Environmental Science & Technology

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Turning Waste into Value: Technoeconomic Analysis and Life Cycle Assessment of Biodiesel-Derived Crude Glycerol Electrooxidation

Published as part of Environmental Science & Technology special issue "Advancing a Circular Economy".

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Cite This: *Environ. Sci. Technol.* 2026, 60, 5492−5504

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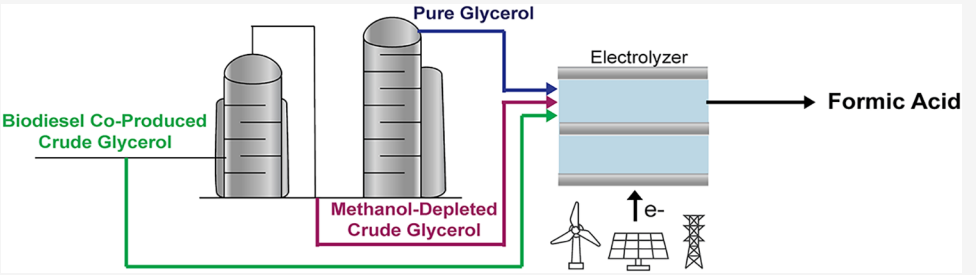

ABSTRACT: The U.S. biodiesel industry faces significant economic challenges, exacerbated by declining glycerol coproduct values and rising feedstock costs and leading to numerous plant closures. In this study, we investigate the technoeconomic and environmental viability of electrochemically upcycling low-value industrial-grade crude glycerol (50 wt % glycerol) and methanol-depleted crude glycerol (80 wt % glycerol) into formic acid, a valuable chemical commodity. Through process modeling, we assess purification processes and electrochemical oxidation pathways for these waste glycerol streams. Our findings indicate that utilizing low-value crude glycerol can produce formic acid at competitive costs, contingent upon advancements in catalyst efficiency and reactor design. Life cycle assessments reveal that this approach could reduce environmental impacts compared to traditional formic acid production, especially as the U.S. electricity grid decarbonizes through additional renewable energy deployment. State-level analyses highlight the influence of regional electricity prices, water costs, policies, and incentives on economic feasibility. By enabling the circular use of biodiesel-derived waste, this work supports more resilient renewable fuel systems and advances sustainable chemical manufacturing.

KEYWORDS: *Electrochemical oxidation, circular economy, biodiesel coproducts, formic acid production, crude glycerol, electrochemical engineering, electrocatalysis, life cycle assessment, technoeconomic analysis*

INTRODUCTION

Biodiesel production in the United States faces economic challenges. Facilities operate on slim, even recently negative, profit margins[1] often sustained by Renewable Identification Number (RIN) credits from the Federal Renewable Fuel Standards (RFS)[2] and supplemented by state-level incentives.[3] Despite these policy mechanisms that support biodiesel production, rising feedstock costs have contributed to the net closure of 46 U.S. biodiesel production plants between 2019 (102 operating plants total)[4] and 2024 (56 plants),[5] with smaller producers being disproportionately affected.

To further compound the economic hardships of U.S. biodiesel production, the value of pure glycerol, coproduced with biodiesel at a 10:1 weight ratio, fell sharply from $2.00 per kg in 1995, to $0.50 per kg in 2010, as U.S biodiesel production ramped upward while glycerol demand remained relatively constant.[6,7] This decline in glycerol value presents a challenge for biodiesel producers, necessitating alternative uses to enhance its economic viability. Electrooxidation of glycerol to value-added chemicals, like formic acid, utilizing low-carbon electricity sources such as wind, solar, and hydropower, offers one such opportunity to increase glycerol's value and improve overall facility margins.[8] As such, extensive research has been conducted on the development of catalysts to improve the efficiencies of this reaction, understand the mechanisms, and improve reactor designs in flow cells.[9−13] Several studies have assessed the technoeconomic[14−17] and environmental[18−20] opportunities of electrochemical glycerol oxidation at industrial scale. However, the existing literature has primarily focused on 99 wt %+ purity glycerol and has found that formic acid,

Received: November 23, 2025
Revised: January 28, 2026
Accepted: January 28, 2026
Published: February 5, 2026

despite being a common oxidation product, is not economically attractive.[14−17] No known literature has assessed the economic or environmental potentials of lower purity, industrially relevant glycerol waste streams. To bridge this gap, a clearer understanding of the industrial purity levels of glycerol from biodiesel facilities is needed, along with a comprehensive evaluation of its economic and environmental viability.

We collected primary data from existing U.S. biodiesel producers, revealing that 99 wt %+ purity glycerol streams are a rarity.[21] Small U.S. biodiesel producers (producing <4 million gallons per year, MMgal/yr) generate crude glycerol streams with approximately 50% glycerol (along with 22.5% methanol, 22.5% water, and 5% NaOH). These producers often lack the capital resources or economies of scale to further purify crude glycerol. In contrast, larger-scale producers typically recover methanol and refine glycerol streams to approximately 80 wt % purity with trace levels of methanol. Experimental studies have shown that both synthetic crude glycerol (CG) (50 wt %) and methanol-depleted crude glycerol (MD-CG) (80 wt %), representative of industrial glycerol streams, can be oxidized to formic acid at high production rates.[21] These experimental results suggest that purifying glycerol to 99 wt % might not be necessary for electrochemical valorization of U.S. biodiesel coproduced glycerol. However, the economic and environmental viability of using CG and MD-CG feedstocks remains unexplored in the literature.

In this work, we conduct the first technoeconomic analysis (TEA) and life cycle assessment (LCA) of the purification and electrooxidation of CG, MD-CG, and pure glycerol (PG) streams to formic acid. We then quantify the U.S. state-level impacts of the utilization of these streams from both economic and environmental perspectives, incorporating temporal and geospatial impacts of a lower-carbon U.S. electric grid. Finally, we provide benchmarks for further advancements in catalyst and reactor design to achieve competitive outcomes. This work demonstrates that with further advancement in reactor design, low-value CG streams can be oxidized to formic acid at an economically competitive cost, and with a lower environmental impact, compared to traditional formic acid production methods.

BACKGROUND

Biodiesel in the United States is produced via transesterification of seed oils derived from soy, corn, canola, and/or waste cooking oil or tallow in an alkaline catalyst (e.g., NaOH, KOH) in methanol.[22,23] Biodiesel was produced in 28 U.S states in 2024, with 70% of that production occurring in the Midwest region, close to ample feedstocks; however, biodiesel is produced at varied scales across the country, including Hawaii. The production capacity of these biodiesel producers varies widely with small scale production ranging from less than 1 MMgal/yr to the largest producer with a capacity of 144 MMgal/yr. Statistical analysis indicates that in 2021, the average biodiesel plant produced approximately 10 million kg per year (10 MMkg/yr) of glycerol with a standard deviation of 10 MMkg/yr, further indicating the wide range of production capacities. A list of U.S. biodiesel production facilities' capacities and estimated glycerol production with descriptive statistics is provided in Supporting Information (SI) Table S1.

The glycerol that is coproduced with this biodiesel is typically separated from the biodiesel using a water-wash column.[24] The separated biodiesel stream is further purified and sold. The CG stream from the wash column is sold as-is (50% glycerol, 22.5% methanol, 22.5% water, 5% NaOH, *vide supra*) or is neutralized, followed by methanol recovery to MD-CG. Water is then further removed via atmospheric distillation to purify the glycerol stream to a target purity, typically above 95%, although the exact percentage varies with the facility design and intended market. A general schematic of the biodiesel production process and glycerol purification train is shown in SI Figure S1.

Electrooxidative conversion of this low-value biodiesel-coproduced PG (no methanol present, but with added hydroxide and water) to value-added chemicals and fuels has been studied on modified and unmodified platinum-group metal (PGM) catalysts (*e.g.*, Pt, Ir, Au)[25−38] and non-PGM catalysts (*e.g.*, stainless steel, Ni).[37,39,40] Most results focus on C_2 and C_3 oxidation products (*e.g.*, glycerate, glycolate, lactate), given their purportedly higher price points. However, studies considering the presence of methanol in waste glycerol streams are limited. Methanol electrooxidation, in contrast to glycerol electrooxidation, produces a single base-stable value-added product: formate. Because glycerol electrooxidation can also produce formate, a single value-added stream can be synthesized from waste glycerol, reducing overall separations costs (which would likely exceed the higher prices from sale of a C_2 or C_3 chemical). Velázquez-Hernández et al. reported on an 85% glycerol purity mixture containing methanol and potassium hydroxide, and Kim et al. reported on a 26.5% glycerol purity mixture containing methanol, potassium hydroxide, and oleate.[40,41] Both works observed significant activity loss over the course of the reaction, attributing this decline to catalyst deactivation. Gaines et al. expanded on this work by using our comprehensive U.S. biodiesel facility primary data to design electrooxidation experiments for a broader range of glycerol streams.[21] Experiments examined glycerol from immediately after the water-wash column (CG) and post-methanol recovery (MD-CG), demonstrating stable performance in industrially-sourced, triglyceride-contaminated waste streams over extended time scales. Through these experiments, we demonstrated that extensive pretreatment and purification of biodiesel-coproduced glycerol streams might not be required to achieve stable performance, contrary to the suggestions of previous literature.

Additionally, the primary product formed in the electrooxidation of CG and MD-CG streams, formic acid, is a valuable chemical with applications in agriculture, leather tanning, and silage preservation, presenting a potential opportunity for glycerol valorization.[42] Commercial production of formic acid is dominated by thermocatalytic pathways, most commonly the carbonylation of methanol to methyl formate followed by hydrolysis, as well as oxidation-based routes involving formaldehyde intermediates.[43,44] These processes rely on fossil-derived methanol, carbon monoxide, or formaldehyde feedstocks that are themselves produced from syngas generated through natural gas or coal reforming.[43,45] Methanol carbonylation typically operates at elevated temperatures (~80−120 °C) and pressures exceeding 30 bar, while upstream methanol and formaldehyde synthesis are energy-intensive and closely coupled to centralized hydrocarbon processing infrastructure.[43,44] As a result, the overall energy demand and carbon intensity of conventional formic acid

https://doi.org/10.1021/acs.est.5c16857
Environ. Sci. Technol. 2026, 60, 5492−5504

production are strongly influenced by fossil fuel-derived feedstocks and thermal energy inputs rather than the formic acid synthesis step alone.[18,43]

Global formic acid production occurs at the scale of nearly 1 million tonnes per year,[46] underscoring the importance of scalable production routes that can meaningfully reduce emissions at industrial scale. In contrast to thermochemical pathways, electrochemical routes enable formic acid production under near-ambient conditions using electricity as the primary energy input.[20,47,48] When paired with low-carbon electricity sources, electrochemical production offers a fundamentally different pathway for formic acid synthesis that can decouple chemical manufacturing from fossil-derived heat and carbon inputs.[18,20] The use of biodiesel-coproduced crude glycerol as a waste-derived carbon source further distinguishes this approach from conventional routes, positioning electrochemical glycerol oxidation as a potentially circular alternative to established fossil-based production methods.[6,21]

MATERIALS AND METHODS

Our U.S. biodiesel primary data collection in Gaines et al. showed that most biodiesel producers obtain a CG stream after the water-wash column with a composition outlined in Table 1.[21] Using these findings, we developed a glycerol purification process model in SuperPro Designer, modifying the BioDiesel Process Model (v11.002) from the SuperPro Designer Process Library, authored by USDA-ARS-ERRC.[49] This model assumes an initial CG composition as shown in Table 1.

Table 1. Biodiesel Coproduced Glycerol Stream Purity Specifications[21]

Glycerol StreamType	Glycerol Content (wt %)	Methanol Content (wt %)	Water Content (wt %)	NaOH Content (wt %)
Crude Glycerol (CG)	50%	22.5%	22.5%	5%
Methanol-Depleted Crude Glycerol (MD-CG)	80%	0.10%	14.0%	6%
Pure Glycerol (PG)	99%	trace	trace	trace

As shown in Figure 1, CG is the initial byproduct of biodiesel production. This stream undergoes purification to remove methanol and other impurities, creating MD-CG. Further processing can produce pure glycerol (PG), depending on the facility's design and market requirements. The compositions of these glycerol streams are provided in Table 1. A detailed description and schematic of the purification process can be found in SI Section S2.

Following their respective purification processes, each of the CG, MD-CG, and PG streams in our model were then combined with an oxidation loop recycle intended to increase the overall glycerol conversion rate and were further diluted with water and/or NaOH to achieve the composition conditions shown in Table 2, which were demonstrated experimentally by Gaines et al. to yield formic acid from both methanol- and glycerol electrooxidation.[21]

Table 2. Glycerol Electrooxidation Reaction Feed Compositions Modeled for CG and MD-CG by Gaines et al.,[21] and Optimal Oxidation Compositions Identified for PG[50]

Glycerol Stream Type	Glycerol Concentration (M)	Methanol Concentration (M)	NaOH Concentration (M)	Source
Crude Glycerol (CG)	6.20	8.10	1.51	21
Methanol-Depleted Crude Glycerol (MD-CG)	4.85	0.02	1.36	21
Pure Glycerol (PG)	2.00	0.00	4.00	50

The glycerol stream is then fed to the anodic side of an electrochemical reactor[51,52] where the glycerol and methanol (if present) are oxidized to formic acid at 100% carbon selectivity. While this selectivity is not yet commercially feasible, recent improvements in reactor design and system optimization for industrial-scale electrolyzers can enable this transition.[21,53−55] This process utilizes a nickel (Ni) catalyst, which is both cost-effective and highly selective for formate production in both glycerol electrooxidation and methanol electrooxidation.[21] Alkaline water splitting was used to produce H_2 at the cathode that is separated and sold. Additional information concerning the electrochemical process can be found in SI Section S3.1. Using SuperPro Designer process modeling software, we represented the stoichiometric reaction for each literature data set in a simulated electrolyzer reactor. We developed an external mathematical model of the electrolyzer unit, considering the respective reactions detailed in SI Sections S3.1 and S3.2, since SuperPro Designer process modeling software lacks built-in electrolyzer units. The model assumes a steady-state reaction and leverages cost estimates from the DOE H2A model.[56] It updates key features,

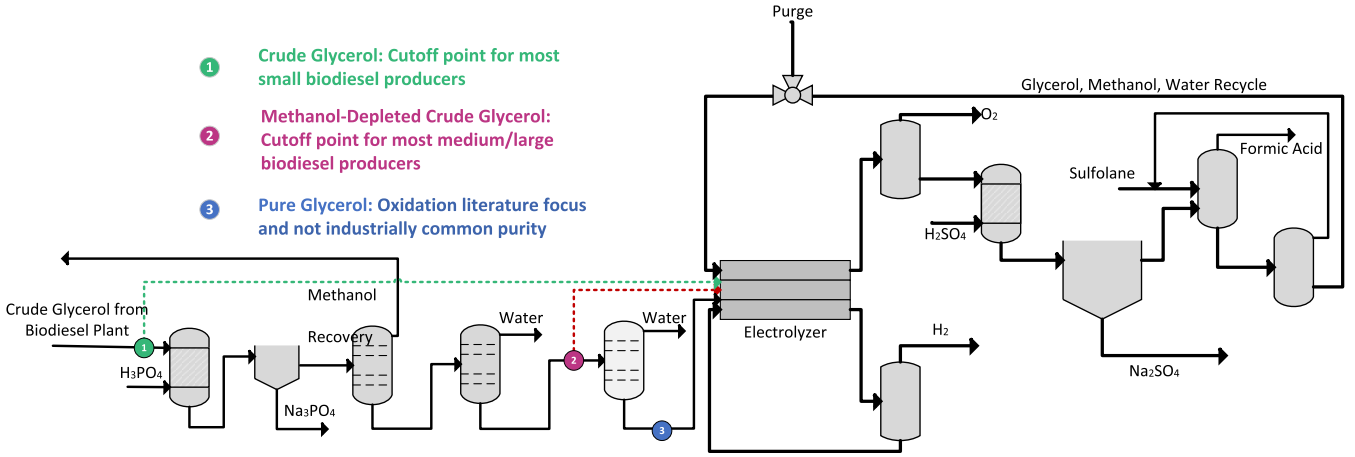

Figure 1. Biodiesel coproduced glycerol purification and electrooxidation process flow diagram for crude glycerol (CG) (green), methanol-depleted crude glycerol (MD-CG) (pink), and pure glycerol (PG) (purple).

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Environ. Sci. Technol. 2026, 60, 5492−5504

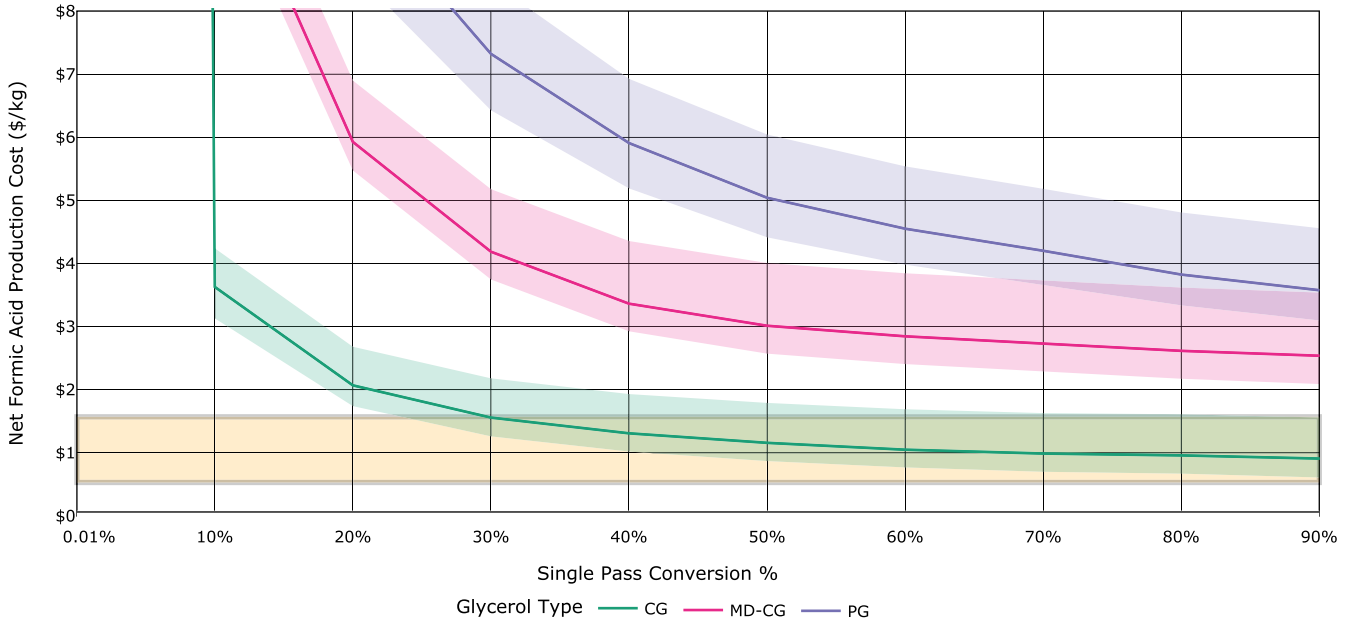

Figure 2. Net formic acid production cost ($/kg) for the electrooxidation of crude glycerol (CG), methanol-depleted crude glycerol (MD-CG), and pure glycerol (PG) streams under varied single pass conversion rates for a biodiesel facility producing 20 MMkg/yr of glycerol. The solid line represents the median value and the shaded region of each plot represents the values between the first and third quartiles of the uncertainty analysis outcomes. The range of market values for formic acid appears in the orange-shaded region. Net formic acid production cost values exceeding $8 per kg are not shown as they are far from the economically feasible region. Full statistical values for this figure can be found in SI Table S3.

like current density, power requirements, and size, to adjust these estimates for the external electrolyzer model.

Following the electrolysis unit, the anodic stream containing unreacted glycerol, methanol, water, NaOH, oxygen, and sodium formate is sent to a flash vessel to recover oxygen in the process model for sale to market. The NaOH present in the anodic stream originates primarily from residual base in the biodiesel-coproduced glycerol feedstock and is utilized as the supporting electrolyte for electrooxidation; any additional NaOH required to maintain the target reaction conditions is explicitly included as a purchased input in the process model. The stream is then neutralized with sulfuric acid where sodium formate and excess NaOH are converted to formic acid and sodium sulfate (Na_2SO_4).[57,58] The stream is then cooled to precipitate out the Na_2SO_4, which is further dried and sold as a byproduct, commonly used in detergents, paper production, and glass manufacturing.[57,58] The glycerol stream is then diluted with sulfolane, shown to be a highly effective extractive distillation agent for formic acid and glycerol mixtures, at a 10:1 weight ratio.[59,60] Formic acid is recovered via vacuum distillation to a 99% purity and the remaining unreacted glycerol, methanol, and water are recycled back to the electrolyzer with a purge stream varied to maintain the reaction conditions specified in Table 2. Further detailed descriptions and process flow diagrams for each model are provided in SI Section S3.

To also assess the impact that electrochemical glycerol oxidation could have on a wide range of U.S. biodiesel producers, we ran simulations for each glycerol feed stream in Table 2 assuming 1, 10, or 20 MMkg/yr of glycerol are fed to the electrolyzer, consistent with the average and plus/minus approximately one standard deviation for U.S. biodiesel production facilities. To provide economic benchmarks for the reaction, we also varied the reactor single pass conversion rate in 10% increments from the current standard in benchtop-scale flow electrolysis of ~0.01% to 90%.[21]

We performed an uncertainty analysis with 90,000 trials for each glycerol feed stream, capacity, and single pass conversion rate, totaling more than 8 million runs to determine the net formic acid production price ($/kg) ranges that could be obtained. The uncertainty analysis parameters are detailed in SI Section S4.1. The net formic acid production cost considers all upfront plant costs (capital equipment, construction, installation, and startup), operating costs (utilities, raw material, maintenance, labor, *etc.*), and taxes less the sale of valuable coproducts produced (H_2, O_2, and Na_2SO_4) represented in 2024 U.S. dollars discounted at a 7% interest rate over a 15-year facility lifetime. The values obtained serve as a proxy for comparison to the traditional methods of producing formic acid whereby the net formic acid production price is compared to the market price of formic acid between 2017 and 2024, which ranged from $0.53 to $1.57 $/kg.[61] The reaction and process design are deemed economically viable if formic acid can be electrochemically produced from these glycerol streams within or below market prices. In addition to assessing the impact that single pass conversion rate has on the process economics, we also performed a sensitivity analysis to determine feasible ranges of current density, overall Faradaic efficiency (FE), electrolyzer lifetime (implicitly accounting for reactor degradation), and other operational values that need to be achieved in electrooxidation research and development to compete with current industrial processes for formic acid at scale.

To assess the impact of state-level variations in electricity,[62] water prices,[63] tax rates,[64] and policies[3] on this process, we analyzed the reaction that maximized economic performance. We assumed electrochemical reactor operating parameters advance to conditions similar to that of commercial proton exchange membrane (PEM) hydrogen electrolyzers (near 100% FE,[65] 1−2 A cm^{-2} current density,[66] 8-year electrolyzer lifetimes,[67] and $12,000 per m^2 total cost[56]). Interpretations of state-level biodiesel production policies and their applicability to a collocated electrochemical glycerol oxidation process are provided in SI Section S5.

Additionally, we conducted an LCA for this process, assessing the impact of the three glycerol feedstock types compared to traditional fossil fuel-based formic acid production.[43] We estimated the required quantities of steel and cement for the plant equipment and infrastructure based on cost data outputs from the SuperPro Designer process simulations and common chemical engineering design heuristics[68−70] (see SI Section S6.1 for details), determined electrolyzer material requirements based on a scaled-up version of the electrolyzer design used by Gaines et al.,[21] identified material demands from our SuperPro Designer process simulations, and quantified electricity requirements for the reaction and process heating with details provided in SI Section S6.4. We used U.S.-centric

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Environ. Sci. Technol. 2026, 60, 5492−5504

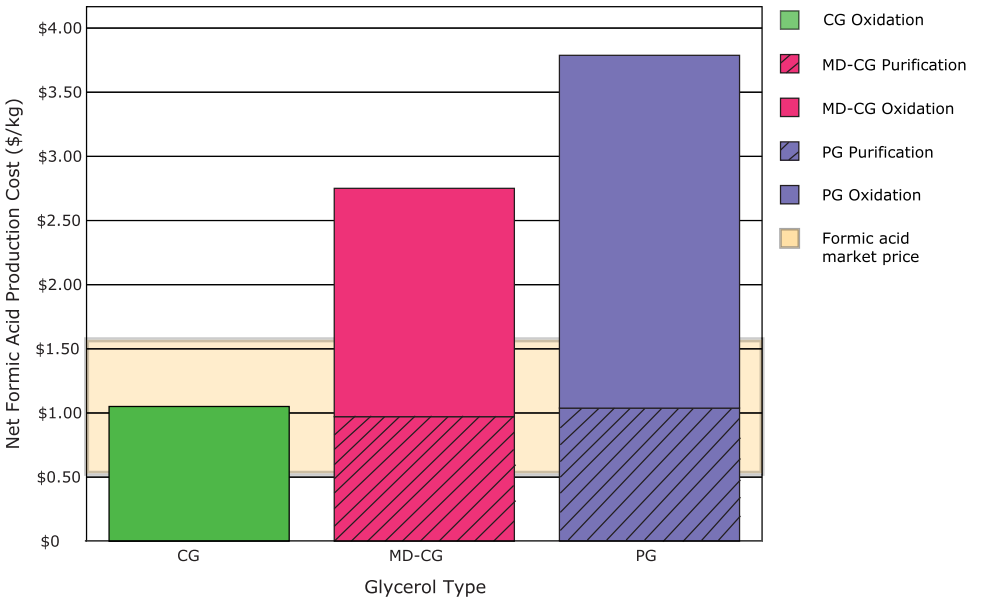

Figure 3. Median glycerol purification and electrooxidation to net formic acid production cost ($/kg) for crude glycerol (CG), methanol-depleted crude glycerol (MD-CG), and pure glycerol (PG) streams for a biodiesel producer making 20 MMkg/yr of glycerol at 90% single pass conversion.

life cycle inventory (LCI) data sets, NREL's USLCI[71] and the U.S. EPA's USEEIO,[72] for each material and utility input. The impacts were determined per kg of formic acid produced for each process feedstock option using OpenLCA 2.3.1 and the TRACI 2.1[73] impact assessment method. The following impact categories were evaluated: acidification (kg SO_2 eq), eutrophication (kg N eq), 100-year global warming potential (kg CO_2 eq), freshwater ecotoxicity (CTUe), and ozone depletion (kg cfc-11 equiv). We then performed a similar uncertainty analysis to compare the economically feasible electrochemical glycerol oxidation cases' environmental impacts to fossil fuel-based formic acid production methods. Because the emissions intensity of the U.S. electric grid varies across locations and over time,[74] we modeled the global warming potential of electrochemical glycerol oxidation to formic acid at the state level. This analysis assumes the same conditions outlined in the TEA methods for reactor design, with a goal of advancing toward conditions similar to those in existing hydrogen PEM electrolyzers. This geospatial state-level LCA uses existing electric grid emissions data and projections for 2040 based on work by Grubert.[75]

RESULTS AND DISCUSSION

In this section we assess the economic feasibility of electrooxidizing CG, MD-CG, and PG to formic acid, finding that while current processes are not viable, advancements in catalyst and reactor design could enable feasibility. Geospatial analysis explores potential deployment, assuming performance benchmarks similar to PEM electrolyzers. Finally, an LCA shows that CG-derived formic acid could reduce environmental impacts compared to conventional production methods, with further benefits as the U.S. grid decarbonizes.

Technoeconomic Analysis

Among the three glycerol feedstocks evaluated in this study across different facility capacities, using CG as a feedstock is the only economically feasible pathway for electrochemical production of formic acid from biodiesel-coproduced glycerol, as shown in Figure 2.

However, current literature on the electrochemical oxidation of CG has demonstrated single-pass conversions of 0.1% or less in flow cells.[50,76,77] To minimize the extent of postreaction separations and sizes of recycle loops, single pass conversions must be at least 30% to be economically competitive with traditional formic acid production processes for biodiesel producers making 20 MMkg/yr of glycerol. Also demonstrated in Figure 2, as the single-pass conversion rate increases, there are increasingly more scenarios in which the electrooxidation of CG to formic acid is economically feasible. Similar results occur for average-sized biodiesel producers (10 MMkg per year), where CG streams are economically favorable to oxidize at single pass conversion of at least 60%, although in much fewer scenarios. For small producers (1 MMkg glycerol per year), electrooxidative production of formic acid is not economical for any glycerol feed compositions. These smaller-capacity facility economics are shown in SI Figures S4 and S5.

While electrooxidation of CG has the potential for economic feasibility, MD-CG and PG streams are economically infeasible for the studied scenarios for several reasons. The first and most obvious reason is the additional cost required to purify CG to MD-CG. The glycerol purification process requires additional capital costs for distillation systems and other process equipment, as well as operational costs for process heating, additional chemical treatment, and labor to achieve an 80 wt % glycerol, MD-CG stream. An additional $0.08 per kg of formic acid relative to MD-CG is required to further purify this glycerol stream to 99% as demonstrated in Figure 3, which is primarily attributed to the additional energy cost to further purify the glycerol stream.

Second, as Gaines et al. demonstrated, the electrochemical oxidation of the methanol available in the CG stream allows for more formic acid production from the feed stream;[21] in the MD-CG and PG cases, methanol is removed at a cost from the feed stream. Electrochemical oxidation of methanol to formic acid necessitates significantly lower electricity input as it requires only four electrons[78] versus eight or more[79] for glycerol, further compounding the lower formic acid production cost compared to the MD-CG and PG feed streams. Lastly, purifying glycerol to 80 or 99 wt % requires additional energy and chemical additives to remove NaOH and water. However, these same components must later be

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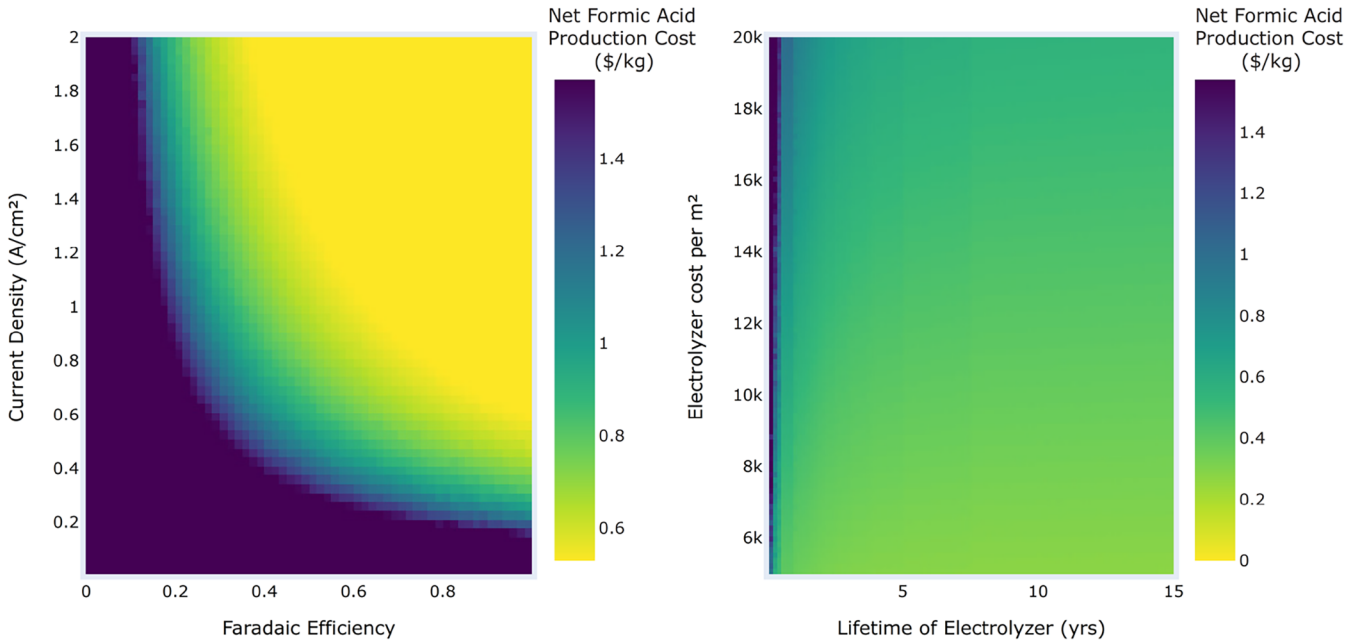

Figure 4. Net formic acid production cost ($/kg) for the electrooxidation of crude glycerol (CG) at 90% single pass conversion for a biodiesel facility producing 20 MMkg/yr of glycerol vs (a) Faradaic efficiency (%) and current density (A cm^{-2}) and (b) electrolyzer lifetime (years) and cost ($ m^{-2}). Sensitivity analysis assumes the mean value of all other parameters assessed under uncertainty detailed in the SI Table S2.

reintroduced into the stream as essential mediums for electrooxidation, adding unnecessary costs. In summary, the electrochemical oxidation of MD-CG and PG streams is economically inefficient, as it incurs unnecessary costs and energy to remove components that are either reactive or essential for the electrochemical process. In contrast, CG streams have been experimentally shown to oxidize to formic acid effectively; however, these reactions are limited in overall selectivity and conversion, underscoring the need for further development of catalysts and reactor systems. Although impurities in crude glycerol streams could potentially lead to catalyst degradation or formation of undesired byproducts, experimental work has demonstrated stable oxidation of industrial CG without measurable catalyst deactivation under appropriate operating conditions.[21] Scaling to larger cells with longer flow paths, higher single-pass conversion rates, and recycle loops could dramatically improve conversion and the economic viability of CG electrooxidation.

To further assess the feasibility of this process, we conducted a sensitivity analysis to identify the reactor design parameters that most significantly affect the economic viability of electrooxidation of CG to formic acid, providing benchmark targets for future research. We analyzed key benchmarks of Faradaic efficiency (overall FE, %), current density (A cm^{-2}), electrolyzer cost ($ m^{-2}), and electrolyzer lifetime (years) shown in Figure 4. Reaction economic feasibility was not highly sensitive to the labor rate or electricity price (SI Figure S6).

Figure 4a indicates that electrochemical CG oxidation reactions to formic acid are not economically feasible at an industrial scale unless the overall FE exceeds a minimum threshold of 20%. Similarly, a current density below approximately 0.3 A cm^{-2} falls below the minimum economically feasible range for industrial implementation. In Figure 4a, our results show that current density and overall FE have a dynamic relationship in contributing to economic viability. As overall FE increases, the required current density to move into the economically feasible region decreases. For example, at a 90% single pass conversion of the CG stream (Figure 4a) and a 20% overall FE, the minimum required current density for economic feasibility is nearly 1.0 A cm^{-2}; however, as the FE rises to 80%, the required current density to competitively produce formic acid falls to 0.3 A cm^{-2}. However, as both current density and FE increase, the cost of producing formic acid decreases, approaching the lowest market price ($0.53/kg) observed since 2000. Current densities must be increased significantly from values observed in literature for CG electrochemical oxidations to formic acid, where the highest current density observed was 0.024 A cm^{-2} in a flow cell.[21,41]

Figure 4b shows that the relationship between electrolyzer lifetime and cost per m^2 is less distinct. Electrolyzer lifetimes that exceed one year lead to formic acid production costs within the economically feasible range, even at higher overall electrolyzer costs. In general, however, lower-cost electrolyzer systems with longer lifetimes lead to more economically viable formic acid production as the production cost further decreases. Durability testing by Gaines et al. (detailed in SI Section S7) indicates that CG electrooxidation can be sustained for up to 16 h under intermittent operating conditions. Additionally, at methanol concentrations greater than 0.5 M, the effects of triglyceride- and other electrolyte impurities are imperceptible, indicating that the formation of byproducts and/or fouling from other operational complexities are not influential in this process.[21] These findings suggest that CG can be stably oxidized over extended periods, even in the presence of impurities, although further studies are needed to optimize long-term reactor operation and assess degradation mechanisms over such timescales.

Our geospatial analysis highlights that the location of electrochemical oxidation of CG significantly affects production costs due to the combined influence of electricity prices, water prices, tax rates, and state policies. In states with higher electricity costs, tax rates, and water prices—such as California,

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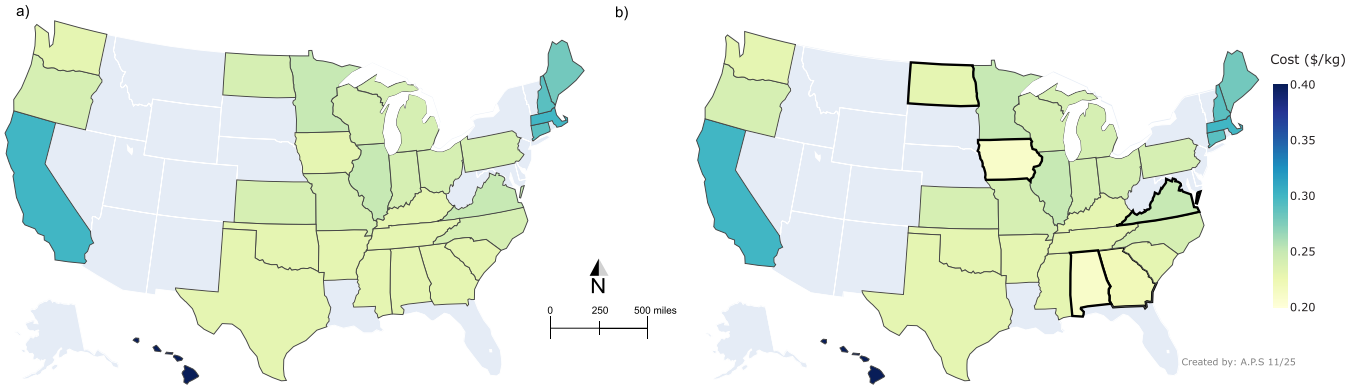

Figure 5. State level net formic acid production cost ($/kg) for the electrooxidation of crude glycerol at 90% single pass conversion, assuming reactor design advancement similar to existing hydrogen PEM electrolyzers for a biodiesel facility producing 20 million kg of glycerol per year (a) without state-level biodiesel production policies considered and (b) with state-level policies considered. States that are greyed out do not produce biodiesel and are therefore excluded from this analysis. Alaska and Hawaii are not shown to scale.

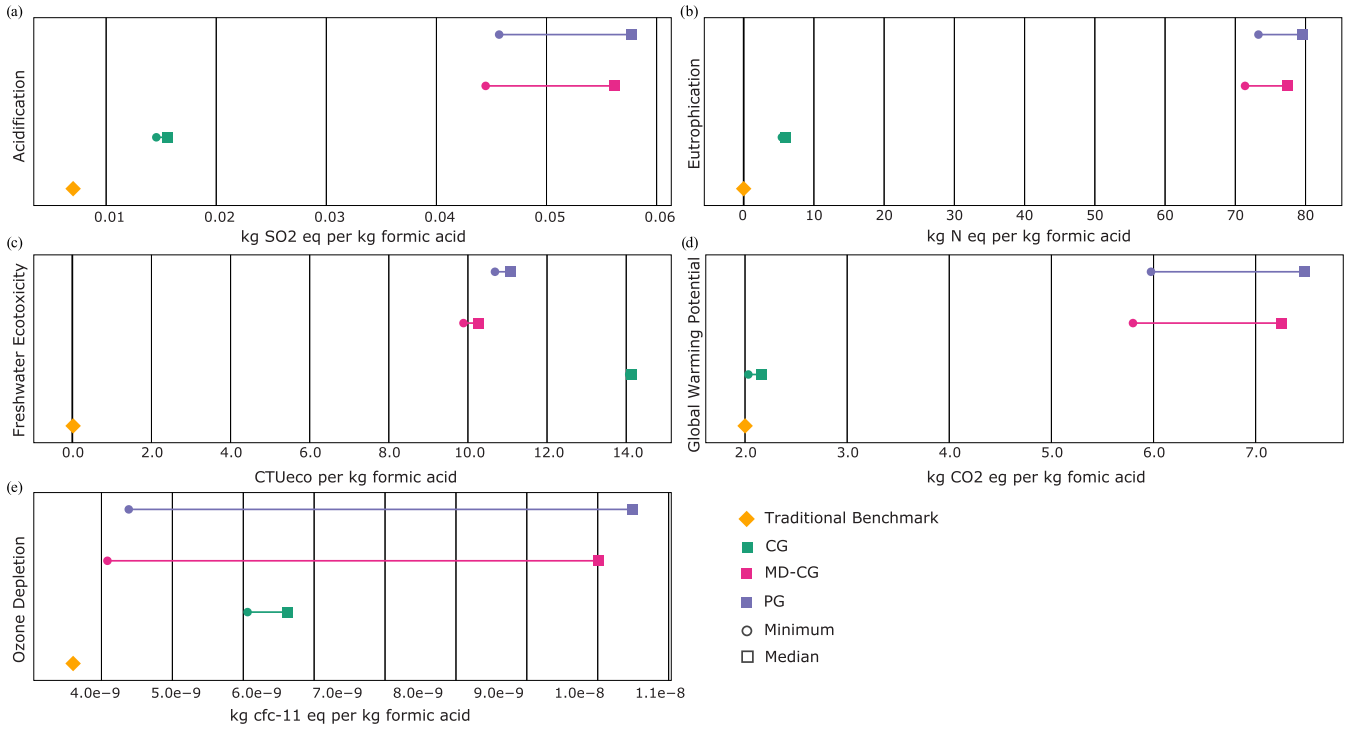

Figure 6. Minimum (circle) and median (square) LCA results per kg of formic acid for (a) acidification (kg SO_2 eq), (b) eutrophication (kg N eq), (c) freshwater ecotoxicity (CTUe), (d) global warming potential (kg CO_2 eq), and (e) ozone depletion (kg cfc^{-11} eq) of crude glycerol (CG, green), methanol-depleted glycerol (MD-CG, pink), and pure glycerol (PG, purple) streams electrochemical oxidation to formic acid at 90% single pass conversion rates and economically feasible operating ranges compared to traditional formic acid production methods (orange diamond). Minimum values for freshwater ecotoxicity align closely to the median value in panel c and may not be visible. See SI Section S6.6 for detailed statistical values.

Hawaii, and the Northeastern United States—the projected production cost of formic acid is substantially higher compared to Midwestern and Southern states, assuming reactor designs comparable to PEM electrolyzers. Biodiesel production incentive policies also play a crucial role in reducing production costs. Currently, 19 U.S. states have pro-biodiesel policies;[3] however, many of these policies specifically target biodiesel production (e.g., per-gallon credits, sales tax exemptions for methanol used in biodiesel) and are not broadly applicable. Only five states (Alabama, Georgia, Iowa, North Dakota, and Virginia; bold outlined in Figure 5b) have more inclusive policies, extending benefits to any biodiesel-producing entity. These inclusive policies typically provide investment tax credits, sales tax exemptions, or job creation incentives, which could be leveraged to support a CG electrooxidation process collocated with a biodiesel production facility. A full list of the biodiesel production policies considered in this geospatial analysis and how they were incorporated or deemed nonapplicable to the electrooxidation of CG is available in SI Table S6.

Altogether, the findings of the TEA bring to light several key insights. Existing literature suggests that electrooxidation of biodiesel-coproduced glycerol to formic acid is not economically viable; however, that literature has focused on the

https://doi.org/10.1021/acs.est.5c16857
Environ. Sci. Technol. 2026, 60, 5492−5504

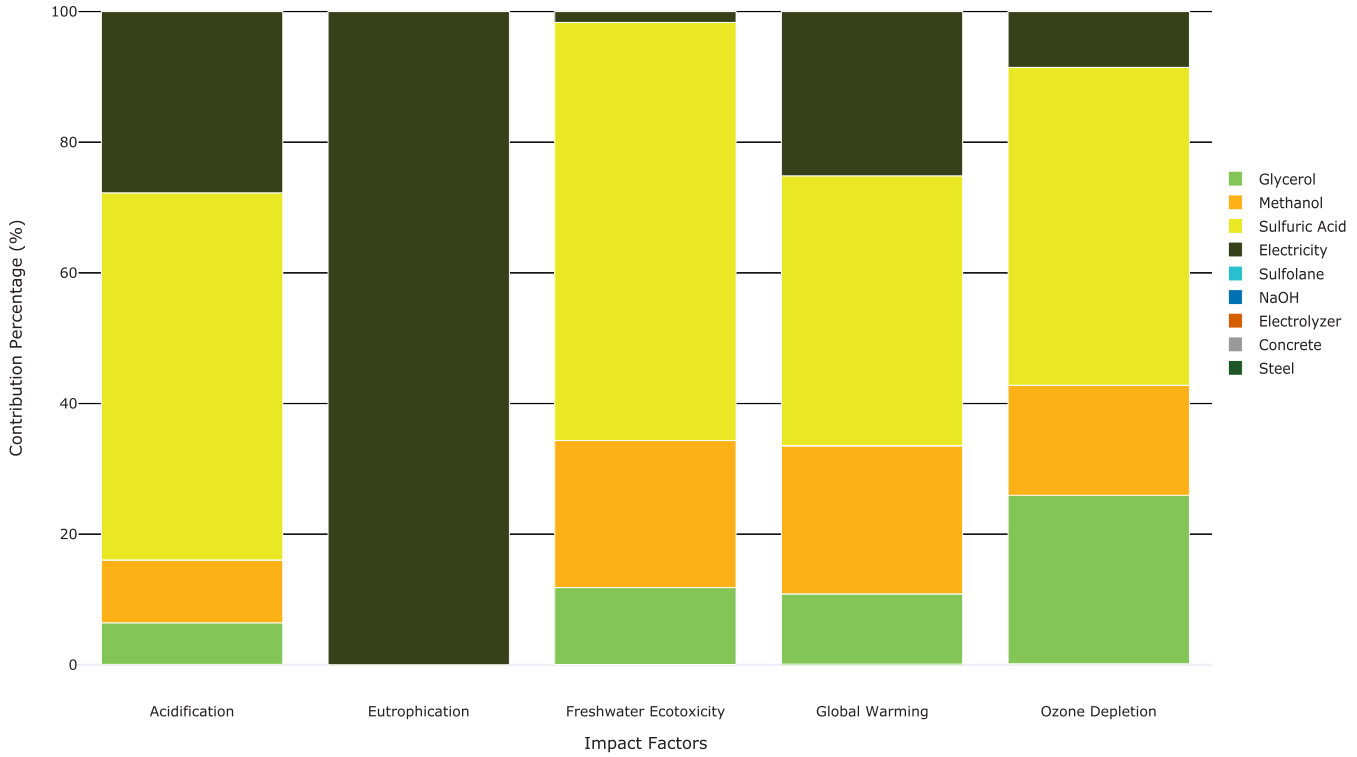

Figure 7. Percentage contribution of each of the material and utility inputs for the electrochemical oxidation of crude glycerol to formic acid at 90% single pass conversion for each of the respective impact factors' median value cases.

electrooxidation of PG. Our results show that, despite the lower purity of the feed stream and the low value of the oxidation product relative to other candidate C_2 and C_3 products, CG is an economically viable feedstock option for formic acid production. This economic feasibility is particularly achievable for large-scale biodiesel producers if reactor designs improve to achieve single-pass conversions of 30%, current densities of 0.3 A cm^{-2}, and electrolyzer lifetimes greater than 1 year. Similar results for related electrocatalytic processes,[76,80,81] including some operating at scale,[48,82] suggest feasibility for CG electrooxidation. This work also demonstrates the geospatial opportunities for CG electrooxidation and importance of policies that are broadly applicable to the entire biodiesel-producing entity, rather than focusing on specific credit mechanisms for biodiesel production itself.

Life Cycle Assessment

Considering the 2016 U.S. electric grid data found in the U.S.-centric life cycle inventory (LCI) data sets[71,72] and the uncertainties detailed in SI Table S10, the LCA results show the three biodiesel coproduct glycerol streams assessed in this study do not outperform traditional fossil fuel-based formic acid production[43] at their median values, as shown in Figure 6.

In Figure 6, our results show that electrochemical oxidation of the CG stream performs better at the minimum and median value than MD-CG and PG feedstocks for acidification, eutrophication, and global warming potential impacts. The only impact factor where MD-CG and PG perform better than CG usage at the median and minimum value is freshwater ecotoxicity. In the median case, CG exhibits lower ozone depletion impacts compared to MD-CG and PG. Although the absolute values are low on a per-kilogram-of-formic-acid basis, the minimum ozone depletion potentials are 6.08×10^{-9}, 4.08×10^{-9}, and 4.38×10^{-9} kg CFC-11 eq for CG, MD-CG, and PG, respectively. Detailed minimum, maximum, median, and mean values for the impact factors are presented for each of the facility capacities, glycerol feedstock types, and single pass conversion rates in SI Section S6.6.

The global warming impact of CG electrooxidation is close to that of traditional formic acid production; however, since the environmental impact of electrochemical glycerol oxidation for formic acid production does not consistently outperform traditional methods, we identify opportunities for optimizing the materials and utilities used in the proposed process. We analyzed the primary contributors to each impact factor for the median case using CG as a feedstock, as shown in Figure 7.

Notably, the environmental impact of the steel and concrete used in the facility's capital infrastructure, along with the materials in the electrolyzer, is overshadowed by the ongoing demand for chemicals and utilities during operations. Chemicals consumed in the production process account for the majority of the impact factor totals, with the use of sulfuric acid as an acidifying agent as the largest impact, followed by methanol and the production of glycerol upstream in the collocated biodiesel facility. While methanol and glycerol inherently exist in the biodiesel-coproduced glycerol stream, replacement of sulfuric acid with a more environmentally friendly neutralizing agent could lower overall environmental impacts. Additionally, as chemical production decarbonizes, the overall environmental impact of our proposed method could decline. However, there is significant uncertainty regarding whether and to what extent this decarbonization will occur, and we do not account for these potential sector-level changes in this study. Electricity usage in the electrochemical process accounts for a substantial portion of the impact factor totals, contributing 27% to acidification, 99% to eutrophication, and 25% to global warming potential, based on 2016 U.S. grid data.

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Environ. Sci. Technol. 2026, 60, 5492−5504

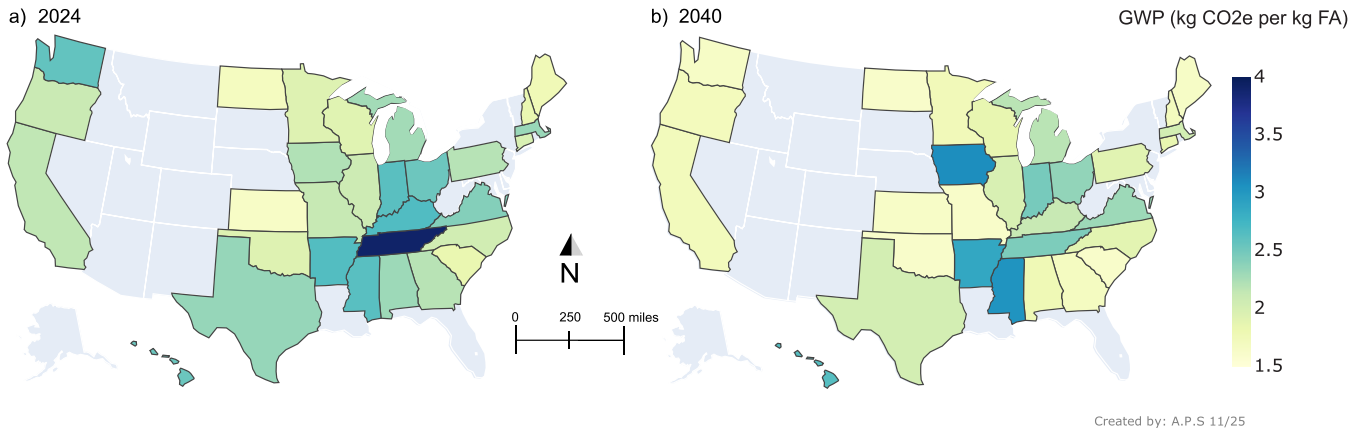

Figure 8. State-level formic acid global warming potential (kg CO_2 eq per kg formic acid) for the oxidation of crude glycerol at 90% single pass conversion, assuming reactor design advancement similar to existing PEM electrolyzers for a biodiesel facility producing 20 million kg of glycerol per year (a) in 2024 and (b) in 2040. States that are greyed out do not produce biodiesel and are therefore excluded from this analysis. Alaska and Hawaii are not shown to scale.

This high eutrophication share arises from the combination of the process's electricity demand and the comparatively large eutrophication impact factor associated with electricity generation. As shown in SI Tables S8 and S10, the eutrophication intensity of electricity is orders of magnitude higher than that of any other material input, which causes electricity to dominate this category even when other feedstocks are consumed in larger mass quantities. Similarly, the limited contribution from NaOH is consistent with the very low impact factors reported for NaOH across all categories in SI Table S8. Although the optimized reaction conditions include 1.51 M NaOH, the overall mass of NaOH consumed in the process is modest, and its impact factors are substantially lower than those of sulfuric acid, methanol, and electricity. Taken together, these factors explain the near-zero NaOH contribution shown in Figure 7.

As the U.S. electric grid continues to decarbonize through more renewable energy, the global warming potential of the proposed CG electrooxidation process to formic acid is subject to change. To assess this impact from a geospatial and temporal perspective, we used state-level CO_2 and methane electricity generation emissions projections from Grubert[75] in 2024 and 2040 in the model while assuming all other impact factors remained constant with results presented in Figure 8.

Our results show that, compared to the initial LCA using 2016 grid data (Figure 6), where the global warming potential of CG electrooxidation exceeds that of traditional production methods, there are nine states (Connecticut, Kansas, Maine, Massachusetts, Minnesota, North Dakota, Oklahoma, South Carolina, and Wisconsin) in the 2024 grid where this process achieves a global warming potential below the traditional fossil fuel-based method threshold of 2.007 kg CO_2 eq per kg of formic acid. With simulated further grid decarbonization by 2040, this number increases to 17 states, including major biodiesel-producing regions such as California and Missouri. When process advances are paired with decarbonization of the electric grid, electrooxidative conversion of waste glycerol to value-added formic acid shows significant potential as an economically-feasible process with reduced environmental impact.

BROADER IMPLICATIONS

In this study, we demonstrate that the electrooxidation of crude glycerol (CG), a coproduct of biodiesel production, has the potential to enhance the biodiesel value chain by converting a low-value waste stream into formic acid, a value-added chemical. Among the possible oxidation products of glycerol, formic acid is not the highest-value chemical; indeed, previous technoeconomic analyses have shown that electrooxidation of 99 wt %+ pure glycerol to formic acid is not economically attractive. However, our analysis demonstrates that even this relatively low-value product can be produced economically from CG under favorable electrochemical performance and system design considerations. Future work could build on this foundation by exploring higher-value product slates and coproduction strategies, which could further enhance the economic potential of glycerol electrooxidation.

The lower-purity, industrially relevant CG and methanol-depleted crude glycerol (MD-CG) streams considered here require less intensive purification and benefit from the additional contribution of methanol oxidation, which enhances the value of the formic acid product. Our results demonstrate that the production of formic acid from electrooxidation of CG specifically can be economically viable with improved Faradaic efficiency, current density, and single-pass conversion rates. The economics of such processes can be further supported by effective policy mechanisms that apply to the whole biodiesel production facility, including coproducts and waste. Critically, the key characteristics that contribute to the perception of CG as a low-value waste (less purification, higher methanol content) led to it outperforming both MD-CG and pure glycerol streams in economic and environmental metrics.

Life cycle assessment results reveal that while current electrochemical processes do not universally outperform traditional formic acid production methods across all impact categories, CG electrooxidation shows promise in reducing global warming potential, particularly in states with low-carbon electricity sources. As the U.S. electricity grid continues to decarbonize, the environmental benefits of electrooxidation of CG are expected to improve, making it a viable pathway for sustainable chemical production.

Ultimately, our findings highlight the need for greater research attention on the electrooxidation of industrially

https://doi.org/10.1021/acs.est.5c16857
Environ. Sci. Technol. 2026, 60, 5492−5504

relevant crude glycerol streams, rather than laboratory-grade purified glycerol. Advancing catalyst and reactor designs to meet performance and durability thresholds will be critical for enabling scalable deployment. As with other alkaline electrolysis systems, large-scale implementation will also require continued attention to electrolyte management, including minimizing losses associated with membrane transport and purge requirements, which are not explicitly resolved in the present steady-state model. These innovations could establish glycerol upcycling as a viable circular economy pathway, transforming a low-value biodiesel byproduct into a valuable chemical input, while enhancing the economic resilience of renewable fuel production and contributing to the decarbonization of the broader chemical sector.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.5c16857.

U.S. biodiesel production and coproduced glycerol estimates; biodiesel and glycerol process schematics; glycerol purification and electrooxidation process models; electrochemical reaction equations and mathematical electrolyzer model; technoeconomic analysis uncertainty and sensitivity parameters; state-level biodiesel policy assumptions; steel and cement use assumptions; life cycle impact factors and uncertainty parameters; sulfolane impact factor characterization; additional technoeconomic and life cycle assessment results and figures (PDF)

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Author Contributions

A.P.S. formulated the analysis, conducted the modeling, and analyzed the results; R.N.G. assisted in formulating the analysis, and assisted in analyzing the results; B.E.F. assisted in formulating the analysis, and assisted in analyzing the results; P.J.A.K. assisted with formulating the analysis and acquired a portion of funding; A.S.S. assisted with formulating the analysis, acquired a portion of funding, and supervised the research; all authors contributed to writing.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the members of the University of Illinois Urbana−Champaign EFRI DCheM research team (David W. Flaherty, Andrew A. Gewirth, and Joaquín Rodríguez-López) for their feedback through the development of this analysis. This work was supported by the National Science Foundation, grant 2029326; the opinions, findings, and conclusions or recommendations are those of the authors and do not necessarily reflect the views of the National Science Foundation.

■ ABBREVIATIONS

RIN: Renewable Identification Number; RFS: Federal Renewable Fuel Standards; SI: Supporting Information; EPA: United States Environmental Protection Agency; EIA: Energy Information Administration; TRACI: Tool for the Reduction and Assessment of Chemicals and Other Environmental Impacts; PG: Pure Glycerol; CG: Crude Glycerol; MD-CG: Methanol-Depleted Crude Glycerol; PEM: Proton Exchange Membrane; LCA: Life Cycle Assessment; TEA: Technoeconomic Assessment; FE: Faradaic Efficiency; LCI: Life Cycle Inventory; DOE: Department of Energy; NSF: National Science Foundation; USDA: United States Department of Agriculture; USLCI: United States Life Cycle Inventory Database; USEEIO: Environmentally-Extended Input-Output Model; NREL: National Renewable Energy Laboratory

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Environ. Sci. Technol. 2026, 60, 5492−5504