Electrocatalysis for Chemical and Fuel Production: Investigating Climate Change Mitigation Potential and Economic Feasibility

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ABSTRACT: The manufacture of goods from oil, coal, or gas to everyday consumer products comprises in more or less all cases at least one catalytic step. Compared to conventional hydrothermal catalysis, electrocatalysis possesses the advantage of mild operational conditions and high selectivity, yet the potential energy savings and climate change mitigation have rarely been assessed. This study conducted a life cycle assessment (LCA) for the electrocatalytic oxidation of crude glycerol to produce lactic acid, one of the most common platform chemicals. The LCA results demonstrated a 31% reduction in global warming potential (GWP) compared to the benchmark (bio- and chemocatalytic) processes. Additionally, electrocatalysis yielded a synergetic potential to mitigate climate change depending on the scenario. For example, electrocatalysis combined with a low-carbon-intensity grid can reduce GWP by 57% if the process yields lactic acid and lignocellulosic biofuel as compared to a conventional fossil-based system with functionally equivalent products. This illustrates the potential of electrocatalysis as an important contributor to climate change mitigation across multiple industries. A technoeconomic analysis (TEA) for electrocatalytic lactic acid production indicated considerable challenges in economic feasibility due to the significant upfront capital cost. This challenge could be largely addressed by enabling dual redox processing to produce separate streams of renewable chemicals and biofuels simultaneously.
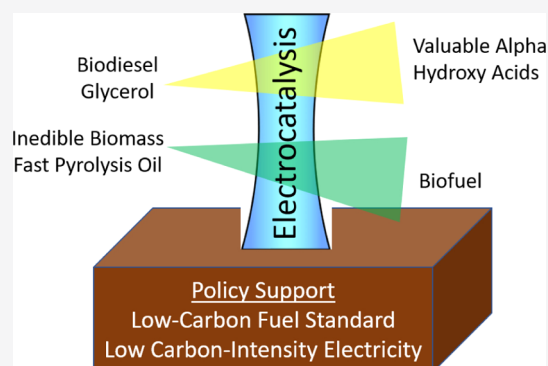
INTRODUCTION

The chemical sector accounts for 10% of the total global energy demand and 7% of global anthropogenic greenhouse gas emissions.[1] With the growing concerns of global climate change, the chemical sector has begun exploring routes to bio-based fuels and chemicals and converting to renewable energy sources. Over the past few decades, different catalytic methodologies have been explored to transform renewable biomass into commodity chemicals, with related efforts focusing on greener methodologies that rely on milder conditions and safer reagents whenever possible. To this end, processes that yield bio-based chemicals while integrating renewable energy sources and utilizing benign reagents can be attractive to mitigate climate impacts from the chemical sector.

Electrocatalysis has emerged as a promising alternative synthetic process to replace traditional synthesis strategies, such as hydrothermal processing. The advantage of electrocatalysis lies in its ability to initiate redox with only a small electric potential difference between the electrodes, bypassing the harsh conditions typically required for delivering the activation energy through thermal inputs. For example, hydrothermal catalytic oxidization of glycerol can be achieved at 150 °C in 4.9 atm of O_2 in 18 h using a platinum oxide catalyst loaded with niobium oxide (glycerol conversion: 82%,

selectivity: 48%),[2] whereas, under the electrocatalytic environment, comparable yields and selectivity can be obtained at 60 °C in an ambient atmosphere (glycerol conversion: 82%, selectivity: 44%) using a cobalt metal oxide catalyst deposited on an anode.[3] A 10 mA cm^{-2} cathodic current density, which is a current density that can be achieved with a small voltage input, can provide roughly 10 bar (9.86 atm) of adsorbed hydrogen on the electrode surface.[4−6] Further, electrocatalysis can make use of water splitting to supply needed redox reagents such as H_2 and O_2.[7] Such advantages make electrocatalysis an important topic in the field of Green Chemistry generally.[8−10] Provided that renewable energy is supplied in the form of electrical energy, electrocatalysis provides the most direct pathway between renewable energy (solar or wind) and biomass transformation into commodity chemicals. On the industrial side, electrocatalysis displays a well-established track record to produce some of the crucial

platform chemicals.[11] For example, BASF has commercialized the Baizer process, which produces adiponitrile, a crucial intermediate to nylon-6,6 production, by a cathodic dimerization of acrylonitrile. Several companies can produce glyoxylic acid, another important synthetic intermediate, by a partial electrochemical reduction of oxalic acid. Other common industrial examples include the electrochemical reduction of glucose to sorbitol, which can be used for vitamin C production.

Numerous electrocatalysis examples for the production of platform chemicals and pharmaceuticals from renewable feedstock have been reported.[7,12−14] One potential application of electrocatalysis is lactic acid production. Lactic acid has gained an increasing popularity due to its importance in the current biorefinery scheme.[15,16] This highly versatile α-hydroxy acid (AHA) plays many important roles in our daily routine and is used in food preservatives, cosmetic ingredients, pharmaceutical precursors, and beverage additives and is the starting material for many other personal care products. Lactic acid provides convenient access to other important platform chemicals, such as acrylic acid, 1,2-propanediol, pyruvic acid, acetaldehyde, and 2,3-pentanedione, and as a precursor to a green solvent, ethyl lactate.[15−17] Most notably, lactic acid is the fundamental building block for polylactic acid, a well-known biodegradable polymer that can potentially contribute to the phase-out of nonbiodegradable plastics.

Current production of lactic acid involves a multistage anaerobic fermentation of carbohydrates derived from starch, which accounts for over 90% of the annual global production.[18] Alternatively, lactic acid can be prepared from glycerol, an abundant byproduct from the biodiesel industry liberated from the long-chain fatty esters when triglycerides undergo transesterification. Several chemo- and biocatalyzed transformations of glycerol to lactic acid have been reported over the past decade.[19−22] Most chemocatalyzed reactions are performed under energy-intensive hydrothermal conditions and require a heterogeneous precious-metal catalyst or a highly alkaline homogeneous environment.[23] The bioconversion of glycerol offers milder conditions and better selectivity but suffers from low reaction rates and requires extensive postprocessing separations. As an alternative route, electro-catalytic oxidation possesses the benefits of mild operational conditions and high product selectivity. Electrochemical transformation of glycerol into various platform chemicals has thus been an ongoing research interest among the renewable chemical research community.[24,25] The disadvant-age of electrocatalytic oxidation, on the other hand, is the prolonged reaction time compared to those of the other two transformation pathways. Therefore, the role of electrocatalysis in a sustainable pathway for lactic acid production hinges upon a thorough understanding of its energy-saving potential, environmental impacts, and economic performance.

Life cycle assessment (LCA) and technoeconomic analysis (TEA) have been conducted to investigate the environmental impacts and economic performance of several glycerol valorization pathways. Morales et al. quantified the global warming potential (GWP) of a hybrid bio- and chemocatalytic production of lactic acid from glycerol, where glycerol is first oxidized to dihydroxyacetone (DHA) enzymatically, followed by a chemocatalyzed rearrangement to lactic acid catalyzed by a tin-loaded MFI zeolite catalyst.[26] A 24% reduction in GWP was observed for this hybrid approach, compared to the benchmark technology (fermentation of glucose).[27] A similar

reduction (35%) in GWP was reported by Lari et al., who also investigated lactic acid production from DHA isomerization.[28] Kim et al. reported a TEA study on electrocatalytic oxidation of glycerol to various AHAs. The authors defined the energy efficiency as the ratio of energy output (energy content of products) to the energy input and concluded that even with a 10.6% energy efficiency, electrocatalysis was still approximately 5.2% more energy-efficient than a nonelectrocatalytic oxidation strategy.[29] These previous works have set the stage to illustrate the economic feasibility and environmental benefits of valorization of glycerol to valuable products. Yet, a comprehensive understanding has not yet been achieved for electrocatalytic oxidation for lactic acid production due to the lack of (1) technoeconomic data for scaling up laboratory configurations and (2) a robust analytical capability for assessing the impact of data uncertainties, which influences the conclusion regarding the sustainability of electrocatalysis of lactic acid.

Therefore, the first objective of this study is to address the abovementioned challenges filling the knowledge gap in the environmental impacts and economic performances of electro-catalytic oxidation for lactic acid production. Second, this study aims to expand the scope of analysis by including fuel production, an area that has been a focus of climate change mitigation for the past few decades, into the electrocatalysis production of lactic acid to enable a coproduction of biofuels and a bio-based chemical. In particular, the objective is to investigate the potential advantages of electrocatalysis in terms of the climate change mitigation measures via milder operational conditions and a shift of energy consumption (e.g., natural gas or coal for heating in the hydrothermal process) to electricity (in electrocatalysis). The third goal is to produce a streamlined modeling framework for evaluating the environmental impacts and economic performance, as well as the contributors to their uncertainty, of a given product system, to support an informed decision regarding R&D effort, investment, and policy design for the chemical industry.

MATERIALS AND METHODS

To evaluate the potential GWP of a plausible full-scale operation of electrocatalytic oxidation for lactic acid production, we scaled a reaction previously reported by Lam et al. accordingly to a 100 kg/hr lactic acid production rate[3] (Table S15). The resulting data of material, energy, and waste flows was fed to both a TEA model and an LCA model for evaluating the metrics of interest (e.g., net present value, global warming potential).

Process Simulation. The electrocatalytic synthesis of lactic acid and the separation unit operations were modeled in Aspen Plus v8.1. Process parameters such as feed, reaction temperature, and pressure were obtained from Lam et al.,[3] who reported the electrochemical oxidation of glycerol in an aqueous alkaline environment using a heterogeneous cobalt-based catalyst to afford lactic acid (lactate) as the main AHA product, accompanied by several organic acid byproducts, namely, glycolic acid (glycolate), formic acid (formate), oxalic acid (oxalate), glyceric acid (glycerate), and unreacted glycerol. The feed requirements for obtaining the required products were linearly scaled assuming the same conversion of glycerol as in the laboratory experiments. The reactor was modeled in the batch environment in Aspen Plus by defining the stoichiometry of the reactions to ensure the formation of desired quantities of products as derived from the laboratory-

scale experiments. While all of the feed requirements were modeled in Aspen Plus to ensure accurate input to the LCA model, the geometry of the reactor and electrodes were accounted for separately while modeling the input to the TEA.

The feed and process parameter inputs to each section of the model are shown in Table S1 in the Supporting Information. The process flow diagram for lactic acid production is shown in Figure S1 in the Supporting Information. The output stream consisted of the lactic acid, glycolic acid, formic acid, oxalic acid, glyceric acid, and unreacted glycerol and was reacted with calcium hydroxide, followed by the addition of sulfuric acid to improve the precipitation of the calcified organic acid products.[30] The calcified organic acids are collected by filtration and then hydrolyzed with sulfuric acid to convert the products back to their respective acids. The acids were then methylated to obtain the methyl esters that are readily separable in a series of distillation columns. The Na_2SO_4 in the filtrate was processed in an electromembrane reactor to regenerate the NaOH and H_2SO_4. The remaining glycerol was recovered along with the methyl esters in a distillation column. The unreacted methanol was separated with residual methyl formate in the top product of the distillation column, DIST1. Methyl lactate and methyl glycolate were separated in the second distillation column with glycerol obtained in the bottom product and recycled. The third distillation column separated methyl lactate and methyl glycolate, which were then hydrolyzed back to their respective acids. A series of distillation columns then separated lactic acid with a 99% purity and glycolic acid with a small fraction of oxalic acid. A comparable separation section of the process was modeled based on Morales et al.[26] Methanol and water used in the processes were recovered by distillation and recycled. Process energy data from each unit block in the simulation was obtained in the form of heating and cooling requirements to provide the total energy requirements. Heat integration was performed on the process model using pinch analysis with the Aspen Energy add-on available in Aspen Plus. Pinch analysis is an energy optimization method that helps in identifying the minimum energy targets for a process by recovering excess energy from one part of the process (heat source) and applying it where needed (heat sink), hence reducing the need for external utilities.[31] The process model was also used for calculating the investment required for setting up a lactic acid production plant for net present value (NPV) calculations. The total capital cost for the process based on the individual equipment cost for each unit operation and the installed cost was calculated using the Aspen Process Economic Analyzer add-on available in Aspen Plus. Default scale-up settings from Aspen Plus were used in capital cost calculations for the process equipment. For the purpose of this analysis, the reactor is linearly scaled up based on the output flow rate from the laboratory experiments, along with the cost of electrodes.

Life Cycle Assessment. *Lactic Acid Production from Electrocatalytic Oxidation of Crude Glycerol.* A cradle-to-gate LCA model was created for the lactic acid production via electrocatalytic oxidation of crude glycerol ("ElectCat LA" pathway). The impact category of interest was the 100 year global warming potential (GWP), evaluated by the "ReCiPe Midpoint (H) 2014" impact assessment method. A detailed description of the reaction mechanism and laboratory conditions of the ElectCat LA pathway can be found in Scheme S1 and Table S15, respectively.[3] The system boundary enclosed major foreground processes including crude glycerol

production, electrocatalytic oxidation, product separation and purification, recycling of unreacted glycerol, and waste treatment. The associated background data such as electricity production and steam generation for the operations was obtained from the "ecoinvent 3.5 cutoff" database (www. ecoinvent.org). The functional unit was set as 1 kg of purified lactic acid. There were four byproducts generated after the electrocatalytic oxidation: glycolic acid, glyceric acid, oxalic acid, and formic acid. Similar to lactic acid, the glycolic acid was separated and recovered as a marketable byproduct, while the remaining three acids (glyceric, oxalic, and formic) were not further purified (due to their low economic values) and were treated together with the unrecovered glycerol as hazardous waste sent for incineration. Mass-based allocation was performed between lactic acid and glycolic acid to allocate the climate change impacts. Allocation was used instead of system expansion due to the lack of an LCA model on the avoided glycolic acid production from conventional means (e.g., catalytic reaction between formaldehyde and syngas). Foreground data of material and energy flows from electro-catalytic oxidation for lactic acid production was obtained from the process simulation (Table 1).

Lignocellulosic Biofuels Based on Electrocatalytic Hydrogenation and Hydrothermal Liquefaction. Two lignocellulosic biofuel production pathways were investigated: (1) fast pyrolysis bio-oil stabilized via electrocatalytic hydrogenation

Table 1. Material and Energy Inputs for 100 kg of Lactic Acid Produced from Electrocatalytic Oxidation of Crude Glycerol

output (kg/h)	per 100 kg lactic acid/h
lactic acid	100
glycolic acid	33.5
glycerol recovered	1166
methanol recovered	346.0
water recovered	175
formic acid[a]	171.2
oxalic acid[a]	20.7
glyceric acid[a]	25.2
CO_2[b]	238.9
input (kg/h)	
glycerol	1677.8
NaOH	1473.7[d]
water	1813.8
$Ca(OH)_2$	158.7
H_2SO_4	336[d]
methanol	362.8
water	181.4
energy (MJ/h)	
minimum heating[c]	28.6
minimum cooling	18.9

[a]Formic acid, oxalic acid, and glyceric acid are treated as hazardous wastes for incineration due to their low economic values. [b]Biogenic carbon from crude glycerol. [c]Minimum heating or cooling refers to the energy consumption after heat integration. [d]NaOH is assumed to be recovered using the electromembrane reactor (converting Na_2SO_4 into NaOH and H_2SO_4). Hence, the actual consumption of NaOH and H_2SO_4 for adjusting pH (to improve the precipitation of the calcified acid products) is assumed to be negligible in LCA and TEA modeling. Accordingly, the amount of H_2SO_4 (336 kg) is only for hydrolyzing the calcified products (e.g., calcium lactate) back to their respective acid products.

("ECH-LB" pathway)[32−34] and (2) hydrothermal liquefaction ("HTL-LB" pathway)[35] for bio-oil (stabilized simultaneously during fuel upgrading step via hydrotreating). For both pathways, the bio-oil was then upgraded through hydrotreating into biofuels that are assumed to be compatible with existing gasoline engines (i.e., "drop-in" biofuels). The LCA models for both pathways were cradle-to-grave, including feedstock (forest residues) harvesting, bio-oil (oxygenated hydrocarbons) synthesis and treatment, hydrotreating of bio-oil to produce biofuels (deoxygenated hydrocarbons), and combustion of biofuels. Biochar was the byproduct of both pathways and was assumed to be used as soil amendment, with 80% of the carbon in biochar assumed to be stably stored in the soil.[35] The feedstock forest residues were collected from the field by loaders, sent to chippers for size reduction, and then loaded to dump trucks for shipment. In the "ECH-LB" pathway, the forest residues were ground and dried before being sent to the fast pyrolysis unit (500 °C, 1 bar). The resulting bio-oil was treated subsequently in the ECH unit (80 °C, 1 bar) for oxygen removal and carbonyl saturation (i.e., "stabilization"). The stabilized bio-oil was reacted with H_2 in the hydrotreating unit (400 °C, 20 bar) to produce the biofuel. The H_2 for ECH and hydrotreating was generated from electrolysis (80 °C, 1 bar, 67% current efficiency) of water. In the HTL-LB pathway, the forest residues underwent size reduction via grinding and were mixed with hot water recycled from the HTL unit to produce biomass−water slurry. The slurry was sent to the HTL unit (335 °C, 203 bar) to produce bio-oil, which was converted into biofuel via hydrotreating (400 °C, 136 bar). H_2 for hydrotreating was produced by steam reforming (850 °C, 31 bar). The aqueous phase recovered after the HTL step, which contained dissolved organics (e.g., alcohols, acids), was fed to an anaerobic digester. The biogas generated from anaerobic digestion was used as a reformer feedstock for H_2 generation, for fired heaters, and for steam generation in boilers. The life cycle inventory data of both models is summarized in Tables S6−S9 in the Supporting Information.

Technoeconomic Analysis. *Lactic Acid Production from Electrocatalytic Oxidation of Crude Glycerol.* The TEA model was created based on a hypothetical facility with an annual production capacity of 0.8 million kg of lactic acid from electrocatalytic oxidation. The economic performance was measured by the net present value (NPV) of constructing and operating the facility for 20 years for lactic acid production. Common financial assumptions were applied, including those for facility lifetime (20 years), discount rate (10%), interest rate (10%), and tax rate (35%). The capital cost (CAPX) was calculated as the sum of the equipment purchase costs and corresponding installation costs, which were determined by the Aspen Process Economic Analyzer. The operational cost (OPEX) was composed of materials and energy costs, labor costs, and other fixed costs (e.g., insurance) incurred during the operation of the facility. The values of all of the costs, as well as the sales prices of lactic acid and glycolic acid, were obtained from the benchmark study and market search.[26] A complete summary of financing options, facility operations, and equipment purchase cost for the TEA model could be found in Section S3 of the Supporting Information. Table 2 summarizes the CAPX, OPEX, and other financial information used for calculating the NPV.

Integrated Modeling Framework for a Multiproduct System. An integrated modeling framework was created to holistically evaluate the environmental impacts and economic

Table 2. Capital Cost (CAPX), Operational Cost (OPEX), and Annual Revenue of the Hypothetical Facility

Capital Cost		Unit
total equipment cost	1 107 135	$
total setup cost	2 097 400	$
total CAPEX	3 204 535	$
Operational Cost and Revenue	**Cost (−)/revenue(+)**	**Unit**
total operation cost	−1 897 847	$/yr
total payroll cost	−145 854	$/yr
total other costs	−30 000	$/yr
total cost	−2 073 701	$/yr
total revenue	2 131 451	$/yr
EBITDA[a]	57 750	$/yr
Interest, Depreciation, and Amortization		**Unit**
straight-line depreciation of equipment	55 357	$/yr
amortization of setup cost	104 870	$/yr
interest expense	320 453	$/1st yr
total interest, depreciation, and amortization	480 680	$/1st yr

[a]Earnings before interest, taxes, depreciation, and amortization.

performance of a product system at any given production scale. The LCA, TEA, and global sensitivity analysis (GSA) models were all programmed using relevant libraries of Python, an open-source programming language, and were linked as modules of the integrated modeling framework (Figure 1). For a multiproduct system, the metric of interest (e.g., GWP) is calculated for each product (e.g., electrocatalytic oxidation for lactic acid production) separately. The individual values of the metric are then multiplied with the quantity of the respective products and are aggregated to quantify the total value of that metric for the multiproduct system.

LCA Module. The LCA module was adapted from the "Brightway2 Life Cycle Assessment Framework" (www.brightway.dev). The foreground database contained the foreground life cycle inventory data for fulfilling one functional unit of a specific product (i.e., materials, energy, and waste flows obtained from process simulation for producing 1 kg of lactic acid from electrocatalytic oxidation), which was documented in an "LCA input file", a spreadsheet with a format that conforms to the requirement for importing. The LCA module imported the foreground database and the relevant background database ("ecoinvent 3.5 cutoff" database for this study). The full LCA model was generated by matching the same flow between the foreground and background databases (e.g., "heat, from steam, in chemical industry | RoW") and linking the associated unit process (e.g., "steam production, as energy carrier, in chemical industry | RoW") in the background database to create a matrix of unit processes, the quantification of which collectively determine the life cycle emissions (e.g., CO_2, CH_4) that were converted into environmental impacts (e.g., GWP) by an impact assessment method. Whenever available, the "Rest of the World (RoW) market average" was chosen as the default geographic location for the data, given its prevalence in the database (and hence maximized the consistency in the geographic scope of this study). The relevant information could be found in Tables S2−S5 and S8−S10 in the Supporting Information. The Monte Carlo simulation method of the LCA module drew random samples for each of the foreground flows of interest, based on the corresponding uncertainty distributions. These random samples were shared between LCA and TEA modules to eliminate the inconsistency
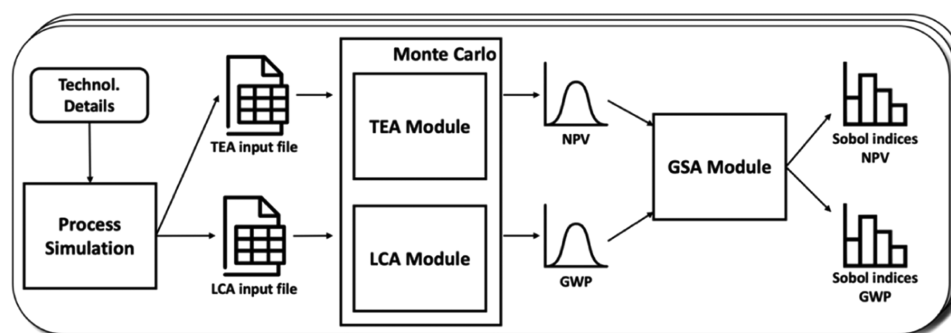
Figure 1. Illustration of the integrated modeling framework (each layer represents the calculation procedure for one product).

between the two assessment modules, when the Monte Carlo simulation was applied for understanding the uncertainties associated with both environmental impacts and economic performance of the product system simultaneously.[36,37] During each iteration of the Monte Carlo simulation (10 000 iterations), new LCA results were calculated based on the updated foreground data.

TEA Module. The TEA module was created using the "xlwings" library (www.xlwings.org). The TEA module calculated the economic performance metrics (e.g., NPV) using the information imported from a "TEA input file" that contains the financial assumptions, equipment purchase costs, and installation factors (for calculating the installation cost of equipment), as well as variable and fixed costs for operation.[38] Given the low-technology readiness level of the electrocatalytic oxidation technology, the TEA modeling did not apply the "n[th]-plant assumptions".[39] For example, the sizes of equipment were not optimized. The same Monte Carlo simulation method described above for the LCA was also applied in the TEA module for uncertainty analysis.

GSA Module. Whereas a local sensitivity analysis evaluates the contribution of each input variable (e.g., electricity consumption during electrocatalytic oxidation) of interest to the model outputs on an individual basis (i.e., changing the value of one variable while keeping others at fixed default values), a global sensitivity analysis determines both the first-order (individual) and second-order (interaction) contributions of model variables while varying their values simultaneously. This GSA module applied the Sobol method to decompose the variance of the Monte Carlo simulation results from LCA or TEA modules into fractions for calculating the Sobol sensitivity indices for the first-order and second-order contributions of each input variable.

Product Systems and Scenarios. Two product systems consisting of multiple main products (lactic acid and fuels) and relevant byproducts were investigated in this study. These two product systems differed in technology options to produce the same amount of main products. The default scenario was the same for both baseline and alternative product systems, comprising 37.9 kilo-tonnes of lactic acid (produced by fermentation of glucose) and 3.8×10^9 MJ of gasoline. In the baseline system, under the "Sustain. Chem." scenario, the technology option for lactic acid production was changed to enzymatic oxidation of glycerol to DHA followed by isomerization. Under the "Sustain. Chem. & Fuel" scenario, gasoline production was displaced by lignocellulosic biofuel by the HTL of biomass feedstock followed by hydrotreating and the byproduct was biochar. On the other hand, the alternative system has featured extensive electricity use. Under the

"Sustain. Chem." scenario, lactic acid was produced by the electrocatalytic oxidation of crude glycerol and the byproduct was glycolic acid. Under the "Sustain. Chem. & Fuel" scenario, lignocellulosic biofuel was produced by pyrolysis of biomass feedstock followed by electrocatalytic hydrogenation (for bio-oil stabilization) and hydrotreating. The product portfolio of each scenario in both baseline and alternative systems is summarized in Table 3.

Table 3. Composition of the Multiproduct System

	default scenario	Sustain. Chem. Scenario	Sustain. Chem. & Fuel Scenario
baseline system			
lactic acid (kilo-tonne)	37.9		
glycolic acid (kilo-tonne)			
gasoline (MJ)	3.8×10^9		
lignocellulosic biofuel (MJ)			3.8×10^9
biochar (kilo-tonne)			16.8
alternative system			
lactic acid (kilo-tonne)	37.9		
glycolic acid (kilo-tonne)		12.7	
gasoline (MJ)	3.8×10^9		
lignocellulosic biofuel (MJ)			3.8×10^9
biochar (kilo-tonne)			32.5

[a]The amount of lactic acid (37.9 kilo-tonnes) was calculated by assuming all crude glycerol from biodiesel production in the United States in 2019 were converted into lactic acid (using electrocatalytic oxidation). The total energy of fuel (3.8×10^9 MJ) was calculated by multiplying 100 million L of lignocellulosic biofuel with 37.9 MJ/L (assumptions from Nie&Bi 2018).

By comparing the modeling results (e.g., GWP) between different scenarios for the same product system, it is possible to identify opportunities to reach impact reduction or economic performance goals. The approach also illustrates how different product systems may respond (e.g., decrease/increase in GWP results) to the same scenario, providing insights regarding the advantage or disadvantage of each product system.

■ RESULTS AND DISCUSSION

Coupled with Low-Carbon Grid, Electrocatalysis Reduced Climate Change Impacts of Lactic Acid

Production by Approximately 50%, Compared to the Benchmark Technology. The GWP result of the electrocatalytic oxidation pathway under a nominal configuration (i.e., assuming no uncertainty associated with the operation conditions) was 38.6 kg CO_2-eq, which is approximately 31 and 40% lower than the benchmark (hybrid bio-/chemocatalytic pathway: 56.0 kg CO_2-eq) and conventional (fermentation of glucose: 64.5 kg CO_2-eq) results, respectively.[26] This reduction was primarily due to the lower-energy consumption of the electrocatalytic pathway, as well as to the biogenic nature of the CO_2 formed during the oxidation process (i.e., assumed to have a GWP value of zero). Procurement of the feedstock (crude glycerol) accounted for the majority (53%) of the impacts, primarily due to the embodied emissions from crude glycerol production. Process energy consumption (34%) included electricity for electrocatalysis, electricity for the recovery of NaOH and H_2SO_4 from Na_2SO_4 using an electromembrane reactor, and steam for heating and cooling water production.[40] The NaOH and H_2SO_4 were recycled for the subsequent glycerol oxidation reaction and postreaction neutralization, respectively. The incineration of formic acid, glyceric acid, oxalic acid, and nonrecoverable glycerol as well as landfill of $CaSO_4$ (waste gypsum from the calcified acid hydrolysis step) made up 11% of the total GWP. As the electrocatalytic oxidation and associated product purification processes were relatively material-efficient (e.g., high methanol recovery rate), the embodied impacts from material manufacturing were insignificant (1%). In addition, by switching from the default electricity grid ("electricity, medium voltage | RoW", 0.73 kg CO_2-eq/kWh) to a lower-carbon-intensity grid, which contains a significant share of hydroelectric power and nuclear power ("electricity, medium voltage | CH", 0.09 kg CO_2-eq/kWh), the GWP of the electrocatalytic oxidation pathway was reduced to 29.3 kg CO_2-eq/kg of lactic acid, which led to 48 and 55% reductions compared to the hybrid bio-/chemocatalytic pathway and fermentation of glucose, respectively. This indicates the unique advantage of electrocatalytic oxidation to leverage on the progress of grid decarbonization to further reduce the climate impacts of lactic acid production.

Since the electrocatalytic oxidation pathway investigated in this study was still at laboratory scale, it was necessary to investigate the uncertainty of the environmental impact results originated from this low-technology readiness level. Hence, a uniform distribution between [+10%, +30%] was applied to the nominal values of three major parameters of the electrocatalytic oxidation pathway (with the default electricity grid of "RoW"): crude glycerol input, electricity consumption, and heat use. Additional crude glycerol input and electricity consumption represent a more conservative assumption of the efficiency of the electrocatalytic oxidation pathway. A higher heat consumption represents a less efficient configuration of heat integration in the facility compared to the nominal case simulated in Aspen Plus. Accordingly, a Monte Carlo simulation was conducted and the 95% confidence interval of the GWP results was [43.5, 44.0] kg CO_2-eq/kg of lactic acid, demonstrating again the advantage of the electrocatalytic oxidation pathway in climate change mitigation, even with more conservative assumptions regarding its operational conditions. In addition, it is also important to understand the individual contribution of the three variables to the total uncertainty, which could assist the planning of future R&D to further improve the electrocatalytic oxidation pathway. The

GSA results showed that only the first-order sensitivity indices were significant, indicating no significant interaction between the three variables, and the changes in crude glycerol input contributed the most to the variance of the GWP results.

Economic Feasibility Needed Improvement for Lactic Acid Production from Electrocatalytic Oxidation. The NPV (in 2020 USD) was negative (Table 4), indicating that it

Table 4. Local Sensitivity Analysis for the Net Present Value (Million USD) of the Hypothetical Lactic Acid Plant

assumptions	no tax credit	with Iowa tax credit[a]	with Maine tax credit[a]
equipment purchase (↓ 50%)	−1.64	−1.29	−1.08
installation factors (↓ 50%)	−2.32	−1.97	−1.76
lactic acid sales price (↑ 50%)	0.91	1.26	1.40
glycolic acid sales price (↑ 50%)	−2.11	−1.69	−1.55
Baseline	−3.60	−3.25	−3.11

[a]Iowa (0.05 USD per lb) and Maine (0.07 USD per lb) Biorenewable Chemical Tax Credit Programs.[47]

was not economically viable for producing lactic acid through the electrocatalytic oxidation pathway with the current assumptions regarding facility configuration and market conditions. As shown in Table 2, the EBITDA was approximately 58 000 USD per year, while the capital cost was significant (3.2 million USD), which reiterated the financial challenges faced by the scaling-up of emerging technology in renewable chemical production.[41,42] Another major driver of the low NPV is the significant amount of electricity consumption for the recovery of NaOH and H_2SO_4 via the electromembrane reactor. The local sensitivity analysis (Table 4) showed that increasing the sales price of lactic acid by 50% (from $2 to $3 per kg) could result in a positive NPV of 900 000 USD. A 50% increase in the sales price of glycolic acid also significantly improved the economic performance (an increase of 1.5 million USD), although the NPV was still not close to break-even. One unique advantage of electrocatalysis is the potential financial improvement gained from the dual processing of organic transformation,[4,13,43] which enables the equipment sharing within a facility. For example, lactic acid is produced from the anodic oxidation of glycerol, while a biofuel precursor or chemicals could also be produced from cathodic reduction (via electrocatalytic hydrogenation of pyrolysis oil[34,44−46]). As a result, by assuming a 50% reduction of the estimated cost for equipment purchase, the NPV could be improved by approximately 2 million USD. Similarly, a 50% reduction of installation factors could also yield a considerable improvement in the economic feasibility.

With the advancement of technology readiness level, more definitive and realistic plant designs, equipment choices, and estimation of installation factors are expected, which could further improve the understanding of the economic viability of the electrocatalytic oxidation pathway. On the other hand, dedicated incentives for promoting renewable chemicals could also be a possible avenue to further improve the economic feasibility of lactic acid production from electrocatalytic oxidation. For example, the Iowa Biorenewable Chemical Tax Credit Program assigns a 0.05 USD per lb of product tax credit for 30 high-value chemicals derived from biomass
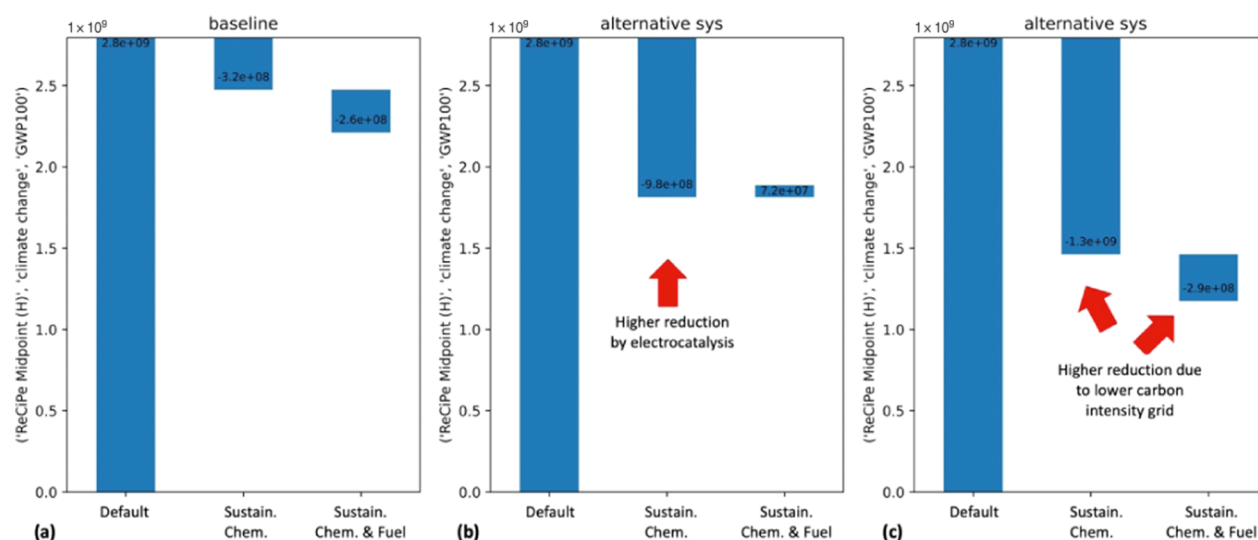
Figure 2. Waterfall chart to illustrate the reduction in GWP of a multiproduct system under different technology options. Default scenario: lactic acid was produced by glucose fermentation, and fuel demand was met by gasoline production. Sustain. Chem. scenario: lactic acid was produced by hybrid bio-/chemocatalytic (baseline system) or electrocatalytic oxidation (alternative system) of crude glycerol from biodiesel production. Sustain. Chem. & Fuel scenario: besides lactic acid, gasoline was displaced by lignocellulosic biofuel produced by HTL + hydrotreating (baseline system) or pyrolysis + electrocatalytic hydrogenation (alternative system).

feedstocks, including lactic acid and glycolic acid.[47] By considering this tax credit, an additional increase of approximately 0.4 million USD in NPV could be achieved, leading to a more positive economic performance when combined with other favorable assumptions mentioned above. A similar tax credit program is also available in Maine (0.07 USD per lb), which could potentially generate an over 0.5 million USD savings through tax reduction.

Electrocatalysis-Based Product Systems Could Augment the Benefits of Climate Change Mitigation Measures. A waterfall chart (Figure 2) illustrates the potential reduction of climate change impacts under different scenarios for the two product systems specified in the Product Systems and Scenarios section. The specific product demand (e.g., 3.8×10^9 MJ of gasoline or lignocellulosic biofuel in Table 3) under each scenario was a plausible representation of market response to a single policy (e.g., biofuel mandate) or a combination of policies. Also, each scenario was inclusive of all policies from preceding scenarios; therefore, the GWP results in the waterfall chart represented the consequences of a cascade implementation of policies. The total GWP under the default scenario was 2.8 million tonnes (Mt) CO_2-eq for both systems. The "Sustain. Chem." scenario reflected the implementation of policies in favor of low-impact feedstock and reducing manufacturing energy. Accordingly, in the baseline system (Figure 2a), the reduction in GWP was approximately 11% by switching to a hybrid bio-/chemo-catalytic process for lactic acid production using crude glycerol from biodiesel production instead of glucose from sugar beet. Under the "Sustain. Chem. & Fuel" scenario, additional policy dedicated to promoting biofuels (e.g., mandate for cellulosic biofuels) could lead to the extra reduction in climate change impacts. For example, by displacing 3.8×10^9 MJ of gasoline with lignocellulosic biofuel, which translated approximately into the mandate volume by Renewable Fuel Standard in the United States in 2019, the GWP of the product system could be further reduced by 9.2%. This additional reduction was due to the use of low-impact feedstock (forest residues are assumed

to bear no environmental burden), reduced process energy consumption, and the credit from applying the biochar (from HTL process) as soil amendments to sequester and carbon in the agricultural land. The cumulative reduction of the baseline system was hence 20% after all policies are implemented.

A different reduction pattern was observed when the same scenarios are applied to the alternative system (Figure 2b). Due to the lower process energy consumption compared to the hybrid bio-/chemocatalytic process, as well as the sharing of the impacts between byproduct and main products (i.e., mass-based allocation between glycolic acid and lactic acid), lactic acid production via electrocatalytic oxidation of glycerol could lead to a significantly larger reduction (35%) under the "Sustain. Chem." scenario. When lignocellulosic biofuel production was considered, however, a slight increase (2.5%) in GWP from the previous scenario was observed. Given that the process energy consumption was similar (0.62 MJ/MJ fuel vs 0.60 MJ/MJ fuel) between the two lignocellulosic biofuel production technologies, the larger emissions in the alternative system could be the result of the carbon intensity of the electricity grid (as electricity is the major source of energy consumption for electrocatalytic hydrogenation and for electrolysis of water for H_2 generation). By switching from the default electricity grid ("electricity, medium voltage | RoW", 0.73 kg CO_2-eq/kWh) to a lower-carbon-intensity grid ("electricity, medium voltage | CH", 0.09 kg CO_2-eq/kWh), another considerable reduction was achieved for lignocellulosic biofuel production (10%) accompanied by an additional reduction for lactic acid production (Figure 2c), yielding a cumulative reduction of approximately 57% in the alternative system. It should be noted that switching to a lower-carbon-intensity grid also enlarged the reduction in baseline system, from 9.2 to 12% (not shown in the waterfall chart), for lignocellulosic biofuels produced from HTL-treated bio-oil.

The results not only demonstrated the advantage of the alternative system (i.e., electrocatalysis-based chemical and fuel production system) over the baseline system in terms of the total reduction in climate change impacts, but also showed

how the two different systems responded to the same policy scenario (e.g., introduction of biofuel mandate) and how the corresponding effects contributed to the overall result. In general, the milder operation conditions of electrocatalysis-based technologies could lead to overall savings in energy and hence reducing climate change impacts from a life cycle perspective. In addition, electrocatalysis-based technologies could increase the share of electricity in the energy consumption patterns for different manufacturing processes, which augmented the benefits of promoting low-carbon-intensity electricity.

The current economic competitiveness is partly diminished by the seemingly low selectivity toward lactic acid, which is at 32%. It should be noted that the optimized product selectivity for lactic acid can reach 44%.[3] The less optimized condition (with respect to lactic acid's selectivity) was selected for this study because it was obtained from a condition that operated at a higher current density and in a lower alkalinity environment. A higher current density can reduce the reaction duration to save energy for heat maintenance, and a lower alkalinity requires less separation effort in downstream processing. Both factors offer a large reduction in energy costs in the TEA analysis. Therefore, this work exemplifies the concept that the reaction condition optimized for selectivity may not be economically optimal; TEA is crucial to reveal economic benefits of technology improvements. For example, one can consider the direct production of methylated AHA, e.g., methyl lactate, which can reduce the usage of NaOH, H_2SO_4, and $Ca(OH)_2$ as it will eliminate the need to methylate the AHA products during product isolation. In light of this, hydrothermal synthesis of methyl lactate has been reported by a number of authors to enable a direct extraction of the AHA products.[48,49]

Electrocatalysis-Based Product Systems Could Create Mutual Benefits with Carbon Pricing Policies. Electrocatalysis-based product system could also benefit from the carbon pricing policies, in addition to the tax credit for renewable chemical production. For instance, the Low Carbon Fuel Standard (LCFS) in California, employs a market-based mechanism for obligated parties (e.g., petroleum refineries, importers of fossil fuels) to choose low-carbon fuels that fit their specific needs for compliance. Each LCFS credit represents 1 tonne of CO_2-eq reduced. The number of credits for compliance (and hence the associated price) of a particular fuel is positively correlated to its carbon intensity (CI). Therefore, by leveraging on the low-carbon-intensity grid, the biofuel derived from electrocatalytic hydrogenation could generate more LCFS credits and a significant revenue through the sales of these credits, given its low CI (e.g., 26.8 g CO_2-eq/ MJ under low-carbon-intensity grid). For example, based on the trading price of LCFS credits in the fourth quarter of 2018 (approximately 196 USD per tonne of CO_2-eq), the biofuel with a CI of 30 g CO_2-eq/MJ could potentially generate an LCFS credit that is worth 1.44 USD per gasoline-gallon equivalent.[50,51] In addition, the electrocatalysis-based product system may also synergize with carbon pricing policies to promote the adoption of alternative energy systems. With major energy consumption shifting toward electricity when electrocatalysis-based product systems scale up, the investment into alternative energy systems to reduce the carbon intensity of electricity production may become incentivized to remain compliant with the relevant carbon pricing policies.

In addition to demonstrating the advantage of an electrocatalysis-based product system in mitigating climate change impacts of manufacturing processes, this study also makes a methodological contribution by creating an open-source, coherently integrated (i.e., TEA, LCA, GSA modules) analytical framework, which streamlines the evaluation of environmental and economic metrics for scaling up emerging technologies and enables the prioritization of research efforts to further improve and/or reduce uncertainties of these metrics. In addition to the "demand side" analysis (e.g., a fixed quantity of lactic acid to be produced from crude glycerol by a technology of choice) of the multiproduct system shown in the previous sections, the integrated analytical framework could also be used to elucidate the plausible environmental and economic implications of different "supply side" scenarios. For example, it would be possible to estimate the indirect benefits of a low-carbon fuel policy that promotes the biodiesel production by quantifying the reduction in GWP when an increased supply of crude glycerol is available to displace conventional feedstocks for lactic acid production.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c07309.

> The equations for TEA calculations are included in the "TEA_user_input_Dec.29 sim results_template.xlsx" and has been uploaded to github repo: https://github.com/SusBioRes-UBC/LacticAcid (XLSX)

> Process simulation; foreground life cycle inventory data; techno-economic analysis; integrated modeling framework for a multi-product system; and reaction information regarding glycerol to lactic acid and other alpha hydroxy acids (PDF)

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Notes
The authors declare no competing financial interest.

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