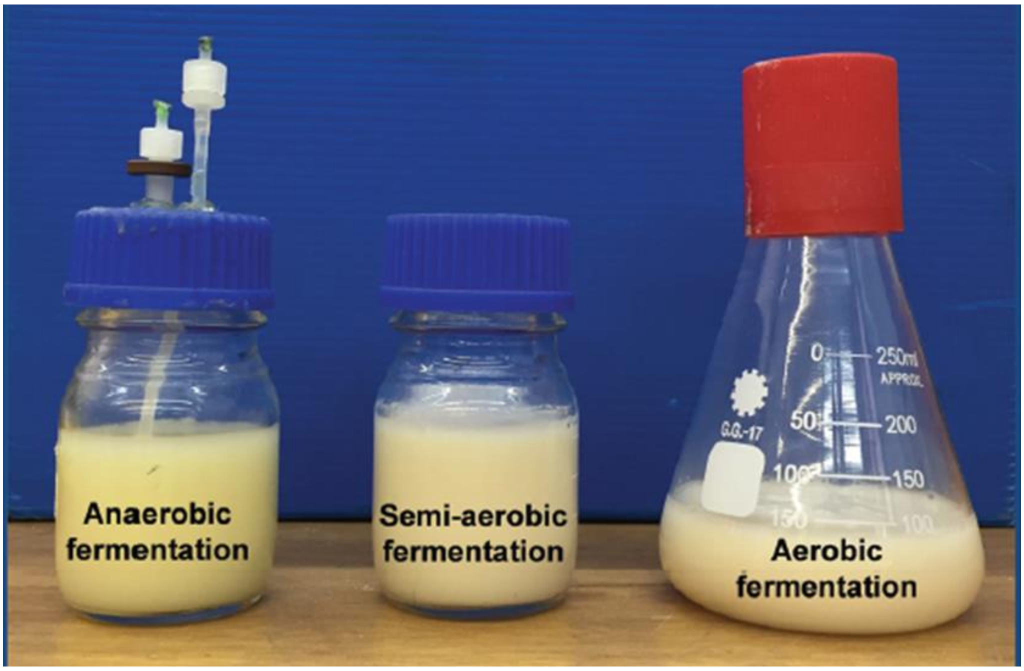

Figure 1. Fermentation of glycerol to 1,3-propanediol (1,3-PDO) using baker's yeast under anaerobic, semi-aerobic, and aerobic conditions.

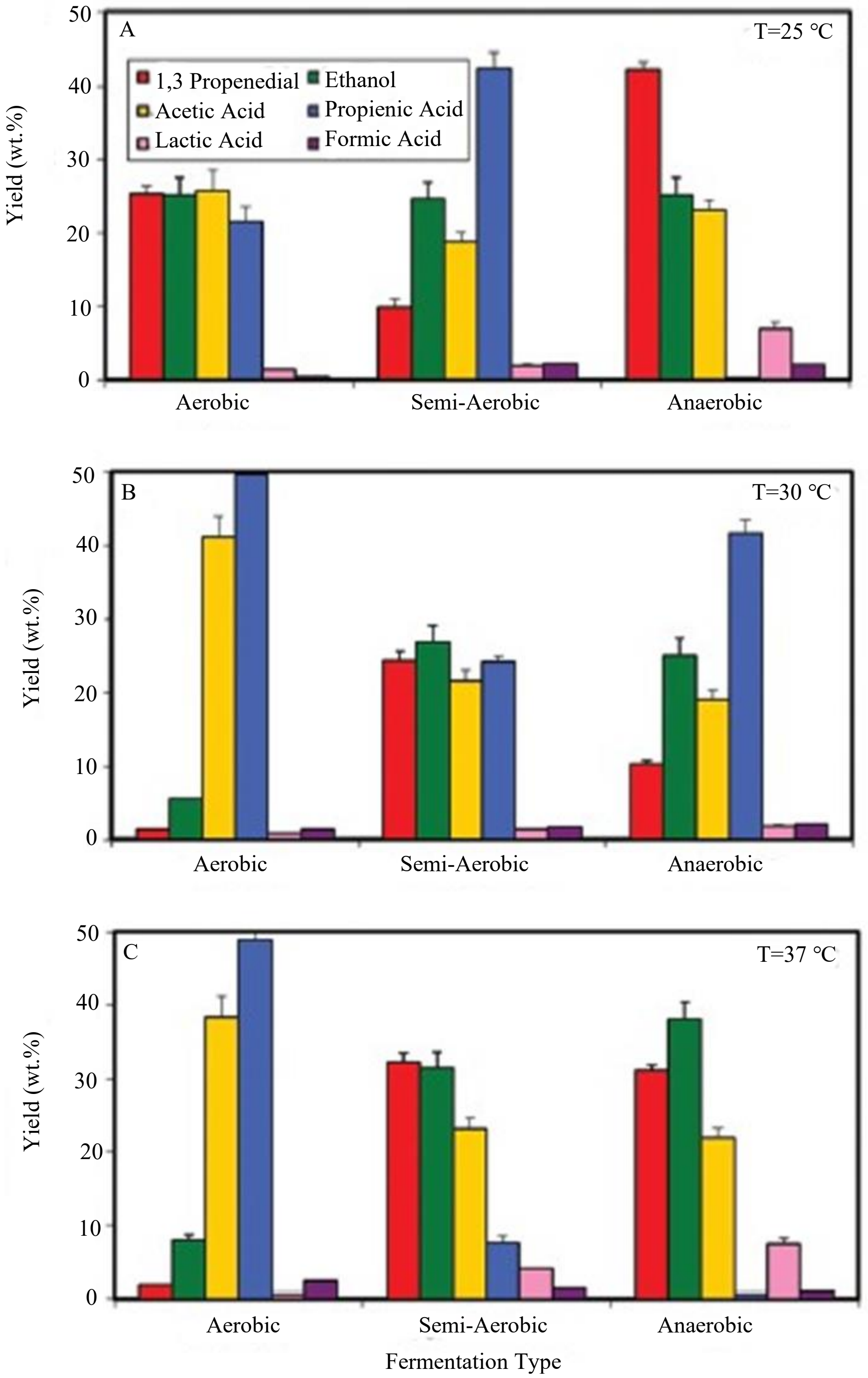

Figure 2. Optimal conditions to produce 1,3-propanediol (1,3-PDO) using baker’s yeast as a biocatalyst.

ADVANCED CATALYSTS FOR GLYCEROL CONVERSION (2021–2026)

Table 1 summarizes representative catalytic systems reported for glycerol valorization under diverse reaction conditions. Various metal, metal oxide, and supported catalysts demonstrate significant differences in glycerol conversion, product yield, and selectivity depending on temperature, pressure, and oxidizing or inert atmospheres. The data highlights the tunability of catalytic pathways toward value-added chemicals such as lactic acid, acrolein, dihydroxyacetone, glyceric acid, hydrogen, and

1,3-propanediol. These comparisons provide insight into catalyst performance and process optimization strategies for sustainable glycerol upgrading.

Table 1. Catalytic conversion of glycerol under various reaction conditions: Catalysts, operating parameters, and product selectivity/yield.

S. N.	Catalyst with reaction conditions	Product	References
1	NaOH, 0.2 M; glycerol, 1.1 M; t = 220 min. ; T = 300°C;	Lactic acid (yield, 82 mol %); glycerol conversion (93 mol %)	[16]
2	Nb_2O_5/SiO_2, T = 500°C, t = 180 min	Acrolein selectivity, 76.25% (15NbSi500)	[17]
3	15NiZr@Al_2O_3	Glycerol conversion (92.4%) H_2 selectivity (76.7%)	[18]
4	2Au/CuO, 0.1 M glycerol, glycerol/Au (mol/mol) = 1,000, 80°C, O_2 10 bar, 900 rpm, 2 h	Glycerol conversion = 20.6% Dihyroxy acetone (DHA) selectivity = 87.5 %	[19]
5	Au/MgO-Al_2O_3, 0.1 M glycerol. 0.1 M glycerol; glycerol/Au = 315 (mol/mol); 900 rpm, 2 h	Glycerol conversion = 16.4% Dihyroxy acetone (DHA) selectivity = 74.1%	[19]
6	Pd-Ag/C, 0.2 M glycerol, glycerol/Pd (mol/mol) = 1,150, 80°C, O_2 1 bar, 1,000 rpm, 4 h	Glycerol conversion = 20.0% Dihyroxy acetone (DHA) conversion = 82.2%	[19]
7	Pt/ZrO_2, 0.1 M glycerol, glycerol/Pt (molar) = 505, 60°C, O_2 10 bar, 500 rpm, 6 h	Glycerol conversion = 92.9% Glyceric acid (GLYA) selectivity = 64.9%	[19]
8	Pt/Si-C, 0.1 M glycerol, glycerol/Pt (molar) = 143, 60°C O_2 1 atm, 10 h	Glycerol conversion = 74.4 % Glyceric acid (GLYA) selectivity = 86.7%	[19]
9	Pt/C, 1.0 M glycerol, glycerol/Pt (molar) = 424, 60°C, O_2 150 cm^3/min, 6 h	Glycerol conversion = 50.0 % Glyceric acid (GLYA) selectivity = 47.4%	[19]
10	Vanadium phosphorous oxide (VPO), T = 320°C, carrier flow rate = 30 mL per min (N_2), resolution = 20 wt%	Glycerol conversion = 99% Acrolein selectivity = 72.3 ± 0.6%	[20]
11	Vanadium phosphorous oxide (VPO), T = 320°C, carrier flow rate = 30 mL per min (N_2), glycerol aqueous solution = 20 wt%	Glycerol conversion = 99% Acetic acid selectivity = 3.4 ± 0.02%	[20]
12	Pt/ZnO, size = 45.0 nm, t = 30 h,T 240°C	Glycerol conversion = 97.0% Lactic acid selectivity = 60%	[21]
13	Cu/SiO_2, t = 6 h, T = 240°C	Glycerol conversion = 75.2% Lactic acid selectivity = 79.7%	[21]
14	10% Pd/C, t = 3h, T = 230°C	Glycerol conversion = 93.8% Lactic acid selectivity = 61.9%	[21]
15	Cu/MgO, t = 3–6 h, T = 240°C	Glycerol conversion = 95.4% Lactic acid selectivity = 90%	[21]
16	Pt/Al_2O_3, P = 40 bar, T = 200°C	Glycerol conversion = 49% 1,3-propanediol yield = 28%	[22]
17	Pt/sulfated-ZrO_2, P =73 bar, T = 170°C	Glycerol conversion = 67% 1,3-propanediol yield = 56%	[22]
18	PKU-1, t = 360 min, T = 45°C, Glycerol: acetone molar ratio = 1:5	Glycerol conversion = 92.8% Acetone selectivity = 98.3%	[23]
19	Co_3O_4/SnO_2, t = 180 min, T = 60°C Glycerol: acetone molar ratio = 1:5	Glycerol conversion = 92% Acetone selectivity = 100%	[23]
20	Mo(VI)/ZrO_2, t = 8 min, T = 60°C, Glycerol: acetone, molar ratio = 1:6	Glycerol conversion = 98% Acetone selectivity = 98%	[23]

FUTURE PERSPECTIVES

The logical design of durable and multipurpose catalysts that can achieve high activity, selectivity, and long-term stability should be the main emphasis of future glycerol valorization research. The creation of metal–acid/base integrated systems and bifunctional acid-base catalysts hold great promise for managing reaction pathways and reducing adverse reactions such as over-oxidation and coke production. It is anticipated that advanced catalyst manufacturing techniques, such as surface-modified catalysts, hierarchical porous support, and nanostructured materials, would improve active-site durability and accessibility. Non-noble metal catalysts should also receive more attention to lower prices and increase industrial viability. Improving catalyst lifetime will require an understanding of catalyst deactivation mechanisms through operando and in situ characterization approaches. To facilitate effective scale-up and process intensification, future research should focus on integrating glycerol conversion into continuous-flow reactors and biorefinery frameworks. Techno-economic research and life cycle assessment will also be crucial in determining how truly sustainable glycerol-based catalytic processes are. In essence, establishing glycerol valorization as a pillar of sustainable chemical manufacture and the growth of the circular bioeconomy would require ongoing developments in catalyst design, mechanistic comprehension, and process optimization [24–35].

CONCLUSION

Glycerol's catalytic valorization has become a crucial tactic for turning biomass-derived feedstocks into industrial chemicals with added value, resolving the financial and environmental issues surrounding the manufacturing of biodiesel. A variety of catalytic systems, including solid acid, solid base, and metal-supported catalysts, have shown promising performance for converting glycerol into value added products, like acrolein, lactic acid, dihydroxyacetone, glyceric acid, hydrogen, and propanediols, as summarized in recent studies (2021–2026). Although catalyst deactivation from coke production is still a significant restriction, solid acid catalysts have demonstrated great activity for glycerol dehydration to acrolein, with high conversion and selectivity under ideal circumstances. In contrast to homogeneous systems, solid base and bifunctional catalysts have demonstrated efficacy in the synthesis of lactic acid, providing enhanced selectivity, softer reaction conditions, and more process sustainability. By facilitating selective oxidation, hydrogenolysis, and reforming routes, metal-supported catalysts have significantly broadened the range of products. Catalyst stability, selectivity control, energy efficiency, and scalability issues still exist despite tremendous advances. Although some of these systems exhibit moderate glycerol conversion, they offer high product selectivity and highlight the versatility of metal–catalyzed pathways. Overall, the reported studies emphasize the critical influence of catalyst type, support properties, and reaction conditions on glycerol conversion and product distribution. These findings underline the strong potential of heterogeneous catalytic systems for glycerol valorization while highlighting the need for further improvements in catalyst stability and process optimization to enable industrial–scale implementation. Overall, the reviewed studies demonstrate how important catalyst composition, metal dispersion, acidity–basicity balance, and reaction conditions are in defining the pathways of glycerol conversion and the distribution of the final product.

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