

Comparative Life Cycle Assessment of Glycerol Valorization Routes to 1,2- and 1,3-Propanediol Based on Process Modeling

Kumar Raja Vanapalli,* Lourembam Nongdren, Sunil K. Maity,* and Vinod Kumar*



Cite This: *ACS Sustainable Chem. Eng.* 2024, 12, 14716–14731



Read Online

ACCESS |



Metrics & More



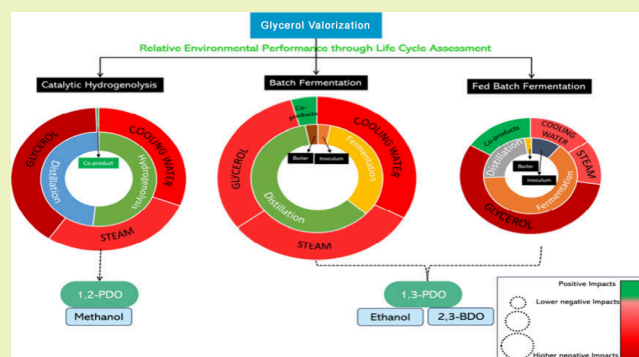
Article Recommendations



Supporting Information

ABSTRACT: Crude glycerol, a high-volume byproduct of the biodiesel industry, has seen a significant surplus due to the industry's rapid growth. It can be a promising feedstock for a range of high-value products via chemical and biochemical routes. This study thus elucidates the relative environmental performance of two prominent glycerol valorization technologies, i.e., catalytic hydrogenolysis to 1,2-propanediol and microbial fermentation (batch and fed-batch) to 1,3-propanediol, using a cradle-to-gate life cycle assessment (LCA). The LCA was performed using an experimental data-driven comprehensive process model to represent an industrial-scale biorefinery, handling 20 833 kg/h of glycerol. The LCA results identified cooling water (18–35.5%) and steam (15.2–33.7%) consumption in the distillation and glycerol sourcing (33.3–68.1%) as the critical environmental hotspots, which should be focused on while designing the process. The fed-batch fermentation process was environmentally more benign, with significantly lower environmental impacts than hydrogenolysis (by 35.2%) and batch fermentation (by 48.2%). Integrating effective process heat recovery using pinch technology reduced the overall environmental impacts by 4.9–11.2%. The environmental performance of the overall processes varied substantially (2.4–62.1%) with changes in glycerol sourcing and production methods. Therefore, energy and material recycling with sustainable water and glycerol sourcing can improve the sustainability of the overall process.

KEYWORDS: Biorefinery, Glycerol, Life Cycle Assessment, Propanediols, Sensitivity



INTRODUCTION

The global transition from fossil fuels to renewable alternatives has enhanced the prominence of the biodiesel industry as a sustainable source of biofuels. Biodiesel, fatty acid methyl/ethyl esters, is produced through the transesterification of triglycerides, such as vegetable oils, animal fats, used cooking oils, greases, etc., with anhydrous methanol/ethanol in the presence of base catalysts.^{1,2} Crude glycerol (CG) is one of the high-volume but low-value coproducts produced during the transesterification process.³ It is estimated that the production of every 100 kg of biodiesel generates ~10 kg of CG. The biodiesel industry has shown tremendous growth in the last few decades, resulting in a glut of CG. An annual average of 6.3 million tons of CG is anticipated to be generated from the biodiesel industry by 2025 with purity levels of 60–80%.⁴ The applications of CG are restricted by its impurity, and needs extensive purification steps to remove impurities to make it suitable for its applications and downstream conversion processes. Pure glycerol has a wide range of applications in the cosmetic, food, and pharmaceutical industries.⁵ Glycerol was thus listed as one of the top platform chemicals by the US Department of Energy. The global market for glycerol is projected to increase from 2.8 million tons (MT) in 2020 to 4 MT by 2027.⁶ The annual growth rate of glycerol is

expected to be 10% from 2022 to 2030.⁷ However, with such revolutionized growth of the biodiesel industry, the CG from the biodiesel industry is expected to be in surplus supply more than the current market demand.⁸

Sustainable valorization of biodiesel-based CG to high-value bulk and specialty chemicals including acrolein, acrylic acid, ethanol, glutamate, polyhydroxyalkanoates, propionic acid, 1,2- and 1,3-propanediol (PDO), lactic acid, succinic acid, etc., via microbial and chemocatalytic routes has been depicted by several studies.^{9–11} Most of these chemicals are currently sourced from fossil-based feedstocks with unsustainable production processes, which have consequences on their commercial viability and environmental sustainability. For instance, 1,2-PDO and 1,3-PDO, which are widely used monomers in the polymer industry and have extensive applications across food, pharmaceuticals, cosmetics, and

Received: June 7, 2024

Revised: September 2, 2024

Accepted: September 3, 2024

Published: September 20, 2024



textiles industries,^{12,13} are typically produced from fossil fuels via catalytic conversion pathways. 1,2-PDO is derived from propylene via hydration of propylene oxide,¹⁴ while 1,3-PDO is produced from ethylene oxide or propylene through hydrogenation of an intermediate product 3-hydroxypropionaldehyde.¹⁵ The catalytic hydrogenolysis of glycerol at high pressure on supported metal catalysts using excess hydrogen is a sustainable alternative pathway for 1,2-PDO production.¹⁶ Among the different monometal and bimetal catalysts studied previously,^{17–19} Cu-based catalysts on acidic support demonstrated high effectiveness in glycerol hydrogenolysis reactions, achieving high 1,2-PDO selectivity.^{20–22} On the other hand, the catalytic glycerol valorization to 1,3-PDO results are not quite promising for commercial process development due to poor 1,3-PDO selectivity with multiple byproducts formation.²³ However, bioconversion of glycerol to 1,3-PDO with high-level production via wild type and genetically modified microbial strains has emerged as a promising and renewable route for 1,3-PDO production.^{24–26} Table S1 summarizes some of the selected previous studies depicting high-level 1,2-PDO and 1,3-PDO production using pure/crude glycerol.

Though experimental results are quite promising, the commercial friendliness of these bioprocesses should be carefully evaluated using sustainability analysis tools to envision their economic and environmental performance. Techno-economic analysis is essential for determining the economic sustainability of these technologies before commercialization. In our previous study, the comprehensive techno-commercial analysis of pure glycerol valorization to PDOs via hydrogenolysis and fermentation was performed.¹⁰ The analysis was based on the detailed process design using current state-of-the-art experimental data in Aspen Plus software using the pinch technology approach. Further, profitability analysis was conducted to estimate the return on investment from PDO production and evaluate the relative economic viability of the processes. Environmental sustainability analysis is another essential tool, especially in the current context, for judging the long-term ecological consequences of these bioprocesses. However, the relative environmental sustainability of these bioprocesses and the critical parameters that influence the environmental performance of these technologies have not been studied before. Life cycle assessment (LCA) has been widely recognized as an efficient tool for determining the environmental impacts of these processes and identifying their critical hotspots. Some previous studies have used LCA to evaluate the environmental performance of biodiesel-derived glycerol conversion technologies to high-value products, including 1,2-PDO,²⁷ dihydroxyacetone (DHA),^{8,28} acrolein,²⁹ 1,2-PDO,³⁰ 1,3-PDO,³¹ propionic acid,¹¹ and lactic acid,³² via different conversion methods, such as hydrogenolysis, fermentation, catalytic oxidation, chemocatalysis, and dehydration. However, the relative environmental consequence of glycerol hydrogenolysis and fermentation technologies for producing PDOs has not been reported in previous literature. The comparative assessment of the environmental consequences of these technologies, in conjunction with their techno-commercial feasibilities, will be instrumental in determining the overall sustainability of the processes and the resultant biorefinery products.²⁷

The current study thus sets a novel objective to evaluate the relative environmental performance of two commercial-scale glycerol valorization technologies to produce 1,2-PDO and 1,3-PDO via catalytic hydrogenolysis and fermentation processes,

respectively. However, the LCA analysis results were greatly influenced depending on the accuracy of resource (energy and material) consumption estimates. The present study estimated the material and energy balance data from our previous comprehensive process design based on the most promising experimental data reported in published literature.¹⁰ The processes were designed with Aspen Plus software using validated thermodynamic property methods for reliable energy consumption estimates. A systematic pinch analysis approach was further applied for process integration with the maximum possible process heat energy utilization to reduce the external heat energy supply. Thereafter, a cradle-to-gate LCA was performed to analyze the environmental effects of these biorefining technologies and determine the critical hotspot processes/pathways of major concern. Based on the identified environmental hotspots, multiple scenario analyses, including integration of pinch technology, glycerol sourcing, and production pathways, were performed to identify the potential strategies for reducing the overall negative impacts of the processes. Moreover, a sensitivity analysis of critical parameters was carried out to determine the relative effects of variation in these parameters on the overall categorical impacts. Further study was conducted to analyze the significance of data uncertainty on the variability of the associated impacts. The novel findings of this study hold tremendous significance to policymakers, investors, and LCA experts in informed decisions on two promising glycerol valorization technologies.

■ PROCESS FLOWSHEETS

The current LCA was performed using our previous techno-economic analysis results,¹⁰ which entailed the development of industrial-scale glycerol valorization process models to manufacture 1,2-PDO and 1,3-PDO. The Aspen Plus simulation software was used to develop the process models, which included databases and property estimation methods. The reaction conditions and process parameters, including input/output composition, were acquired from lab-scale experimental results reported in the literature.^{33–35} These parameters formed the basis for the industrial-scale process simulations to estimate energy, material, and elementary flows. Based on these process data, the relative environmental performance of two glycerol valorization processes was evaluated: (1) catalytic hydrogenolysis to produce 1,2-PDO and (2) fermentative manufacturing of 1,3-PDO. The study further assessed the relative environmental impact of integrating “with pinch technology”, which involved an optimal heat exchanger network design for maximizing the utilization of heat energy within the process, compared to “without pinch technology”.

Glycerol Catalytic Hydrogenolysis to 1,2-Propanediol (1,2-PDO). The hydrogenolysis reaction of glycerol for the selective conversion to 1,2-PDO using supported Cu-based catalyst under high-pressure conditions with excess hydrogen was adopted for process modeling in the current study. This process occurs in a fixed-bed reactor in a single stage, involving two sequential reactions: (i) the dehydration of glycerol over either acidic or basic sites to hydroxyacetone (HA) and (ii) subsequent HA hydrogenation into 1,2-PDO on the metal centers (Figure 1). This step also involves several unavoidable side reactions to a lesser extent, such as C–C cleavage of glycerol and 1,2-PDO, over Cu-based bifunctional catalysts, forming insignificant quantities of several coproducts, including methanol, HA, ethylene glycol (EG), and ethanol. The glycerol hydrogenolysis process model adopted in this study was divided

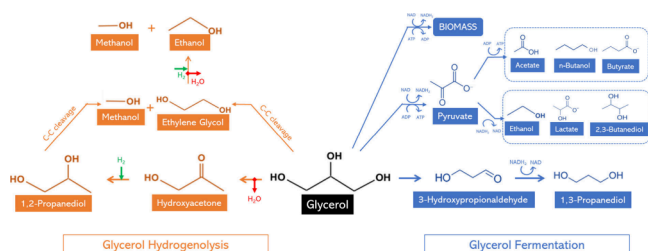


Figure 1. Pathways for catalytic hydrogenolysis and fermentation of glycerol to produce 1,2-propanediol and 1,3-propanediol, respectively, along with byproduct formation.

into two subsections: hydrogenolysis and downstream separation processes. In the former subsection, a 10 wt % glycerol–water mixture at 5 MPa was preheated to 220 °C and pumped to the reactor for glycerol hydrogenolysis. Simultaneously, compressed hydrogen (5 MPa of pressure) was fed to the same reactor by using a double-stage compressor. The output stream from the hydrogenolysis reactor was directed to a vapor–liquid flash vessel after cooling, where excess hydrogen gas was separated from the product liquid mixture. The hydrogen separated from the flash vessel was pressurized to 5 MPa and recycled back to the reactor to supplement the process hydrogen demand. The liquid product mixture from the flash drum further underwent a downstream separation process, which included a series of distillation columns (DC). Methanol and ethanol, which are the low boiling point compounds in the liquid mixture, were distilled in the first distillation column (DC1), along with an azeotropic quantity of water. The methanol was separated from the methanol–ethanol–water mixture in the second column (DC2) from the DC1 distillate, while the

bottom product of DC2 contained ethanol and water, from which fuel-grade ethanol was obtained by extractive distillation (DC3) using EG as the entrainer. Finally, EG was regenerated from the EG–water mixture in another distillation column (DC4) and recycled to DC3 after cooling. The bottom product of DC1, which consisted of water, HA, EG, and 1,2-PDO, was separated sequentially through three additional distillation columns based on the volatility of the components: DC5 (water), DC6 (HA), and DC7 (EG and 1,2-PDO). The water separated from DC5 was recycled back to the hydrogenolysis reactor to supplement the water demand for glycerol dilution and hydrogenolysis reaction. Detailed flowsheets showing the modeled individual processes for the glycerol hydrogenolysis to manufacture 1,2-PDO are depicted in our previous study.¹⁰

Microbial Glycerol Fermentation to 1,3-Propanediol (1,3-PDO). Microbial fermentation of glycerol to 1,3-PDO was performed under two different modes with cogeneration of 2,3-butanediol (2,3-BDO) and ethanol: batch fermentation using wild strain and fed-batch fermentation using genetically engineered *Klebsiella* sp. HE-2 microorganisms. In *Klebsiella* sp., glycerol is metabolized by oxidative and reductive pathways.³⁶ The oxidative pathway entails the conversion of glycerol to several organic acids and alcohols through pyruvate using a glycerol dehydrogenase reaction (Figure 1). Conversely, in the reductive pathway, a two-step pathway, glycerol is dehydrated to 3-hydroxypropionaldehyde by vitamin B12 dependent enzyme glycerol dehydratase. In the next step, 3-hydroxypropionaldehyde is reduced to 1,3-PDO by 1,3-PDO oxidoreductase using NADH as a cofactor.³⁶ The process model adopted for glycerol fermentation was divided into four subsections: inoculum preparation, fermentation, downstream separation process, and other auxiliary processes. Initially,

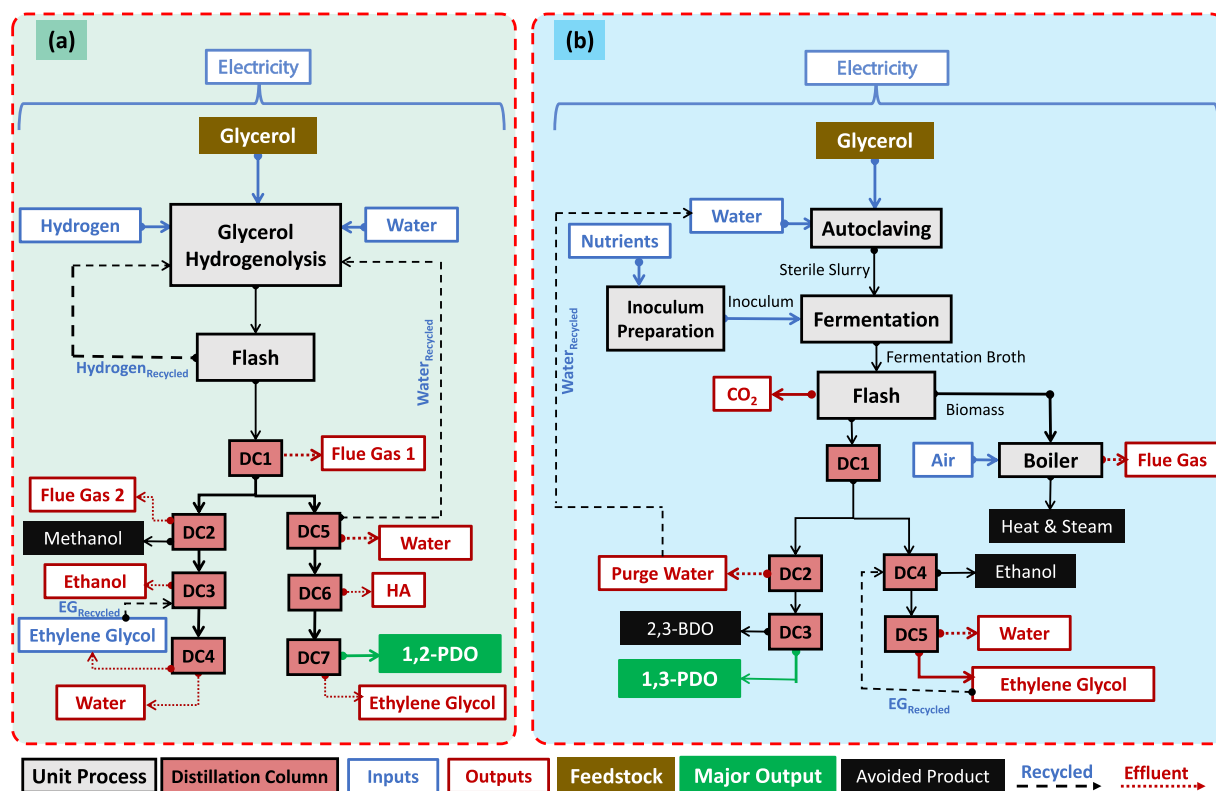


Figure 2. System boundaries for (a) 1,2-PDO and (b) 1,3-PDO production from glycerol. DC, distillation column; HA, hydroxyacetone; EG, ethylene glycol; and 2,3-BDO, 2,3-butanediol.

Table 1. Life Cycle Inventory Data for 1,2-PDO Production per Hour by Glycerol Hydrogenolysis with and without Pinch Analysis

		input/output per hour		
		unit	without pinch	with pinch
glycerol hydrogenolysis	glycerol (input)	kg	20.83×10^3	20.83×10^3
	hydrogen (input)	kg	459.4	459.4
	hydrogen recycled (input/output)	kg	1818	1818
	water recycled (input)	kg	18.75×10^4	18.75×10^4
	cooling water (input)	kg	10.15×10^6	42.15×10^5
	steam (input)	kg	57.93×10^3	99.72×10^2
	electricity (input)	kWh	19.58×10^2	19.58×10^2
downstream separation	capital goods (input)	kg	0.538	0.538
	electricity (input)	kWh	758	758
	cooling water (input)	kg	33.57×10^6	31.33×10^6
	steam (input)	kg	35.77×10^4	32.53×10^4
	capital goods (input)	kg	7.84	8.36
	ethylene glycol recycled (input/output)	kg	83.75	83.75
	water for recycling (output)	kg	18.75×10^4	18.75×10^4
	methanol (output)	kg	108.4	108.4
	hydroxyacetone (output)	kg	125	125
	ethylene glycol (output)	kg	100	100
	ethanol (output)	kg	124.9	124.9
	1,2-propanediol (output)	kg	16.79×10^3	16.79×10^3
	gas 1 (output)			
	water	kg	0.062	0.062
	hydrogen	kg	0.19	0.19
	methanol	kg	0.348	0.348
	ethanol	kg	0.251	0.251
	gas 2 (output)			
	water	kg	≈ 0	≈ 0
	hydrogen	kg	1.1×10^{-3}	1.1×10^{-3}
	methanol	kg	6.8×10^{-3}	6.8×10^{-3}
	ethanol	kg	≈ 0	≈ 0
	wastewater (discharge) (output)			
	water	kg	40.47×10^2	40.47×10^2
	ethylene glycol	kg	1.4×10^{-3}	1.4×10^{-3}
	hydroxyacetone	kg	7.7×10^{-3}	7.7×10^{-3}
	methanol	kg	≈ 0	≈ 0
	ethanol	kg	0.414	0.414

sterilized diluted glycerol (to 50 g/L) was fed into the fermentation reactor as the feed. The reactor was inoculated with *Klebsiella* sp. (5% v/v) to initiate the fermentation, and CO₂ emitted as part of the fermentation process was continuously vented out. The cell biomass generated during fermentation was recovered by centrifugation. The cell biomass was further directed to a boiler to produce high-pressure steam, which was utilized to partially complement the process heating energy requirements.

The fermentation broth obtained from the process further underwent the downstream separation process, which included a series of five distillation columns (DC). The cell-mass-free fermentation broth was separated into two streams in the first distillation column (DC1): azeotropic ethanol–water distillate and 1,3-PDO–2,3-BDO–water bottom stream. The bottom stream from DC1 was processed through a series of two distillation columns to separate water (DC2) from 1,3-PDO (DC3 bottom) and 2,3-BDO (DC3 distillate). The fuel-grade ethanol was separated from the ethanol–water stream by extractive distillation (DC4 and DC5) by using EG as the entrainer. The separated EG was cooled and recycled back into DC4. The composition and quantum of different byproducts obtained during the batch and fed-batch fermentation processes varied and were subject to variable culture conditions. Finally, the water separated from DC2 was recycled to complement the

water demands of the fermentation process. Figure 1 depicts the individual pathways for glycerol catalytic hydrogenolysis to produce 1,2-PDO and glycerol fermentation to produce 1,3-PDO. Detailed flowsheets depicting the modeled individual processes for the glycerol fermentation to manufacture 1,3-PDO are illustrated in our previous study.¹⁰

LCA METHODOLOGY

Goal and Scope. This study aims to determine the relative environmental performance of two glycerol valorization routes to produce important value-added chemicals, 1,2-PDO and 1,3-PDO, using a cradle-to-gate LCA. Figure 2 illustrates the system boundary for the production of 1,2-PDO and 1,3-PDO from glycerol as adopted in the LCA modeling. Based on the techno-economic analysis from our previous study,¹⁰ the technical and economic performance of glycerol hydrogenolysis and fermentation processes was evaluated at simulated plant capacities of 100, 500, 1000, and 2000 metric tons/day. The economic analysis identified an optimal glycerol feed capacity of 500 metric tons/day (equivalent to 20 833 kg/h). Consequently, in the current study, we have selected this economically optimum glycerol feed rate of 20 833 kg/h as the functional unit for the LCA of both processes. Based on our previous process design,¹⁰ the purity of 1,2-PDO and 1,3-PDO was considered as >99.5% on a mass basis. Further, the purity of all other coproducts was considered to be >99% on a mass basis. It is important to note that while the production rates of main and byproducts, such as 1,2-PDO from hydrogenolysis and 1,3-PDO and 2,3-BDO from batch/fed-batch fermentation, may vary across the

Table 2. Life Cycle Inventory Data for 1,3-PDO Production per Hour by Glycerol Fermentation using Batch and Fed-Batch Processes with and without Pinch Analysis

			1,3-PDO production (input/output per hour)				
			batch process		fed-batch process		
		unit	without pinch	with pinch	without pinch	with pinch	
inoculum cultivation (nutrients)	glycerol (input)	kg	11.64×10^2	11.64×10^2	24.51×10^2	24.51×10^2	
	K ₂ HPO ₄ (input)	kg	21.9	21.9	40.84	40.84	
	KH ₂ PO ₄ (input)	kg	6.33	6.33	245.1	245.1	
	(NH ₄) ₂ SO ₄ (input)	kg	5.10	5.10	590.77	590.77	
	CaCO ₃ (input)	kg	0.464	0.464	-	-	
	MgSO ₄ (input)	kg	46.39	46.39	37.93	37.93	
	C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O (input)	kg	-	-	70.02	70.02	
	yeast extract (input)	kg	35.02	35.02	157.54	157.54	
	acetic acid (input)	kg	13.52×10^2	13.52×10^2	-	-	
	CaCl ₂ ·2H ₂ O (input)	kg	-	-	3.9×10^{-4}	3.9×10^{-4}	
	ZnCl ₂ (input)	kg	16.4×10^{-4}	16.4×10^{-4}	4.7×10^{-4}	4.7×10^{-4}	
	FeCl ₃ ·6H ₂ O (input)	kg	-	-	3.7×10^{-3}	3.7×10^{-3}	
	MnCl ₂ ·4H ₂ O (input)	kg	23.4×10^{-4}	23.4×10^{-4}	13.7×10^{-4}	13.7×10^{-4}	
	H ₃ BO ₃ (input)	kg	14.1×10^{-4}	14.1×10^{-4}	4.29×10^{-5}	4.29×10^{-5}	
	CoCl ₂ ·2H ₂ O (input)	kg	46.9×10^{-4}	46.9×10^{-4}	3.2×10^{-4}	3.2×10^{-4}	
	CuCl ₂ ·2H ₂ O (input)	kg	4.7×10^{-4}	4.7×10^{-4}	1.2×10^{-4}	1.2×10^{-4}	
	NiCl ₂ ·6H ₂ O (input)	kg	5.9×10^{-4}	5.9×10^{-4}	-	-	
	Na ₂ MoPO ₄ ·2H ₂ O (input)	kg	5.9×10^{-4}	5.9×10^{-4}	3×10^{-6}	3×10^{-6}	
	HCl (37%) (input)	kg	0.208	0.208	-	-	
	FeSO ₄ ·7H ₂ O (input)	kg	0.234	0.234	-	-	
glycerol fermentation	electricity (input)	kWh	265.4	265.4	72.5	72.5	
	glycerol (input)	kg	20.83×10^3	20.83×10^3	20.83×10^3	20.83×10^3	
	inoculum (input)	kg	13.94×10^3	13.94×10^3	19.03×10^3	19.03×10^3	
	water recycled (input)	kg	39.6×10^4	39.6×10^4	39.6×10^4	39.6×10^4	
	cooling water (input)	kg	90.6×10^5	18.62×10^5	26.89×10^5	92.46×10^5	
	steam (input)	g	79.91×10^3	91.75×10^2	19.43×10^3	20.86×10^2	
	capital goods (input)	kg	1.214	1.214	0.236	0.236	
	biomass (output)	g	36.36×10^2	36.36×10^2	908.9	908.9	
	CO ₂ (output)	kg	38.52×10^2	38.52×10^2	39.25×10^2	39.25×10^2	
	downstream separation	electricity (input)	kWh	25.22×10^2	25.22×10^2	740.9	740.9
cooling water (input)		kg	53.96×10^6	54.59×10^6	13.91×10^6	13.37×10^6	
steam (input)		kg	58.5×10^4	58.13×10^4	13.66×10^4	13.14×10^4	
capital goods (input)		kg	8.24	8.73	2.92	3.05	
ethylene glycol recycled (input/output)		kg	18.9×10^2	18.9×10^2	472.5	472.5	
water for recycling (output)		kg	39.6×10^4	39.6×10^4	39.6×10^4	39.6×10^4	
1,3-propanediol (output)		kg	42.99×10^2	42.99×10^2	92.91×10^2	92.91×10^2	
wastewater (discharge) (output)		water	kg	35.96×10^2	35.96×10^2	26.9×10^2	26.9×10^2
		ethanol	kg	0.0772	0.0772	0.064	0.064
		2,3-butanediol	kg	0.361	0.361	1.254	1.254
boiler	ethanol (output)	kg	28.05×10^2	28.05×10^2	701.4	701.4	
	2,3-butanediol (output)	kg	2644	2644	3315	3315	
	biomass (input)	kg	36.36×10^2	36.36×10^2	908.9	908.9	
	air (input)	kg	32.02×10^3	32.02×10^3	78.42×10^2	78.42×10^2	
	electricity (input)	kWh	932.5	932.5	223.8	223.8	
	capital goods (input)	kg	1.79	1.79	0.475	0.475	
	heat (output)	kJ	90.18×10^6	90.18×10^6	22.54×10^6	22.54×10^6	
	flue gas (output)	H ₂ O	kg	26.99×10^2	26.99×10^2	674.8	674.8
		CO ₂	kg	80.3×10^2	80.3×10^2	20.1×10^2	20.1×10^2
		O ₂	kg	363.6	363.6	53.14	53.14
	N ₂	kg	24.56×10^3	24.56×10^3	60.16×10^2	60.16×10^2	
steam (output)	kg	44.05×10^3	44.05×10^3	11.01×10^3	11.01×10^3		

processes, we standardized the glycerol feed rate at 20 833 kg/h as the functional unit for comparison purposes. However, 1,2-PDO and 1,3-PDO are chemical intermediaries with extensive postproduction applications. Therefore, their downstream processing, including transport, postprocessing to subsidiary products and their end use,

and end-of-life phases, were excluded from the scope of the current study. The European Union (EU) is a leading producer and consumer of biodiesel, with a projected compound annual growth rate (CAGR) of 5.5% from 2024 to 2029.³⁷ This growth is primarily driven by the Renewable Energy Directive (RED II) targets for 2030, which mandate

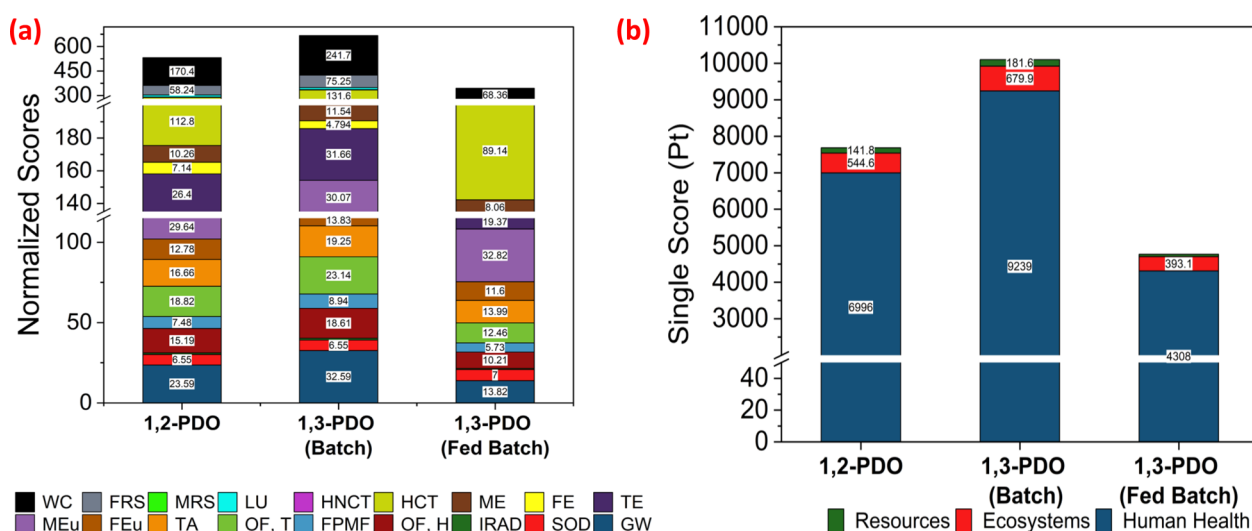


Figure 3. Comparison of midpoint and endpoint normalization results between various glycerol valorization routes: (a) classification according to midpoint impact categories and (b) classification according to endpoint damage categories. FE: freshwater ecotoxicity; FEu: freshwater eutrophication; FPMF: fine particulate matter formation; FRS: fossil resource scarcity; GW: global warming; HNCT: human noncarcinogenic toxicity; HCT: human carcinogenic toxicity; IRAD: ionizing radiation; LU: land use; ME: marine ecotoxicity; MEu: marine eutrophication; MRS: mineral resource scarcity; OF, H: ozone formation, human health; OF, T: ozone formation, terrestrial ecosystems; SOD: stratospheric ozone depletion; TA: terrestrial acidification; TE: terrestrial ecotoxicity; and WC: water consumption.

that EU member states achieve a minimum share of 3.5% advanced biofuels in their total energy consumption for transport.^{38,39} Consequently, the geographical scope of the current study was limited to European countries.

Life Cycle Inventory (LCI). The LCI for the commercial-scale 20 833 kg/h glycerol valorization to 1,2-PDO through catalytic hydrogenolysis and 1,3-PDO by batch and fed-batch fermentation is presented in Tables 1 and 2, respectively. The environmental assessment included material (raw materials, products, byproducts, waste, etc.) and energy (electricity, heat, etc.) flows, along with the manufacture of the general biorefinery process equipment (reactors, distillation columns, heat exchangers, etc.). The inoculum cultivation phase, which included nutrients supply, was adopted from Wong et al.³⁴ for the batch process and Wang et al.²⁵ and Wang et al.⁴⁰ for fed-batch processes. The process inventory depicting mass flow rates and electricity consumption in various unit operations/subprocesses of the biorefining facility was obtained from our process simulation designed in Aspen Plus software.¹⁰ The background data on the environmental footprint of the individual compounds and bioprocesses in LCI were taken from the EcoInvent 3.10 database (Table S2). It is important to note that the electricity demands of all the unit operations, such as centrifugation, pumping, gas compression, sterilization, etc., were depicted in their individual processes in the LCI (Figure 2). Further, the chemicals used as nutrients for inoculum preparation were separately depicted as the inoculum cultivation phase in LCI. The LCI data were compiled on the basis of the following assumptions.

- As K_2HPO_4 , KH_2PO_4 , $ZnCl_2$, $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2$, $Na_2MoO_4 \cdot 4H_2O$, and $C_6H_5Na_3O_7 \cdot 2H_2O$ were not directly included in the EcoInvent 3.10 database, their requirement was derived from their stoichiometry of corresponding substitutes: (H_3PO_4 , KCl), (H_3PO_4 , KOH), (Zn, HCl), (Mn, H_2O , HCl), ($Co(OH)_2$, HCl), (CuO , H_2O , HCl), ($NiSO_4$, Cl_2), (MoO_3 , H_2O , NaOH), and (citric acid, NaOH), respectively. Previous studies^{8,11,41} have utilized a similar approach involving stoichiometric equations for the substituted chemicals unavailable in the EcoInvent 3.10 database.
- Pure glycerol available in the market of Europe as represented by the data set “market for glycerine in the region of Europe (RER)” in the EcoInvent 3.10 database was selected in the current study. This data set represents the environmental impacts of the activities associated with the production and supply of glycerol from industries in the European region to the

consumer. It accurately reflects the available glycerol mix in the European market (Table S3).

- The inoculum was considered to be prepared under neutral pH conditions.
- All data inputs into the LCA, including chemicals, electricity production mix, and other secondary data, were based on European-based averages as available in the EcoInvent 3.10 database.
- The steel consumption (kg) for commissioning of the process was estimated from the individual equipment sizing specifications, which were obtained from the Aspen Plus process simulation model.²⁷ The impacts corresponding to infrastructure manufacturing were evaluated based on this data. The hourly average infrastructural impacts were calculated assuming 20 years as the design life of the equipment.¹⁰ The details of simulated major process equipment including their sizes and volumes used in developing the simulated processes are provided in Table S8.
- The environmental impacts related to the installation of infrastructure, its maintenance, and usage of land area were excluded from the present analysis owing to the unavailability of pertinent data sets in the EcoInvent 3.10 database. A similar approach was also adopted in previous LCA studies based on techno-economic analysis using process design in Aspen Plus.^{41–43}
- The recycled material streams were not included in the calculation of the environmental impacts of individual subprocesses for simplification of analysis. This consideration was based on the assumption that the net impact of such materials on the overall process is insignificant.
- The coproducts of the hydrogenolysis (methanol) and fermentation (2,3-BDO, ethanol, and steam) technologies were added as avoided products in the LCA, which implied that the environmental impacts of these products were negated from the total environmental impacts of the corresponding processes. This approach enables determining the environmental impacts associated with the production of the major products (1,2-PDO and 1,3-PDO) from their respective processes.
- The environmental emissions from the collection and transportation of glycerol and other chemicals to the biorefinery were presumed to be relatively similar and negligible for all the

scenarios and thus not included in the current study. Earlier LCA analyses have also considered the relative environmental impacts of the collection and transportation of feedstock and utilities as negligible in comparative LCAs.^{41,44,45}

Life Cycle Impact Assessment (LCIA). The LCA was modeled with the ReCiPe 2016 (H) method, one of the most widely utilized LCIA methodologies using SimaPro v9.6 PhD software. The environmental impacts of the processes were carried out using this method at both the midpoint level, which evaluated the level of individual environmental problems, and depicted environmental impacts at higher aggregation levels through cause-effect aggregation principles at the endpoint level. The midpoint impact categories adopted in this study encompass 18 different categories: freshwater ecotoxicity (FE), freshwater eutrophication (FEu), fine particulate matter formation (FPMF), fossil resource scarcity (FRS), global warming (GW), human noncarcinogenic toxicity (HNCT), human carcinogenic toxicity (HCT), ionizing radiation (IRAD), land use (LU), marine ecotoxicity (ME), marine eutrophication (MEu), mineral resource scarcity (MRS), ozone formation, human health (OF, H), ozone formation, terrestrial ecosystems (OF, T), stratospheric ozone depletion (SOD), terrestrial acidification (TA), terrestrial ecotoxicity (TE), and water consumption (WC). The endpoint impact categories include damages to ecosystems, human health, and resources. Furthermore, this study adopted the “avoided burden” and “system expansion and substitution” approaches for impact allocation following the recommendations of ISO 14044, thereby ensuring a comprehensive understanding of the environmental implications across the entire life cycle of the processes.

Sensitivity and Uncertainty Analysis. Some specific input/output subprocesses and parameters with the highest contribution to their respective processes' overall environmental impacts were identified as critical hotspots. The sensitivity of these critical input/output subprocesses and parameters can have a major influence on the variability of the overall environmental impacts of the process. A sensitivity analysis was therefore conducted for these parameters with variations set at $\pm 5\%$ and $\pm 10\%$ to determine their effects of fluctuations on the overall contribution analysis. Furthermore, uncertainty analysis of the processes was also performed using the Monte Carlo method through 10 000 simulations at a 95% confidence interval. This analysis was carried out through SimaPro software using the ReCiPe 2016 midpoint (H) method.

RESULTS AND DISCUSSION

Life Cycle Impact Assessment. The relative environmental impacts of manufacturing 1,2-PDO by hydrogenolysis (scenario 1) and fermentative production of 1,3-PDO through batch (scenario 2) and fed-batch (scenario 3) from glycerol were evaluated at the midpoint (Figure 3a) and endpoint levels (Figure 3b). These impacts were calculated for the valorization of 20 833 kg/h of glycerol. To facilitate effective comparison across different impact categories and determine the cumulative impacts, midpoint and endpoint normalized scores were used. Further, the detailed characterization of midpoint data for all the processes/subprocesses is depicted in the Supporting Information (Tables S4 and S5). The relative contribution of individual subprocesses and pathways to the total environmental impacts were evaluated to determine the primary hotspots of interest. Moreover, the relative significance of the impact categories was analyzed to understand the potential areas of highest environmental concern.

The midpoint environmental impacts of all of the glycerol valorization processes depicted that water consumption (WC), human carcinogenic toxicity (HCT), and fossil resource scarcity (FRS) were the primary impact categories of concern. Their respective contributions were 19.8–36.3% (WC), 19.7–25.8% (HCT), and 8.3–11.3% (FRS) of the total midpoint environ-

mental impacts. These impact categories were especially prominent in scenario 2, where they exhibited the highest contributions compared to other scenarios (Table S9). Further, the marine eutrophication (MEu) category was also identified as an area of concern in scenario 3, which represented 9.5% of the total midpoint impacts. The distillation process was the highest contributor to the WC impact category (74.2–83.3%) in all three scenarios. The hydrogenolysis process in scenario 1 (63.7%) and the fermentation process in scenarios 2 and 3 (55.5–74.2%) accounted for the highest contributions to the HCT impact category (Table S4). For the FRS category, the distillation process contributed to a higher proportion of impacts in scenario 1 (59.5%) and scenario 2 (70.8%). However, in scenario 3, the fed-batch fermentation process represented the highest proportion of effects (63%). With respect to total midpoint impacts of the technologies, distillation alone contributed to 24.1–58.2%, while hydrogenolysis and fermentation processes accounted for 51.6% and 41.2–66.1%, respectively, depicting them as the major environmental hotspots.

Further, other impact categories, including marine eutrophication (MEu) (4.5–9.5%), global warming (GW) (4–4.89%), terrestrial ecotoxicity (TE) (4.75–5.61%), and effects of ozone formation on terrestrial ecosystems (OF, T) (3.5–3.6%) also contributed significant proportions to the overall midpoint impacts of the technologies (Table S9). Distillation (40.1–66.8%) and hydrogenolysis/fermentation (33.2–59.9%) processes were the major subprocesses, individually contributing to GW, TE, and (OF, T) in scenarios 1 and 2. However, in the case of scenario 3, the distillation process (61.4–89.7%) was identified as the major factor contributing to the effects of all these parameters, depicting the environmental significance of this subprocess to fed-batch fermentation. Previous studies have also identified the associated environmental impact categories of heating and cooling demand, including GW, TE, eutrophication, aquatic ecotoxicity, and climate change, as hotspot categories of concern during glycerol valorization in a biorefinery system.^{8,27,30} However, it should be noted that due to the adoption of different LCA methodologies for the evaluation of the environmental impacts in those studies, an accurate comparison of the impact categories is not feasible.

The environmental impacts related to the ME category exhibited an interesting case, where the distillation process depicted positive impacts in scenarios 2 and 3, negating 1–3% of the impacts contributed by the fermentation subprocess. This could be attributed to the positive contributions of the coproducts recovered from the fermentation process (2,3-BDO and ethanol), which were considered as avoided products in this LCA study. The positive environmental effects of recovering value-added coproducts in an integrated circular bioeconomy-based biorefinery have been depicted by previous studies.^{46–48} However, it should be noted that coproduct handling methods in LCA, including mass allocation, energy allocation, economic allocation, and substitution method (as adopted in the current study), have a significant influence on the environmental impacts of the overall process in a multiproduct biorefinery.^{49–52}

Human health was the most impacted category (90.4–91.5%) across all the glycerol valorization processes, with the highest contributions to the total endpoint negative impacts. Distillation was the major process contributing up to 53.1–62.7% of the overall impact of all the subprocesses in scenarios 1 and 2. However, glycerol fermentation exhibited the highest contribu-

tion (63.1%) to the human health impact category in scenario 3. Further, the glycerol hydrogenolysis (44.5%) in scenario 1 and the glycerol fermentation (31.3%) process in scenario 2 also had significant effects on the human health damage category. Ecosystem (6.73–8.25%) and resources (1.4–1.85%) also depicted significant contributions to the total endpoint impacts. Glycerol batch fermentation depicted the highest endpoint impacts, which were 1.3–2.1 times higher than those of the other two processes. The adoption of the fed-batch fermentation process alone reduced the overall endpoint impacts by 1.23 fold during the fermentation stage and 4.6 fold in the distillation stage compared to their respective stages in the batch process. This emphasizes the environmental relevance of fed-batch fermentation, which could be attributed to the higher product titer, yielding better output with a relatively lower consumption of resources.

Comparatively, the inoculum cultivation phase in the fed-batch process resulted in an increase of 119% of the cumulative endpoint impacts compared to the batch process. However, the relative positive impacts of the boiler, which were able to negate 234.5 Pt in batch fermentation, reduced to 58.7 Pt in fed-batch fermentation. This can be due to relatively lower biomass production in the fed-batch process compared to that in the batch process. However, it should be noted that the proportionate contribution of the boiler process to the individual endpoint impact categories did not depict any significant changes among the batch and fed-batch processes. Table 3 highlights the environmental hotspot subprocesses and impact categories identified in various LCA studies on glycerol valorization to high-value products. However, it is important to note that variations in the reported impact categories arise from differences in LCA methodologies employed across those studies.^{27,29,31} Furthermore, direct comparison of impact category values is not feasible due to the adoption of various functional units,^{8,30} differences in the goal and scope of the LCAs, and inconsistent coverage of impact categories across studies.⁸

Detailed Contribution Analysis. The detailed contribution analysis representing the classification of respective midpoint and endpoint impacts by individual processes is depicted in panels a and b of Figure 4, respectively. Considering each individual process, the distillation stage as well as hydrogenolysis (in scenario 1) and fermentation processes (in scenarios 2 and 3) were determined as the major environmental hotspots with the highest environmental impacts among the glycerol valorization techniques. The environmental impacts of the distillation stage were primarily influenced by the cooling water and steam consumption, which were responsible for 48.8–62.6% and 50.2–59.3%, respectively, of the total impacts of the distillation process. While the cooling water impacts were majorly responsible for the high environmental impact contribution to WC, the steam utility contributed to FRS, HCT, and (OF, T) midpoint impact categories. Cooling water and steam as utilities were also identified as critical hotspots in glycerol valorization processes by previous LCA studies.^{8,11,27,28} In this study, cooling water and steam were considered externally sourced and used as inputs for different processes. The environmental impacts of these products were mostly associated with the raw water sourcing and its processing to the desired quality along with energy demands for their respective heating/cooling application. Therefore, integrating closed-loop recycling systems for steam and cooling water in the biorefinery to substitute the raw water demand for the processes while

reducing wastewater discharge can be a sustainable practice.^{41,53} In particular, the integration of near-zero liquid discharge systems to successfully enhance the sustainability of the industrial processes through water treatment and recirculation has been depicted by other studies.^{54,55} Water recycling has already been a substantial part of this study, where the water used in catalytic hydrogenolysis (scenario 1) and fermentation subprocesses (scenario 2 and 3) was entirely recycled from the distillation process. However, stringent evaluation of the techno-economic feasibility and environmental sustainability of such integrated wastewater treatment processes is necessary to produce cooling water and steam of adequate quality. Further, considering energy demands as a substantial part of the process in a biorefinery, heat integration for energy utilization within the systems can reduce the load on cooling/heating systems, resulting in substantial enhancement of environmental sustainability of the overall process.^{28,31}

On the other hand, the impacts of hydrogenolysis and fermentation processes can be majorly attributed to the glycerol feed, which accounted for 76.2% (scenario 1), 54.2% (scenario 2), and 92.2% (scenario 3) of these respective subprocesses. The upstream processing of glycerol was alone responsible for 33.3–68.1% of the total midpoint impacts of the glycerol valorization technologies. Previous studies^{27,29–31} have also emphasized the environmental significance of upstream pure glycerol production processes, including raw glycerol sourcing and purification, making them a critical hotspot during glycerol valorization in their LCA studies (Table 3). The glycerol consumption majorly contributed to the ME, TE, HCT, and FRS impact categories. Cespi et al.²⁹ have also reported that the raw biomass cultivation phase in glycerol production was responsible for the majority of these midpoint environmental impacts, which further contributed to the human health category in the endpoint impacts. This emphasizes the importance of glycerol sourcing, which influences the upstream environmental impacts of the material. In the fermentation techniques, apart from glycerol consumption as the feed, a part of it was consumed in the microbial growth,¹⁰ which was responsible for 5.3% (batch) and 10.5% (fed-batch) of the total impacts of the glycerol consumption. Wong et al.³⁴ also reported 28% of the total glycerol consumption during the biomass (*Klebsiella* sp. HE-2 cells) growth stage during fermentative production of 1,3-PDO. Its importance was more prominent in the fed-batch fermentation technique, where the contribution of environmental impacts from glycerol consumption increased by 34.8% compared to the batch fermentation technique. This could be attributed to a relative decrease in the overall impacts of other processes in the fed-batch fermentation process. Further, Cespi et al.²⁹ and Minh Loy et al.³⁰ have also highlighted the environmental prominence of CG purification as one of the significant phases in glycerol production, mostly contributed by water and energy consumption during the process.

The coproducts of the processes, namely methanol (hydrogenolysis) and 2,3-BDO and ethanol (batch and fed-batch fermentation), were able to compensate for 0.1%, 7.6%, and 23.4% of the environmental impacts of their respective subprocesses. This translated to overall reductions of 0.1% (hydrogenolysis), 4.5% (batch fermentation), and 19.5% (fed-batch fermentation) in the total environmental impacts. Similarly, the burning of biomass in the boiler process, which was responsible for generating steam and heat energy, was jointly able to negate 1.2–2.4% of the total impacts in the fermentation techniques. Considering steam consumption as

Table 3. Comparison of the Current Study with Other LCA Studies on Glycerol Valorization to Different High-Value Products

s. no	main product	conversion method	LCA methods	environmental hotspots	major environmental impact categories	reference
1.	1,2-PDO	isothermal and nonisothermal hydrogenolysis	midpoint method CML2001 (cradle-to-gate LCA)	<ul style="list-style-type: none"> glycerol production heating demand 	<ul style="list-style-type: none"> photochemical oxidation global warming potential eutrophication potential 	Gonzalez-Garay et al. ²⁷
2.	1,2-PDO and 1,3-PDO	hydrogenolysis	greenhouse gases, regulated emissions, and energy use in transportation (GREET) model	<ul style="list-style-type: none"> glycerol production energy input from natural gas hydrogen and dipotassium phosphate 	<ul style="list-style-type: none"> life cycle greenhouse gas emissions fossil energy consumption 	Adom et al. ³¹
3.	1,2-PDO	hydrogenolysis	ReCiPe 2016 method (gate-to-gate LCA)	<ul style="list-style-type: none"> glycerol production wastewater generation greenhouse gas emissions 	<ul style="list-style-type: none"> ozone depletion potential aquatic ecotoxicity global warming potential 	Loy et al. ³⁰
4.	dihydroxyacetone (DHA)	microbial fermentation and catalytic oxidation	LCA impact categories: fossil resource scarcity, global warming, human noncarcinogenic toxicity, land use, terrestrial ecotoxicity, and water consumption (cradle-to-gate LCA)	<ul style="list-style-type: none"> heat energy utility glycerol production use of acetone as raw material 	<ul style="list-style-type: none"> terrestrial ecotoxicity land use global warming 	Thanahiranya et al. ⁸
5.	lactic acid	cascade bio/chemocatalysis	LCA metrics: <ul style="list-style-type: none"> cumulative energy demand (CED) global warming potential (GWP-100a) 	<ul style="list-style-type: none"> DHA production from crude glycerol energy consumption in enzymatic process methanol recovery and catalyst reusability 	<ul style="list-style-type: none"> GWP₁₀₀ CED 	Morales et al. ³²
6.	propionic acid	fermentation	eco indicator 99 (EI99) (cradle-to-gate LCA) global warming potential using CO ₂ equivalent emissions (cradle-to-gate LCA)	<ul style="list-style-type: none"> glycerol production cooling water steam refrigerant heat energy utility process waste 	<ul style="list-style-type: none"> global warming potential 	Thanahiranya et al. ¹¹
7.	dihydroxyacetone (DHA)	biocatalysis and chemocatalysis	LCA metrics: <ul style="list-style-type: none"> cumulative energy demand (CED) global warming potential (GWP-100a) eco indicator 99 (EI99) (cradle-to-gate LCA) ReCiPe 2008 midpoint, ReCiPe 2008 endpoint	<ul style="list-style-type: none"> glycerol production pathways 	<ul style="list-style-type: none"> agricultural land occupation climate change terrestrial ecotoxicity 	Lari et al. ²⁸
8.	acrolein	dehydration				Cespi et al. ²⁹
9.	1,2-PDO	hydrogenolysis	ReCiPe 2016 midpoint (H)	<ul style="list-style-type: none"> cooling water utility in distillation 	<ul style="list-style-type: none"> water consumption 	current study

Table 3. continued

s. no	main product	conversion method	ReCiPe 2016 endpoint (H) (cradle-to-gate LCA)	LCA methods	environmental hotspots	major environmental impact categories	reference
	1,3-PDO	fermentation			<ul style="list-style-type: none"> glycerol production steam utility 	<ul style="list-style-type: none"> human carcinogenic toxicity fossil resource scarcity 	

one of the major hotspots of the overall fermentation process, the steam generated from the boiler process was able to compensate for 6.6% (batch) and 7.1% (fed-batch) of the total steam midpoint impacts. The relatively lower quantity of biomass production in the fed-batch fermentation compared to that in the batch fermentation also resulted in a proportionate reduction (by 12%) of the environmental effects contributed by the boiler unit. This emphasizes the need for sustainable management of resources, which significantly reduces the negative impacts of the processes. The environmental significance of integrated biorefinery system with a recovery boiler unit for the generation of high-pressure steam from waste biomass was also demonstrated in other studies.^{56–58} However, it is necessary to integrate the in situ boiler system with air pollution control equipment to reduce the environmental impacts from gaseous and particulate pollutants to meet ambient standards.⁵⁹

The total contribution of capital goods was only responsible for 0.28–0.46% of the total midpoint environmental impacts, rendering it very insignificant. Previous studies have also emphasized the insignificant contribution of infrastructure and capital goods to the overall environmental impacts in large-scale biorefinery processes with prolonged service life.^{41,60,61} The nutrients in the inoculum process contributed 32.1–44.3% of the inoculum growth stage during the fermentation; their overall share to the total impacts of the fermentation process was 1.4% (batch) and 3.82% (fed-batch), which was highly significant. Further, hydrogen consumption, which was responsible for 1.4% of the impacts of the hydrogenolysis process, contributed to 0.73% of the impacts. It should be noted that these impacts represent only 20.2% of the total hydrogen demand of the process. The recycling of hydrogen, which was an integral part of the hydrogenolysis subprocess, was responsible for a substantial reduction in hydrogen consumption and further reduced the overall environmental impacts. Further, Minh Loy et al.³⁰ depicted the potential of an integrated design, where the use of in situ hydrogen can eliminate the need for hydrogen storage and transportation and significantly improve the overall sustainability of the process. Electricity, which was an essential part of all the subprocesses, only represented 0.1–0.4% of the overall environmental impacts of the processes.

Comparing the individual glycerol valorization routes, scenario 3 exhibited the lowest environmental footprint compared to scenario 2 (by 48.2%) and scenario 1 (by 35.2%) processes. This can be directly related to the relatively lower consumption of cooling water (by 2.6–3.8 times) and steam (by 2.9–4.3 times) in the fed-batch fermentation process. This translated to reduced environmental impacts during the fermentation and distillation subprocesses. The midpoint environmental impacts of hydrogenolysis and batch fermentation subprocesses were comparable; the fed-batch fermentation depicted 16.8–17% lower impacts. Additionally, there were 67.7–78.5% lower impacts exhibited by the distillation process in scenario 3. However, higher glycerol consumption in scenario 3 translated to 5.9–11.8% higher environmental impacts compared to the other scenarios. This led to 44.4% higher environmental impacts compared to the inoculum cultivation subprocesses of fed-batch and batch fermentation techniques. Additionally, the differences in nutrient consumption (during the inoculum growth stage), electricity, and infrastructure contributed to minor variations in the overall environmental impacts among the techniques.

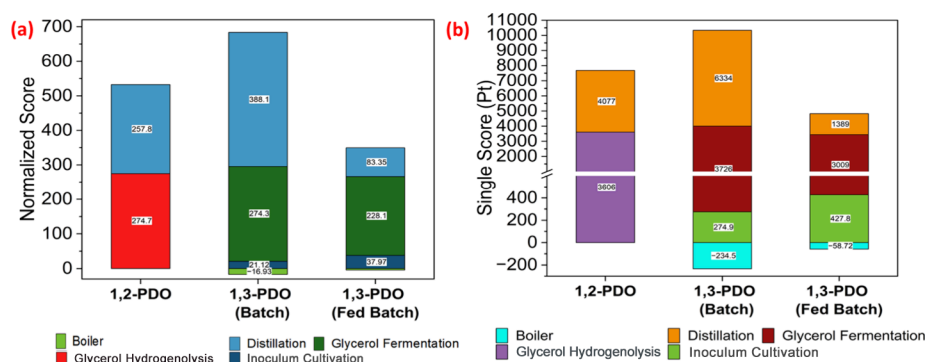


Figure 4. Detailed contribution analysis of individual processes: (a) classification of midpoint impacts and (b) classification of endpoint impacts.

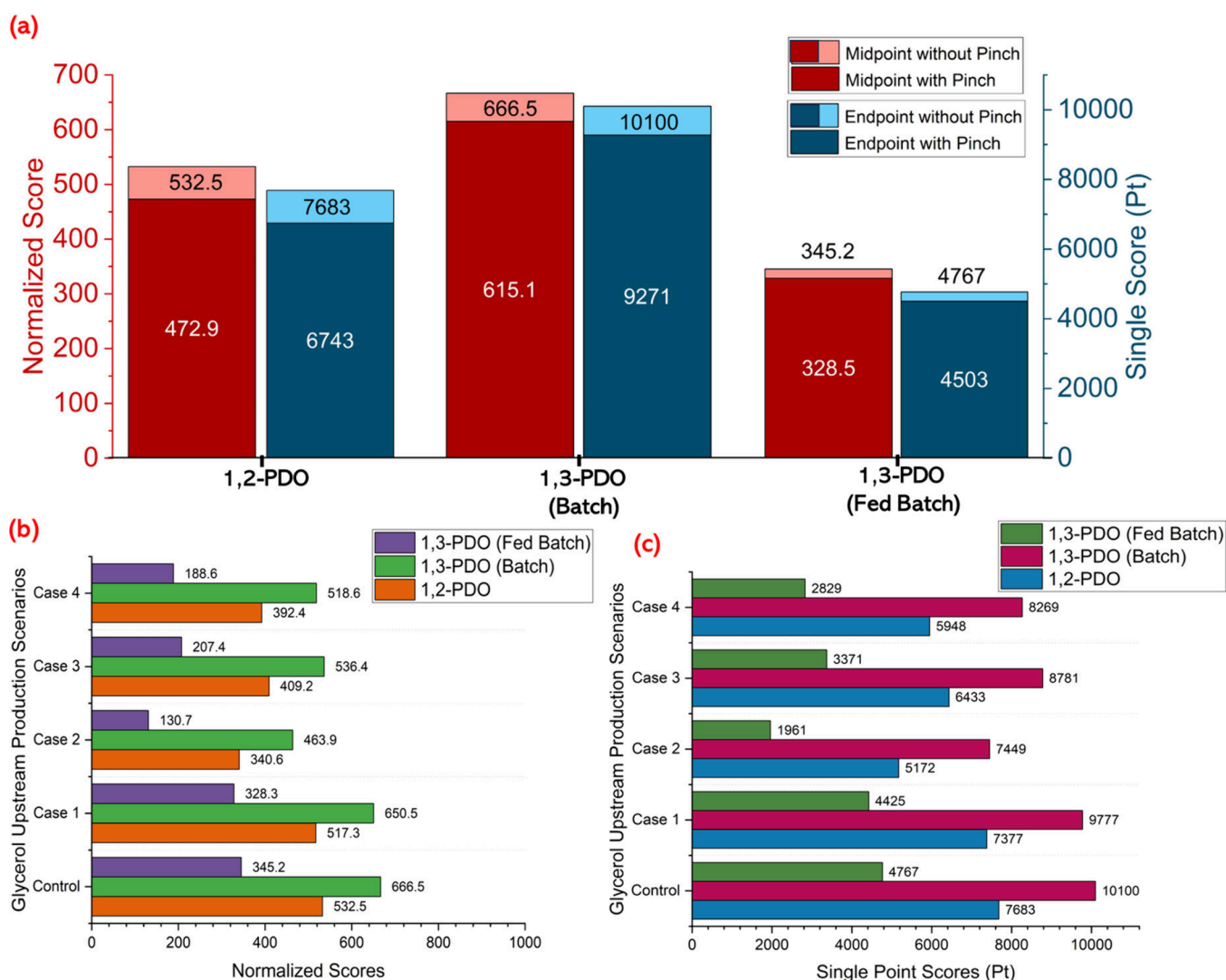


Figure 5. Scenario analysis for conversion of glycerol to 1,2-PDO through catalytic hydrogenolysis and 1,3-PDO through batch/fed-batch fermentation. (a) Variation in midpoint and endpoint impacts in with pinch vs without pinch technologies. Influence of glycerol feedstock sourcing on (b) midpoint impacts and (c) endpoint impacts.

Thus, the fed-batch fermentation technique was determined to be the most environmentally efficient among the compared glycerol valorization routes. Further, cooling water and steam utility during the distillation subprocess as well as glycerol consumption were identified as the critical hotspots, which should be of significant importance while designing the systems. Castro Oliveira et al.⁵⁵ suggested simultaneous improvement of

water and energy use efficiently through the integration of water and energy integration systems (WEIS) and water-heat nexus (WHN) based on process integration and system retrofitting principles. It entails implementing technologies that facilitate water recirculation for both heat recovery and supplemental water supply purposes. Specifically, these technologies include recirculating waste heat streams to thermal processes,⁶²

redirecting waste heat streams to water system heaters,⁶³ integrating waste heat streams into heat-driven wastewater treatment units,⁶⁴ and utilizing sludge generated from wastewater treatment as an additional energy source.⁴⁷ Mussatto et al.⁶⁵ suggested a combination of mass and energy integration as the optimal approach for achieving higher environmental performance in a biorefinery, although mass integration yielded relatively better results than energy integration in their study.

Scenario Analyses. Integration with Heat Recovery and Recirculation. The current study identified cooling water and steam utility as one of the major contributors to the total load of environmental impacts of glycerol valorization technologies. So, the environmental sustainability of these scenarios can substantially improve with the recycling of this heat energy generated across different processes to supplement the energy demands of the overall process. Pinch technology is a widely adopted process integration technique that connects cold and hot streams within the process through an optimal design of a heat exchanger network. By facilitating effective trading between recoverable internal and external heat energy demand (majorly through steam) through in-process cooling water recirculation, pinch technology aims to enhance the overall thermal efficiency of industrial processes. Hence, in this section, the relative environmental impacts of the base scenarios (without pinch) are compared to process integration with pinch technology for effective heat recovery and recirculation (Figure 5a).

Compared to the base scenarios, pinch technology-based process integration improved the environmental performance of the technologies by reducing the overall midpoint (by 4.9–11.2%) and endpoint (by 5.5–12.2%) impacts. This variation in the environmental impacts can be primarily accredited to the reduction in the cooling water consumption (by 12–18.7%), and steam demand (by 12–19.3%) in the processes facilitated by cooling water recirculation-assisted heat exchange within the system. A substantial reduction in the cooling water and steam utility was observed in the hydrogenolysis subprocess (scenario 1) by 58.46% and 82.79%, respectively, which corresponded to a 14.4% reduction in the midpoint impacts of the subprocess. Similarly, the integration of pinch technology resulted in a decrease in cooling water (by 65.6–79.5%) and steam (by 88.5–89.3%) utility in batch/fed-batch fermentation (scenarios 2 and 3). This resulted in a 5.7–19.2% decrease in the midpoint impacts of the subprocess. The consequent decrease in the environmental midpoint impacts with cooling water recycling was also observed in the distillation subprocess (by 4.7–7.8%) in pinch technologies of scenarios 1 and 3. However, the 1.18% higher consumption of cooling water in the distillation stage of scenario 3 caused a minor increase in the midpoint impacts by 0.3% (Table S9). Gonzalez-Garay et al.²⁷ and Thanahiranya et al.⁸ also depicted better environmental performance from process integration with heat exchangers in their glycerol valorization technologies. Overall, scenario 1 achieved the highest reduction in total environmental impacts, decreasing by 11.2% (midpoint) and 12.2% (endpoint), thereby significantly enhancing its relative environmental performance compared to other scenarios. However, it should be highlighted that scenario 3, with heat exchange, demonstrated superior environmental performance with the lowest overall environmental impacts. Specifically, scenario 3 resulted in 30.5–46.6% lower midpoint impacts and 33.2–51.4% lower endpoint impacts compared to the other scenarios. Moreover, utilization of the heat energy recovered in the boiler process generated from burning the waste biomass produced during fermentation in scenarios 2 and

3 (input as avoided product) can further reduce the heat required in the overall process and thus improve the sustainability of the technologies in the current study.

Glycerol Feedstock Sourcing. Glycerol feed has been one of the prominent input factors identified as the environmental hotspot in all of the scenarios. The environmental impacts of glycerol feed are mostly associated with feedstock sourcing for CG production along with its upstream purification processes.²⁹ The glycerol selected in the current study corresponds to the production and supply of glycerol within the European market as adopted from the EcoInvent 3.10 database. To understand the influence of glycerol feedstock sourcing from different biomass sources in various geographic locations on the overall environmental performance of the technologies, scenario analysis was performed (Figure 5b,c). In this context, four different data sets of glycerol production available in the EcoInvent 3.10 database were used as scenarios and compared to the control scenario as adopted in the current study: case 1, glycerol from transesterification of rape oil (Europe without Switzerland); case 2, glycerol from the treatment of waste cooking oil, purified by transesterification (France); case 3, glycerol from transesterification of palm oil (rest of the world); and case 4, glycerol from transesterification of soybean oil (United States). These cases encompass the recovery of glycerol from the base-catalyzed transesterification process of different oil feedstocks, producing multiple products, including methyl esters, crude glycerol, and other byproducts. It should be noted that the data sets do not specify the purity of crude glycerol or whether its processing to pure glycerol is included in the data sets. However, the glycerol as an output of these processes was directly incorporated into the data set “market for glycerine in the region of Europe (RER)”, which was used for the base scenario (control). So, the relative significance of crude glycerol purification among the different cases in the study was assumed to be negligible. Consequently, for the current study, it was assumed that the purification of glycerol to standard European market quality was also integrated with transesterification processes in all cases, irrespective of the output crude glycerol quality from various feedstocks. This should be considered as an assumption in this scenario analysis.

The results revealed that glycerol produced from the treatment of waste cooking oil, purified by transesterification (France), yielded the best results with substantially lower environmental impacts (91.2%) compared to the glycerol of the control scenario. This factor led to significant improvement in the environmental performance of the overall processes by 30.4–62.1% and 26.3–58.9% in the midpoint and endpoint impact categories, respectively. Similarly, the other glycerol feedstocks also yielded better results compared to the control in the midpoint and endpoint impacts in the order of case 4 (22.2–45.4% and 18.1–40.7%) < case 3 (19.5–39.9% and 13.1–29.3%) < case 1 (2.4–4.9% and 3.2–7.2%). Comparing the individual glycerol valorization technologies studied, the highest reduction was observed in the fed-batch fermentation technique, considering the highest contribution of glycerol to its overall impacts. For instance, the lowest environmental impacts of 130.7 and 1961 Pt (midpoint and endpoint) were observed compared to the control scenario 3 values of 345.2 and 4767 Pt. Adom et al.³¹ also suggested the relative environmental significance of sourcing glycerol from waste feedstocks (such as algae and corn-stover-derived sugars) compared to first-generation agricultural feedstocks. Moreover, with the integration of pinch technology, the environmental impacts were

further reduced by 12.8–13.5%, which resulted in an overall reduction of the environmental impacts in the fed-batch fermentation technology by 67% (midpoint) and 64.4% (endpoint). This depicts the necessity for the combined adoption of sustainable sourcing of glycerol feedstock and heat energy recycling to improve the overall environmental performance of the technologies.

Sensitivity and Uncertainty Analysis. Sensitivity analysis was carried out to determine the variability in the environmental impacts of the overall processes with the changes in identified environmental hotspot input parameters (cooling water, steam, and glycerol feed) by $\pm 5\%$ and $\pm 10\%$ (Figure 6a,b). The

of the fed-batch process by 3.4–6.8% (midpoint) and 3.2–6.3% (endpoint). As the glycerol consumption rate for specific products is process dependent, this variation in environmental impacts of glycerol indirectly corresponds to the multiple parameters influencing its source feedstock and processing techniques, as identified by previous studies^{29,31} as a significant factor. The effect of glycerol variation (by 5% and 10%) also yielded significant variation in the environmental impacts of scenario 1 (0.5–2% and 1–4%) and scenario 2 (0.5–1.7% and 1.1–3.3%). So, this emphasizes the importance of adopting sustainable practices, including renewable sourcing of feedstock and process integration with heat and product recycling, which can have a significant positive influence on the overall environmental impacts of the processes.

The uncertainty analysis for midpoint impacts of all of the scenarios was conducted through Monte Carlo simulations (Table S7). This involved 10 000 simulation runs with a 95% confidence interval for processing 20 833 kg/h of glycerol to 1,2-PDO and 1,3-PDO. The analysis showed a moderately lower coefficient of variation (C_v) in hotspot midpoint impact categories including WC (3–3.3%), HCT (2.7–2.9%), FRS (2.8–3%), ME (3.4–3.76%), GW (2.7–2.9%), TE (2.7–2.9%), and (OF, T) (2.7–2.9%) across all the scenarios.

CONCLUSIONS

This investigation examines the relative environmental performance of two promising glycerol valorization routes: catalytic hydrogenolysis to 1,2-PDO and batch and fed-batch fermentation to 1,3-PDO. The utility (steam and cooling water) consumption in downstream product recovery by distillation and upstream glycerol production pathways were recognized as the prominent environmental hotspots. Fed-batch fermentation with a high product titer was environmentally superior to batch fermentation and glycerol hydrogenolysis processes due to higher byproduct yield and lower resource consumption. Heat integration by designing an optimal heat exchanger network using pinch technology further slashed the environmental consequences of these technologies. Moreover, the shift to sustainable feedstock and glycerol production pathways proved environmentally beneficial. Therefore, simultaneous in-process energy utilization through process integration, material recycling, and system retrofitting can improve the overall sustainability of these processes. Considering the global emphasis on the sustainable valorization of low-value biodiesel glycerol, the findings of this LCA study will enable targeted multi-hotspot parameters optimization to enhance the environmental sustainability of these technologies. Further, a techno-economic and environmental optimization of an operational glycerol-based biorefinery plant considering all the location-specific data sets of upstream processes and infrastructural elements in real time is essential for accurate assessment of the environmental footprint.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c04691>.

Summary of selected previous studies depicting high-level 1,2-PDO and 1,3-PDO production using pure/crude glycerol, background data sets adopted from EcoInvent for the LCA analysis, midpoint characterization data for all the processes and subprocesses, midpoint character-

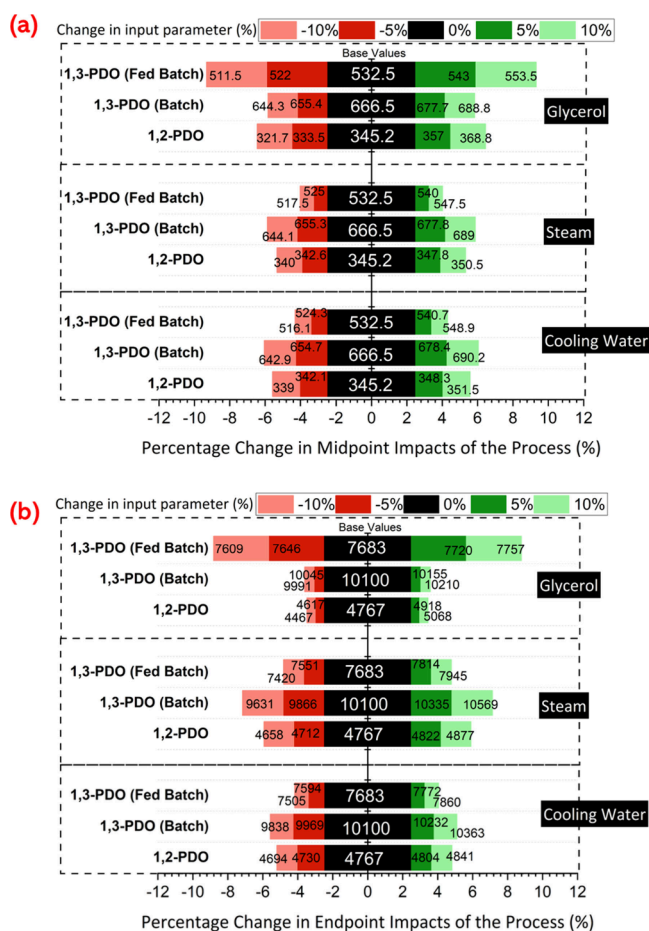


Figure 6. Sensitivity analysis for (a) midpoint impacts and (b) endpoint impacts, with changes in the cooling water utility, steam utility, and glycerol consumption rate.

detailed midpoint characterization data for the sensitivity analysis for all the scenarios are depicted in Table S6. The sensitivity analysis indicated that a 5% and 10% change in cooling water utilization would alter the total midpoint impacts of the process by 0.9–1.5% and 1.8–3.6%, which corresponded to 0.8–1.3% and 1.6–2.6% variability in the endpoint impacts, respectively. Similarly, a 5% and 10% change in steam utility affected the overall environmental impacts by 0.8–1.7% and 1.5–3.4% (midpoint) and 1.1–2.3% and 2.3–4.6% (endpoint), respectively. It was observed that the variability of both these input parameters had their highest influence on batch fermentation technique, followed by hydrogenolysis and fed-batch processes. In contrast, the variation in the glycerol consumption rate was more influential in changing the impacts

ization data for the sensitivity analysis, uncertainty analysis, simulated major process equipment details, and proportionate distribution of midpoint and endpoint characterization results for individual impact categories (PDF)

AUTHOR INFORMATION

Corresponding Authors

Kumar Raja Vanapalli – Department of Civil Engineering, National Institute of Technology Mizoram, Aizawl, Mizoram 796012, India; Email: kumar.ce@nitmz.ac.in

Sunil K. Maity – Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Sangareddy, Telangana 502284, India; orcid.org/0000-0002-1832-5060; Email: sunil_maity@che.iith.ac.in

Vinod Kumar – Faculty of Engineering and Applied Sciences, Cranfield University, Cranfield MK43 0AL, United Kingdom; Department of Biosciences and Bioengineering, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand 247667, India; orcid.org/0000-0001-8967-6119; Phone: +44 (0) 1234754786; Email: vinod.kumar@cranfield.ac.uk

Author

Lourembam Nongdren – Department of Civil Engineering, National Institute of Technology Mizoram, Aizawl, Mizoram 796012, India

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acssuschemeng.4c04691>

Author Contributions

Kumar Raja Vanapalli: Conceptualization, Methodology, Writing—original draft. **Lourembam Nongdren**: Methodology, Analysis, Writing—original draft. **Sunil K. Maity**: Conceptualization, Data curation, Writing—review and editing. **Vinod Kumar**: Conceptualization, Writing—review and editing.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) *Advanced Biofuels in European Union: Status Report on Technology Development, Trends, Value-Chains and Markets* (EUR 31287 EN); Publications Office of the European Union, Ispra, Italy, 2022. www.etipbioenergy.eu/images/Advanced%20Biofuels%20-%20CETO%20Report%202022.pdf.
- (2) Mandari, V.; Devarai, S. K. Biodiesel Production Using Homogeneous, Heterogeneous, and Enzyme Catalysts via Transesterification and Esterification Reactions: A Critical Review. *Bioenergy Res.* **2022**, *15* (2), 935–961.
- (3) Quispe, C. A.; Coronado, C. J.; Carvalho, J. A., Jr. Glycerol: Production, Consumption, Prices, Characterization and New Trends in Combustion. *Renewable and sustainable energy reviews* **2013**, *27*, 475–493.
- (4) Attarbach, T.; Kingsley, M. D.; Spallina, V. New Trends on Crude Glycerol Purification: A Review. *Fuel* **2023**, *340*, No. 127485.
- (5) Dhabhai, R.; Koranian, P.; Huang, Q.; Scheibelhoffer, D. S. B.; Dalai, A. K. Purification of Glycerol and Its Conversion to Value-Added Chemicals: A Review. *Sep. Sci. Technol.* **2023**, *58* (7), 1383–1402.
- (6) Global Glycerol Industry (2020 to 2027) - Market Trends and Drivers - ResearchAndMarkets.com. Business Wire. <https://www.businesswire.com/news/home/20210115005399/en/Global-Glycerol-Industry-2020-to-2027---Market-Trends-and-Drivers---ResearchAndMarkets.com> (accessed 2024-05-12).
- (7) Biodiesel Market Size, Share & Trends Analysis Report By Feedstock (Vegetable Oils, Animal Fats), By Application (Fuel, Power Generation), By Region (Europe, APAC), And Segment Forecasts, 2022 - 2030. Grand View Research, 2022. <https://www.grandviewresearch.com/industry-analysis/biodiesel-market> (accessed 2024-05-12).
- (8) Thanahiranya, P.; Sadhukhan, J.; Charoensuppanimit, P.; Soottitantawat, A.; Arpornwichanop, A.; Thongchul, N.; Assabumrungrat, S. Sustainability Assessment of Dihydroxyacetone (DHA) Production from Glycerol: A Comparative Study between Biological and Catalytic Oxidation Routes. *ACS Sustainable Chem. Eng.* **2023**, *11* (49), 17425–17439.
- (9) Mangayil, R.; Efimova, E.; Kontinen, J.; Santala, V. Co-Production of 1, 3 Propanediol and Long-Chain Alkyl Esters from Crude Glycerol. *New biotechnology* **2019**, *53*, 81–89.
- (10) Shrirame, B. S.; Varma, A. R.; Sahoo, S. S.; Gayen, K.; Maity, S. K. Techno-Commercial Viability of Glycerol Valorization to 1, 2-and 1, 3-Propanediol Using Pinch Technology. *Biomass and Bioenergy* **2023**, *177*, No. 106943.
- (11) Thanahiranya, P.; Charoensuppanimit, P.; Soottitantawat, A.; Arpornwichanop, A.; Thongchul, N.; Assabumrungrat, S. Sustainable Process Design of Propionic Acid Production from Glycerol: A Comparative Study of Bio-Based and Petroleum-Based Technologies. *ACS Sustainable Chem. Eng.* **2022**, *10* (45), 14761–14774.
- (12) Pan, D.; Wang, X.; Wang, J.; Shi, H.; Wang, G.; Xiu, Z. Optimization and Feedback Control System of Dilution Rate for 1,3-propanediol in Two-stage Fermentation: A Theoretical Study. *Biotechnol. Prog.* **2022**, *38* (1), No. e3225.
- (13) Restrepo, J. B.; Paternina-Arboleda, C. D.; Bula, A. J. 1, 2-Propanediol Production from Glycerol Derived from Biodiesel's Production: Technical and Economic Study. *Energies* **2021**, *14* (16), 5081.
- (14) Azri, N.; Irmawati, R.; Nda-Umar, U. I.; Saiman, M. I.; Taufiq-Yap, Y. H. Promotional Effect of Transition Metals (Cu, Ni, Co, Fe, Zn)—Supported on Dolomite for Hydrogenolysis of Glycerol into 1, 2-Propanediol. *Arabian Journal of Chemistry* **2021**, *14* (4), No. 103047.
- (15) Zhu, Y.; Wang, Y.; Gao, H.; Wang, H.; Wan, Z.; Jiang, Y.; Xin, F.; Zhang, W.; Jiang, M. Current Advances in Microbial Production of 1,3-propanediol. *Biofuels Bioprod Bioref* **2021**, *15* (5), 1566–1583.
- (16) Poddar, M. K.; Pandey, A.; Jha, M. K.; Andola, S. C.; Ali, S. S.; Bhandari, S.; Sahani, G. K.; Bal, R. Aqueous Phase Hydrogenolysis of Renewable Glycerol to 1, 2-Propanediol over Bimetallic Highly Stable and Efficient Ni-Cu/Al₂O₃ Catalyst. *Molecular Catalysis* **2021**, *515*, No. 111943.
- (17) Liu, L.; Ye, X. P. Simultaneous Production of Lactic Acid and Propylene Glycol from Glycerol Using Solid Catalysts without External Hydrogen. *Fuel processing technology* **2015**, *137*, 55–65.
- (18) Zhang, D.; Yu, W.; Li, Z.; Wang, Z.; Yin, B.; Liu, X.; Shen, J.; Yang, C.; Yan, W.; Jin, X. Strong Metal-Support Interaction of Palladium Carbide in PtPd/C Catalysts for Enhanced Catalytic Transfer Hydrogenolysis of Glycerol. *Biomass and Bioenergy* **2022**, *163*, No. 106507.
- (19) Zhang, X.; Cui, G.; Wei, M. PtIn Alloy Catalysts toward Selective Hydrogenolysis of Glycerol to 1,2-Propanediol. *Ind. Eng. Chem. Res.* **2020**, *59* (29), 12999–13006.
- (20) Akiyama, M.; Sato, S.; Takahashi, R.; Inui, K.; Yokota, M. Dehydration-Hydrogenation of Glycerol into 1, 2-Propanediol at Ambient Hydrogen Pressure. *Applied Catalysis A: General* **2009**, *371* (1–2), 60–66.
- (21) Lee, M.; Hwang, Y. K.; Chang, J.-S.; Chae, H.-J.; Hwang, D. W. Vapor-Phase Hydrogenolysis of Glycerol to 1, 2-Propanediol Using a Chromium-Free Ni-Cu-SiO₂ Nanocomposite Catalyst. *Catal. Commun.* **2016**, *84*, 5–10.
- (22) Pandhare, N. N.; Pudi, S. M.; Biswas, P.; Sinha, S. Selective Hydrogenolysis of Glycerol to 1,2-Propanediol over Highly Active and Stable Cu/MgO Catalyst in the Vapor Phase. *Org. Process Res. Dev.* **2016**, *20* (6), 1059–1067.
- (23) Agrawal, D.; Budakoti, M.; Kumar, V. Strategies and Tools for the Biotechnological Valorization of Glycerol to 1, 3-Propanediol: Challenges, Recent Advancements and Future Outlook. *Biotechnology Advances* **2023**, *66*, No. 108177.

- (24) Liberato, V. S.; Martins, F. F.; Maria S Ribeiro, C.; Alice Z Coelho, M.; Ferreira, T. F. Two-Waste Culture Medium to Produce 1, 3-Propanediol through a Wild *Clostridium Butyricum* Strain. *Fuel* **2022**, 322, No. 124202.
- (25) Wang, W.; Yu, X.; Wei, Y.; Ledesma-Amaro, R.; Ji, X.-J. Reprogramming the Metabolism of *Klebsiella Pneumoniae* for Efficient 1,3-Propanediol Production. *Chem. Eng. Sci.* **2021**, 236, No. 116539.
- (26) Yun, J.; Zayed, H. M.; Zhang, Y.; Parvez, A.; Zhang, G.; Qi, X. Co-Fermentation of Glycerol and Glucose by a Co-Culture System of Engineered *Escherichia Coli* Strains for 1, 3-Propanediol Production without Vitamin B12 Supplementation. *Bioresour. Technol.* **2021**, 319, No. 124218.
- (27) Gonzalez-Garay, A.; Gonzalez-Miquel, M.; Guillen-Gosalbez, G. High-Value Propylene Glycol from Low-Value Biodiesel Glycerol: A Techno-Economic and Environmental Assessment under Uncertainty. *ACS Sustainable Chem. Eng.* **2017**, 5 (7), 5723–5732.
- (28) Lari, G. M.; Mondelli, C.; Papadokonstantakis, S.; Morales, M.; Hungerbühler, K.; Pérez-Ramírez, J. Environmental and Economic Assessment of Glycerol Oxidation to Dihydroxyacetone over Technical Iron Zeolite Catalysts. *React. Chem. Eng.* **2016**, 1 (1), 106–118.
- (29) Cespi, D.; Passarini, F.; Mastragostino, G.; Vassura, I.; Larocca, S.; Iaconi, A.; Chierigato, A.; Dubois, J.-L.; Cavani, F. Glycerol as Feedstock in the Synthesis of Chemicals: A Life Cycle Analysis for Acrolein Production. *Green Chem.* **2015**, 17 (1), 343–355.
- (30) Minh Loy, A. C.; Ng, W. L.; Samudrala, S. P.; Bhattacharya, S. Technical, Economic, and Environmental Potential of Glycerol Hydrogenolysis: A Roadmap towards Sustainable Green Chemistry Future. *Sustainable Energy & Fuels* **2023**, 7 (11), 2653–2669.
- (31) Adom, F.; Dunn, J. B.; Han, J.; Sather, N. Life-Cycle Fossil Energy Consumption and Greenhouse Gas Emissions of Bioderived Chemicals and Their Conventional Counterparts. *Environ. Sci. Technol.* **2014**, 48 (24), 14624–14631.
- (32) Morales, M.; Dapsens, P. Y.; Giovino, I.; Witte, J.; Mondelli, C.; Papadokonstantakis, S.; Hungerbühler, K.; Pérez-Ramírez, J. Environmental and Economic Assessment of Lactic Acid Production from Glycerol Using Cascade Bio- and Chemocatalysis. *Energy Environ. Sci.* **2015**, 8 (2), 558–567.
- (33) Sun, D.; Yamada, Y.; Sato, S. Effect of Ag Loading on Cu/Al₂O₃ Catalyst in the Production of 1,2-Propanediol from Glycerol. *Applied Catalysis A: General* **2014**, 475, 63–68.
- (34) Wong, C.-L.; Huang, C.-C.; Chen, W.-M.; Chang, J.-S. Converting Crude Glycerol to 1,3-Propanediol Using Resting and Immobilized *Klebsiella* Sp. HE-2 Cells. *Biochemical Engineering Journal* **2011**, 58–59, 177–183.
- (35) Zhu, S.; Gao, X.; Zhu, Y.; Fan, W.; Wang, J.; Li, Y. A Highly Efficient and Robust Cu/SiO₂ Catalyst Prepared by the Ammonia Evaporation Hydrothermal Method for Glycerol Hydrogenolysis to 1,2-Propanediol. *Catal. Sci. Technol.* **2015**, 5 (2), 1169–1180.
- (36) Kumar, V.; Park, S. Potential and Limitations of *Klebsiella Pneumoniae* as a Microbial Cell Factory Utilizing Glycerol as the Carbon Source. *Biotechnology advances* **2018**, 36 (1), 150–167.
- (37) Europe Biofuel Market Size & Share Analysis - Growth Trends & Forecasts (2024 - 2029). Modor Intelligence, 2023. <https://www.modorintelligence.com/industry-reports/europe-biofuel-market> (accessed 2024-06-02).
- (38) Commission Delegated Regulation (EU) 2023/1640 of 5 June 2023 on the Methodology to Determine the Share of Biofuel and Biogas for Transport, Produced from Biomass Being Processed with Fossil Fuels in a Common Process. European Union, 2023. http://data.europa.eu/eli/reg_del/2023/1640/oj/eng (accessed 2024-06-02).
- (39) Ershov, M. A.; Savelenko, V. D.; Makhova, U. A.; Makhmudova, A. E.; Zengkov, A. V.; Kapustin, V. M.; Abdellatif, T. M. M.; Burov, N. O.; Guik, T.; Abdelkareem, M. A.; Olabi, A. G. Current Challenge and Innovative Progress for Producing HVO and FAME Biodiesel Fuels and Their Applications. *Waste Biomass Valor* **2023**, 14 (2), 505–521.
- (40) Wang, X.; Zhang, L.; Liang, S.; Yin, Y.; Wang, P.; Li, Y.; Chin, W. S.; Xu, J.; Wen, J. Enhancing the Capability of *Klebsiella Pneumoniae* to Produce 1, 3-Propanediol by Overexpression and Regulation through CRISPR-dCas9. *Microbial Biotechnology* **2022**, 15 (7), 2112–2125.
- (41) Vanapalli, K. R.; Bhar, R.; Maity, S. K.; Dubey, B. K.; Kumar, S.; Kumar, V. Life Cycle Assessment of Fermentative Production of Lactic Acid from Bread Waste Based on Process Modelling Using Pinch Technology. *Science of The Total Environment* **2023**, 905, No. 167051.
- (42) Tiwari, B. R.; Bhar, R.; Dubey, B. K.; Maity, S. K.; Brar, S. K.; Kumar, G.; Kumar, V. Life Cycle Assessment of Microbial 2,3-Butanediol Production from Brewer's Spent Grain Modeled on Pinch Technology. *ACS Sustainable Chem. Eng.* **2023**, 11 (22), 8271–8280.
- (43) Vinardell, S.; Cortina, J. L.; Valderrama, C. Environmental and Economic Evaluation of Implementing Membrane Technologies and Struvite Crystallisation to Recover Nutrients from Anaerobic Digestion Supernatant. *Bioresour. Technol.* **2023**, 384, No. 129326.
- (44) Cok, B.; Tsiropoulos, I.; Roes, A. L.; Patel, M. K. Succinic Acid Production Derived from Carbohydrates: An Energy and Greenhouse Gas Assessment of a Platform Chemical toward a Bio-Based Economy. *Biofuels, Bioproducts and Biorefining* **2014**, 8 (1), 16–29.
- (45) Moussa, H. I.; Elkamel, A.; Young, S. B. Assessing Energy Performance of Bio-Based Succinic Acid Production Using LCA. *Journal of Cleaner Production* **2016**, 139, 761–769.
- (46) Cai, H.; Han, J.; Wang, M.; Davis, R.; Biddy, M.; Tan, E. Life-Cycle Analysis of Integrated Biorefineries with Co-Production of Biofuels and Bio-Based Chemicals: Co-Product Handling Methods and Implications: Co-Product Handling Methods and Implications of Life-Cycle Analysis of Biofuel and Bio-Chemical Co-Producing Biorefineries. *Biofuels, Bioproducts and Biorefining* **2018**, 12 (5), 815.
- (47) Hafyan, R. H.; Mohanarajan, J.; Uppal, M.; Kumar, V.; Narisetty, V.; Maity, S. K.; Sadhukhan, J.; Gadkari, S. Integrated Biorefinery for Bioethanol and Succinic Acid Co-Production from Bread Waste: Techno-Economic Feasibility and Life Cycle Assessment. *Energy Conversion and Management* **2024**, 301, No. 118033.
- (48) Spataro, S.; Stadel, A.; Adler, P. R.; Kar, S.; Parton, W. J.; Hicks, K. B.; McAlloon, A. J.; Gurian, P. L. The Role of Biorefinery Co-Products, Market Proximity and Feedstock Environmental Footprint in Meeting Biofuel Policy Goals for Winter Barley-to-Ethanol. *Energies* **2020**, 13 (9), 2236.
- (49) Asdrubali, F.; Cotana, F.; Rossi, F.; Presciutti, A.; Rotili, A.; Guattari, C. Life Cycle Assessment of New Oxy-Fuels from Biodiesel-Derived Glycerol. *Energies* **2015**, 8 (3), 1628–1643.
- (50) Canter, C. E.; Dunn, J. B.; Han, J.; Wang, Z.; Wang, M. Policy Implications of Allocation Methods in the Life Cycle Analysis of Integrated Corn and Corn Stover Ethanol Production. *Bioenerg. Res.* **2016**, 9 (1), 77–87.
- (51) Sills, D. L.; Van Doren, L. G.; Beal, C.; Raynor, E. The Effect of Functional Unit and Co-Product Handling Methods on Life Cycle Assessment of an Algal Biorefinery. *Algal Research* **2020**, 46, No. 101770.
- (52) Wang, M.; Huo, H.; Arora, S. Methods of Dealing with Co-Products of Biofuels in Life-Cycle Analysis and Consequent Results within the U.S. Context. *Energy Policy* **2011**, 39 (10), 5726–5736.
- (53) Lamolinara, B.; Pérez-Martínez, A.; Guardado-Yordi, E.; Guillén Fiallos, C.; Diéguez-Santana, K.; Ruiz-Mercado, G. J. Anaerobic Digestate Management, Environmental Impacts, and Techno-Economic Challenges. *Waste Management* **2022**, 140, 14–30.
- (54) Alnouri, S. Y.; Linke, P.; El-Halwagi, M. M. Accounting for Central and Distributed Zero Liquid Discharge Options in Interplant Water Network Design. *Journal of Cleaner Production* **2018**, 171, 644–661.
- (55) Castro Oliveira, M.; Iten, M.; Matos, H. A. Review on Water and Energy Integration in Process Industry: Water-Heat Nexus. *Sustainability* **2022**, 14 (13), 7954.
- (56) Marinova, M.; Mateos-Espejel, E.; Jemaa, N.; Paris, J. Addressing the Increased Energy Demand of a Kraft Mill Biorefinery: The Hemicellulose Extraction Case. *Chem. Eng. Res. Des.* **2009**, 87 (9), 1269–1275.
- (57) Mongkhonsiri, G.; Anantpinijwatna, A.; Charoensuppanimit, P.; Arpornwathan, A.; Gani, R.; Assabumrungrat, S. Novel Biorefinery-Integrated-Kraft-Pulping Network for Sustainable Development. *Chemical Engineering and Processing - Process Intensification* **2021**, 163, No. 108373.

- (58) Ng, R. T. L.; Tay, D. H. S.; Ng, D. K. S. Simultaneous Process Synthesis, Heat and Power Integration in a Sustainable Integrated Biorefinery. *Energy Fuels* **2012**, *26* (12), 7316–7330.
- (59) Bhatt, A.; Ravi, V.; Zhang, Y.; Heath, G.; Davis, R.; Tan, E. C. D. Emission Factors of Industrial Boilers Burning Biomass-Derived Fuels. *J. Air Waste Manage. Assoc.* **2023**, *73* (4), 241–257.
- (60) Bhar, R.; Tiwari, B. R.; Sarmah, A. K.; Brar, S. K.; Dubey, B. K. A Comparative Life Cycle Assessment of Different Pyrolysis-Pretreatment Pathways of Wood Biomass for Levoglucosan Production. *Bioresour. Technol.* **2022**, *356*, No. 127305.
- (61) Smidt, M.; den Hollander, J.; Bosch, H.; Xiang, Y.; van der Graaf, M.; Lambin, A.; Duda, J.-P. Life Cycle Assessment of Biobased and Fossil-Based Succinic Acid. In *Sustainability Assessment of Renewables-Based Products: Methods and Case Studies*; John Wiley & Sons, Ltd., 2015; p 307–321. DOI: [10.1002/9781118933916.ch20](https://doi.org/10.1002/9781118933916.ch20).
- (62) Chin, H. H.; Foo, D. C. Y.; Lam, H. L. Simultaneous Water and Energy Integration with Isothermal and Non-Isothermal Mixing – A P-Graph Approach. *Resources, Conservation and Recycling* **2019**, *149*, 687–713.
- (63) Zhang, C.; Yang, M.; Lu, M.; Shan, Y.; Zhu, J. Experimental Research on LiBr Refrigeration – Heat Pump System Applied in CCHP System. *Applied Thermal Engineering* **2011**, *31* (17), 3706–3712.
- (64) Cuvilla-Suárez, C.; Colmenar-Santos, A.; Borge-Diez, D.; López-Rey, Á. Heat Recovery in Sanitary-Ware Industry Applied to Water and Energy Saving by Multi-Effect Distillation. *Journal of Cleaner Production* **2019**, *213*, 1322–1336.
- (65) Mussatto, S. I.; Moncada, J.; Roberto, I. C.; Cardona, C. A. Techno-Economic Analysis for Brewer's Spent Grains Use on a Biorefinery Concept: The Brazilian Case. *Bioresour. Technol.* **2013**, *148*, 302–310.



DSPACE

<https://dspace.org/>

Comparative life cycle assessment of glycerol valorization routes to 1,2- and 1,3-propanediol based on process modeling

Vanapalli, Kumar Raja; Nongdren, Lourembam; Maity, Sunil K.; Kumar, Vinod

2024-10-07

American Chemical Society

<https://doi.org/10.1021/acssuschemeng.4c04691>

Vanapalli KR, Nongdren L, Maity SK, Kumar V. (2024) Comparative life cycle assessment of glycerol valorization routes to 1,2- and 1,3-propanediol based on process modeling. ACS Sustainable Chemistry & Engineering, Volume 12, Issue 40, October 2024, pp. 14716-14731