Green Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2024, **26**, 11303

Comparative techno-economic and life cycle assessment of electrocatalytic processes for lignin valorization

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This study explores the potential of using electrochemical (EC) methods for valorizing lignin, a lignocellulosic biomass cell wall component, into biofuels and high-value compounds. Traditional direct electroreduction as well as oxidation of lignin have faced challenges in efficiency and selectivity due to the requirement of high oxidation potentials and expensive, toxic electrodes, leading to uncontrolled degradation. We propose using a hydrogen atom transfer (HAT) mediator to achieve benzylic oxidation, enhancing efficiency and selectivity under milder conditions. The research employs the NREL model for producing ethanol to evaluate the commercial viability of EC lignin conversion. We carried out a techno-economic analysis (TEA) and a life cycle assessment (LCA) using BioSTEAM and GREET® 2022, respectively, to evaluate the process's economic and environmental impacts over 20 years. Sensitivity analysis has been conducted to examine base case values extracted from the catalytic performance of phthalimide-*N*-oxyl type HAT mediators. Our findings suggest that a 2000 metric tonnes per day biorefinery using this method could produce approximately 49.56 tpd of chemicals, with the EC unit consuming 3.5% of the input energy. The TEA operating cost for chemical production was estimated at $16.86 per kg, with a total capital expenditure of $403 769 MM. The LCA revealed that producing by-products in ethanol production can lead to around 10 to 46% reduction in total CO_2 emissions, depending on the employed allocation methods. The study indicates that integrating an EC unit using a HAT mediator into second-generation biorefineries for lignin oxidation followed by a reduction in chemicals could offer additional revenue streams and lower environmental impacts compared to conventional methods.

Received 20th April 2024,
Accepted 16th September 2024

DOI: 10.1039/d4gc01963f

rsc.li/greenchem

1. Introduction

Lignocellulosic biomass, comprised of cellulose, lignin, and hemicellulose, can potentially be used in biorefineries, which produce biofuels and chemicals by fermenting sugar from carbohydrates found in cell walls.[1] Studies on the valorization of lignin through its deconstruction into renewable aromatic and phenolic chemicals have increased due to the recognition that the economic viability of biorefinery depends on the co-utilization of cell wall carbohydrates and lignin.[2,3] However, the heteropolymeric structure of lignin, alongside its functional groups, interunit linkage diversity, and slight branching, complicates depolymerization. Chemically modified lignin like sulfonated Kraft lignin, common in biorefineries, poses additional challenges by altering reactivity and accessibility, hindering selective bond cleavage. The economic viability of biorefineries depends on satisfactory lignin deconstruction. Thus, efficiently obtaining desired monomers while reducing unwanted byproducts is a significant challenge in lignin valorization. While pyrolysis, a high-temperature thermal decomposition process, has been a well-studied and valuable method for lignin valorization for producing liquid fuels, its nonselective nature results in wide product distribution, lower stability and associated low liquid product yields. In contrast, the electrocatalytic approach prioritizes the selective cleavage of β-O-4 bonds, tailored to specific needs and thus offering distinct advantages. In the spirit of maximizing monomer yields while minimizing unwanted byproducts and pathways, the low-temperature, selective properties of electrocatalytic methods may provide superior outcomes compared to more common but nonselective methods like pyrolysis.[4–6]

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Electrochemical (EC) depolymerization, which generates reactive, high-energy electrons despite operating at milder temperatures and pressure conditions, has gained popularity as a method for targeting aryl–ether bonds and facilitating selective depolymerization. Electrochemical technologies have emerged as promising alternatives to traditional fossil-based methods for the sustainable synthesis of chemicals. Similarly, electrocatalytic and photo-assisted electrocatalytic routes have been investigated for the degradation of lignin, offering efficient pathways to convert biomass into valuable products.[7,8]

Among the several approaches to the EC depolymerization of lignin, one involves the EC oxidation of the Cα alcohol of the β-O-4 linkage to a ketone.[9,10] This oxidized lignin linkage is more susceptible to cleavage under mild chemo-, electro-, or photo-catalytic conditions. Such advancements in EC depolymerization techniques highlight the potential to offer low-cost, reagent-free, and environmentally friendly solutions for lignin depolymerization, making it a promising and sustainable technique.[11] Due to their ability to be conducted at low temperatures and pressures, EC methods can be extremely important in refining the selectivity of reactions and preventing unintended secondary reactions during lignin depolymerization.[12] These advantages of electrochemical lignin valorization have not gone unnoticed, and several strategies on both model compounds and real lignin have recently been a subject of interest.[6,13–16]

Nonetheless, direct oxidation of the Cα alcohol is made complicated by the polymeric structure of lignin, which poses transport limitations toward the electrode surface. Typical ways to combat this drawback include the need for high potentials and the use of costly and toxic electrodes, leading to unselective oxidation and potential uncontrolled degradation.[9] To address these challenges, the employment of a mediator proves beneficial. The mediator, in this case, is a smaller, more mobile molecule that readily oxidizes on the electrode surface and then diffuses towards target functional groups to deliver the desired oxidation reaction. In doing so, the mediator acts as a catalyst by lowering the necessary potential for targeted oxidations, resulting in gentler conditions, improved selectivity, and enhanced overall efficiency. Specifically, employing a hydrogen atom transfer (HAT) mediator for lignin proves effective, as it facilitates the desired selective benzylic oxidation through the abstraction of benzylic hydrogen. According to Wang and Stahl's study, mediators can dramatically reduce the overpotentials needed for the EC oxidation of organic molecules. This is especially true for mediators that can facilitate hydride and HAT reactions.[17] As reported by Luo and Liu, mediated electro-oxidation has a high chemical selectivity when it comes to breaking the β-O-4 linkage, which effectively reduces side reactions and keeps lignin-derived products from being overoxidized.[18]

Tu *et al.* discovered that integrating electrocatalysis with a low-carbon-intensity power grid can lower the global warming potential (GWP) by 57% when producing lactic acid and lignocellulosic biofuel, compared to a conventional fossil-based system that produces similar products.[19] Moreover, several authors have examined market data to identify market opportunities for lignin-derived products. Techno-economic analysis (TEA) evaluates economic feasibility, optimizes resource utilization, and supports decision-making in scaling up processes and helps assess costs, risks, and market competitiveness for informed project planning.[20,21] Also, to compare conventional products with organic alternatives, life cycle assessments (LCAs), need to be used to evaluate the environmental benefits of lignin-derived products.[22] Utilizing suitable techniques for analysis and environmental effect evaluation, LCA serves as a standardized approach for modeling a product's or mechanism's entire life cycle, from the extraction of resources until the end of life.[23,24]

There have been numerous studies that investigate the TEA and LCA of lignin conversion to chemicals and fuel. In order to convert biorefinery lignin into higher-value industrial chemicals while simultaneously producing hydrogen, NaderiNasrabadi *et al.* proposed a TEA for incorporating an EC reactor into a lignocellulosic biorefinery. They discovered that at greater lignin conversion levels, the break-even output stream value might range from \$1.00 to \$2.00 per kg, based on capital cost as well as manufacturing expenses like a decrease in value, making it potentially attractive to the industry.[25] In an evaluation of the minimum selling price (MSP) of ethanol for a corn stover biorefinery incorporated with hydrothermal liquefaction, Bbosa *et al.* found that taking into account lignin-derived biochemicals, the MSP of ethanol was \$1.03 per gal. The price of feedstock, fixed capital investment, and internal rate of return (IRR) were found to be crucial variables.[26] Khwanjaisakun *et al.* explored the valorization of Kraft lignin waste into vanillin through oxidation. They optimized reaction temperature, lignin feed content, and oxygen partial pressure to maximize vanillin production, achieving a yield of 9.25% with specific conditions. Three distinct separation situations have been studied: Case I involved solvent extraction and distillation, Case II used solvent extraction only, and Case III involved vacuum distillation. According to their analysis, Case I produced the largest return on investment, with an IRR of 22.63% as well as a payback period of 6.19 years.[27]

Although there are many studies in lignin valorization, the research in the TEA and LCA of a combined system consisting of an EC reactor for producing chemicals and ethanol production from lignocellulosic biomass remains limited. Moreover, the additional process design requirements cost of the HAT mediators, and the potential for HAT mediator degradation or lost, the economic benefit of HAT mediator use is unclear.

The present study aims to evaluate the sustainability of a novel EC conversion technology as a strategy for lignin valorization to produce commodity and specialty chemicals. The research contributes detailed TEA and LCA analysis to understand the economic potential and GHG emissions across the products' lifecycle. Sensitivity analysis is conducted to identify key TEA parameters. Various GHG product allocation methods are evaluated to understand their impact on the LCA. Finally, we discuss the limitations of the study and opportunities for improving the development of EC biorefineries.

2. Methodology

2.1. Process overview

Fig. 1 shows the simplified process flow diagram of three main sections: electrocatalytic oxidation using HAT mediators, followed by chemo-catalytic reduction to depolymerize oxidized lignin into monomers as well as corn stover to ethanol biorefinery including heat recovery and waste treatment.

The lignin stream is initially separated in the lignin splitter section using dilute-acid pretreatment to break it down into intermediate molecular-weight compounds, although there are more advanced pretreatment methods for biomass that could offer more efficiency and yield.[28] This extracted lignin then undergoes EC depolymerization, facilitated by an oxidation step employing electrocatalytic oxidation with HAT mediators, which specifically targets Cα alcohols in the β-O-4 lignin linkage to ketones. This selective benzylic oxidation, achieved by abstracting benzylic hydrogen atoms, is integrated into our EC system for TEA and LCA. A subsequent chemo-catalytic reduction step is then utilized to depolymerize oxidized lignin into monomers, following which target chemical products and intermediates are isolated *via* multi-stage distillation and purification methods. Notably, the Bosque *et al.* method, combining electrocatalytic oxidation *via* HAT mediators with photocatalytic reduction, showcases effective cleavage of crucial lignin linkages.[29]

The ethanol production part is derived from earlier research conducted by the National Renewable Energy Laboratory (NREL).[28] As can be seen in Fig. 1, the corn stover biomass first undergoes dilute-acid pretreatment to extract lignin, and the resulting pretreated lignocellulosic biomass is then exposed to enzymatic hydrolysis to form hydrolysate. Cellulose and hemicellulose are broken down into fermentable sugars during enzymatic hydrolysis. Various phases of the synthesis of cellulosic ethanol can employ ammonia to aid in the breakdown of lignocellulosic biomass. Ammonia functions as a pH buffer and aids in establishing the ideal conditions for enzymatic hydrolysis, which transforms cellulose and hemicellulose into fermentable sugars. The activity and stability of the enzymes are increased when the pH is brought into the correct range, generally pH 4–5, with the aid of ammonia.[28] The main end product of the fermentation process is Ethanol. The ethanol should be extracted from the fermentation broth. To extract and concentrate the ethanol from the mixture, distillation is performed. High-purity ethanol can be obtained by adding further purification stages.

The final section is the heat recovery and waste treatment step. This section receives lignin from the ethanol and chemical production steps. The ethanol production step results in a lignin waste stream. The lignin from the chemical production step is split based on the energy requirements of the plant. Lignocellulosic biorefineries export excess heat and power from lignin combustion. Thus, the EC conversion section employs only a portion of the lignin that is not required for process heat and power. Wastewater treatment is a required step. Common techniques for treating wastewater include physical (like filtration or sedimentation), biological (like aerobic or anaerobic treatment), and chemical (like coagulation, flocculation, or oxidation) procedures. These procedures assist in ensuring wastewater complies with environmental regulations by removing organic material, suspended particles, and other pollutants.[28]

2.2. EC oxidation of lignin

In this study, the electroanalytical analysis of the electro-oxidation of a β-O-4 model compound was used to assess the

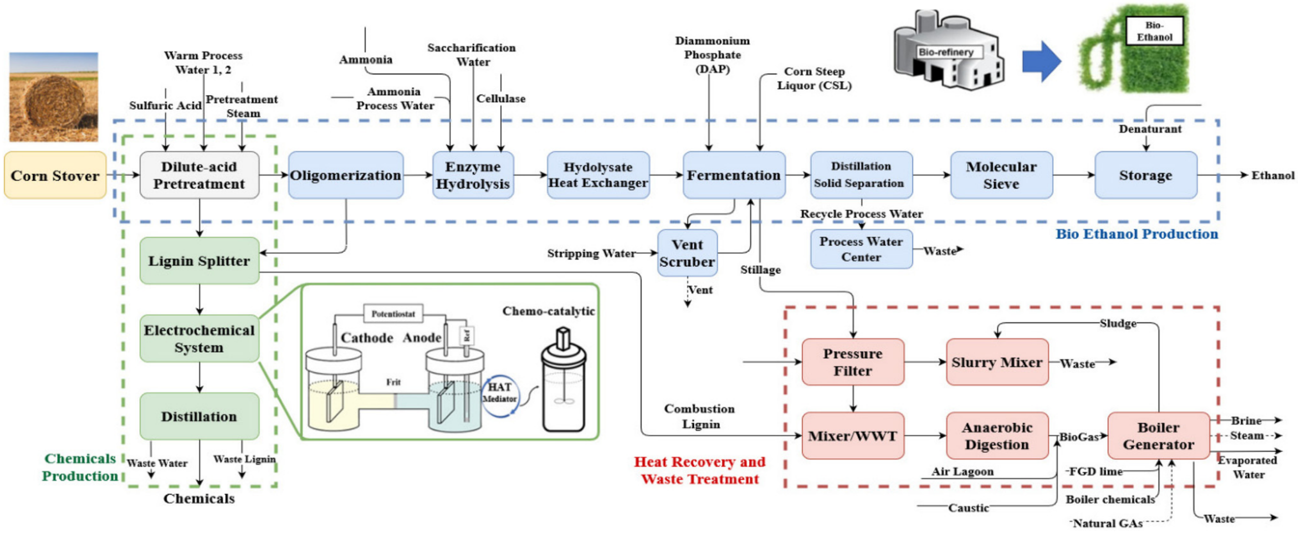


Fig. 1 Simplified process flow diagram for a dilute-acid pretreatment of corn stover to ethanol biorefinery with lignin EC conversion to chemicals.

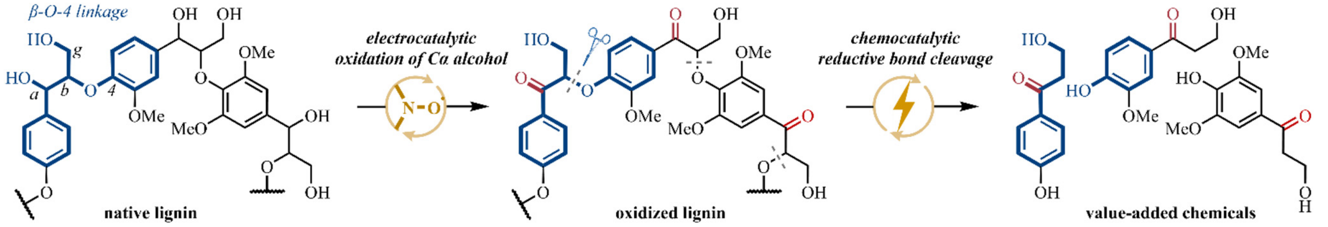


Fig. 2 Electrocatalytic oxidation of lignin model compound.

efficacy of phthalimide-*N*-oxyl (PINO) type catalysts mediated EC oxidation (Fig. 2). All EC oxidation was conducted in an undivided vessel using a three-electrode configuration. A self-assembled glassy carbon plate (1 cm × 2 cm, from GoodFellow) has been utilized as an anode, and reticulated vitreous carbon (RVC, 100 ppm, 1 cm^3, from Duocel) was used as the cathode. All the reactions were referenced by a hand-made silver nitrate/silver ($AgNO_3$, 0.01 M/Ag) reference electrode. An electrolyte solution of 0.1 M KPF_6 in MeCN was used as a reaction media solution. NHPI-type catalyst precursors (0.016 mmol, 10 mmol%) and pyridine (0.32 mmol, 2 equiv.) were added to 8 mL of the reaction solution. Cyclic voltammetry was performed to measure the anodic peak potential (E_{pa}) of the redox couple. Then, the lignin model (0.16 mmol, 1 equiv.) was added to the reaction solution. EC reactions were acquired using μStat 4000 Multi-Channel Potentiostat/Galvanostat (from Metrohm USA). Electrolysis was performed at ambient temperature under air with a constant potential of 0.15 V above E_{pa} to provide a head-to-head comparison. After the reaction was completed, the reaction solution was analyzed by ^1H NMR to determine conversions and yields by adding internal standard 1,3,5-trimethoxybenzene. The total charges passing through the EC cell were calculated by integrating chronoamperometry (*i*–*t* curve). Faraday's efficiency was determined accordingly.

Scaling up any electrochemical reactor is challenging due to transport requirements. While other processes have addressed similar issues, the purpose of our TEA and LCA is to provide a model for early-stage research, highlighting key areas like oxidation yield that could significantly impact the overall process.

2.3. Catalysts

Experimental data for this analysis is based on PINO-type catalysts. In this study focuses on *N*-hydroxytetrachlorophthalimide (TCNHPI). The catalytic activities of PINO-type HAT species are influenced by their chemical structure, in particular, the substituents on the phthalimide ring.[30] On the basis of our previous mechanistic study, the base strength has an impact on catalytic efficiency by influencing the catalyst decomposition path.[31] When using NHPI as a mediator, 70% of the starting material was converted, and the catalytic reaction gave 77% of the desired oxidation product at an applied potential of 0.8 V *vs.* Fc+/0. During the course of the reaction, 0.72 mmol electrons passed through the electrodes, which yielded 15% Faraday efficiency. Introducing electron-withdrawing groups to the phthalimide ring (catalysts 2–4, 6) activates the HAT mediator through the polar effect but destabilizes their corresponding catalysts.[30] In the same amount of reaction, we observed increased yields and conversions, but these processes require higher applied potentials. Installing bulky phenyl groups to the phthalimide core (catalyst 5) deactivated the catalyst, and only gave <5% conversion and yield and very low Faraday efficiency. Changing the backbones of the NHPI (catalyst 7–8) gave lower yields/conversions/Faraday efficiencies (Fig. 3). Our 70% yield is on the same order of magnitude as previously reported yields of other catalytic depolymerization processes.[32,33] However, the scope of this study is to evaluate the early-stage electrochemical lignin valorization technology, and more data would be required to make more detailed comparisons with established technologies. The stability of PINO-type catalysts was investigated in a recent study.[34] Based on those findings, new, more stable PINO catalysts have been developed.[35] Future experimental studies will investigate the stability of PINO catalysts for lignin electrochemical oxidation applications.

Product composition data for the EC process is based on the Alherech *et al.* study shown in Table 1.[36] The molecular structure (drawn in ChemDraw software) in the table was gathered from the reference.[36] Characterization for lignin model substrates and products can be found in ref. 37 The tetrachloroNHPI catalyst is commercially available through online merchants.

Chemo-catalysis is an alternative approach to recovering lignin chemicals.[38] Chemocatalysis employs a catalyst to accelerate chemical reactions by lowering activation energy. Reactants interact with the catalyst, facilitating bond breaking and product formation. After the reaction, products detach, and the catalyst can be reused. This process boosts reaction rates, selectivity, and efficiency while reducing energy con-

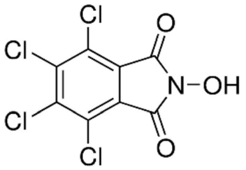
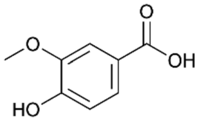
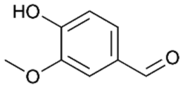
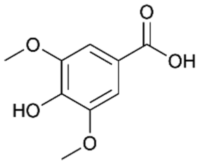
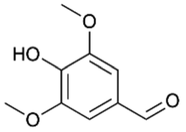
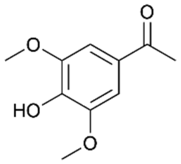
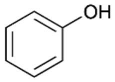


Fig. 3 TCNHPI electrocatalytic oxidation of lignin catalyst performance (yield, conversion, oxidation, faradaic Efficiency, and potential).

Table 1 The product composition data.[36]

Product	Molecular structure	Yield (wt%)
Vanillic acid		2.1
Vanillin		6.1
Syringic acid		1.8
Syringaldehyde		13.7
Acetosyringone		1.9
Phenol		35.8

sumption and waste generation, making it vital in various industries. Although we did not model this pathway, it presents an intriguing avenue for future investigation, especially considering its potential to yield aromatics from lignin. Quinones were not formed, and the reduction was not performed in this study. Product distributions were extracted from ref. 36 and 38.

2.4. TEA approach

The goal of the TEA would be to assess the profitability of the corn stover to ethanol with lignin EC biorefinery. The primary profitability metric for this study is the MSP of the lignin chemicals. In order to estimate capital and operational costs, the TEA employs energy as well as material data from the process design, and a multiyear discounted cash flow rate of return evaluation to determine the Net Present Value (NPV). The MSP is determined by varying the chemical prices until an NPV of zero is achieved at a target IRR. The TEA assumes that the biorefinery operates as a N^{th} plant model, which has resolved all the critical engineering and scientific challenges required to operate commercially.

The process model is implemented in BioSTEAM.[39] BioSTEAM is a chemical process design framework financed by U.S. Department of Energy. It includes validated packages based on the NREL's corn stover to ethanol biorefinery design.[40] For this project, we modified the BioSTEAM stover to ethanol design to incorporate the EC conversion step.

The TEA estimates capital costs based on the material and energy flow stream data. Equipment purchase costs are based on power-law economies-of-scale calculations utilizing cost elements gathered by NREL from equipment vendors. The purchase cost is then multiplied by the bare module factor to determine the installation cost. This approach does not rely on a LANG factor to estimate the facility's fixed capital investment.

Operating costs are calculated based on the material and energy flow rates and fixed cost factors. Raw materials include corn stover and chemicals such as ammonia, sulfuric acid, and boiler chemicals. Fixed cost factors include equipment maintenance, labor and overhead, and field expenses. The operating cost calculation also accounts for revenues from electricity generation, ethanol production, and chemical sales.

Considering a 20-year project lifetime with 350 operating days annually, the profitability analysis is performed. The biorefinery is initially built over a 2-year period prior to operation. During that period, the facility incurs labor and operation costs and generates a fraction of total sales. Forty percent of the capital investment is done throughout the initial year of the construction period. The facility is financed through 40% equity and 60% loan at an 8% interest rate with a 10-year payback period.[28] The facility equipment depreciates over a 7-year period based on a MACRS7 depreciation schedule and the steam power plant depreciates over a 10-year period (MACRS20) due to its technological maturity. The income tax rate is 35%, which is comparable to NREL's tax rate in the original study. The target IRR is 10%.[28] Table 2 displays the financial assumptions and various parameters related to the profitability analysis.

The design of the EC system is based on the study by Orella *et al.*[41] Their study builds upon the U.S. Department of Energy H2A model.[42] They estimated costs for 50 tonne per day hydrogen EC system was about \$5 per kg consisting of ~\$3.4 (electricity), ~\$0.4 per kg (capital), ~\$0.5 per kg (balance of plant), and ~\$0.65 per kg (additional) costs. The model was modified to account for the performance of the catalysts employed in this study. Based on the NREL report,[43] we assumed a catalyst cost of \$44 per kg with a 2-year replacement cycle for our analysis. According to recent research,[44] HAT catalysts are potentially more cost-effective compared to traditional catalysts. Since market prices for HAT catalysts are not currently available, this assumption is considered conservative.

The EC process generates a wide range of lignin-derived chemicals. We gathered market average price data for various chemicals, as shown in Table 3.[45] These are commodity prices that may not reflect the greater economic value of biobased chemicals. Some bio-based chemicals are more expensive than fossil-based alternatives. However, NREL evaluated various bio-based chemicals and determined that their market supply remains too low to affect market prices and more development is needed to determine their market competitiveness.[46] We believe our conservative assumption is necessary to establish a baseline. Future work may evaluate the value of specialty chemicals as we learn more about the composition, separation process, and performance of the products.

Table 2 Corn stover to ethanol and EC lignin chemicals financial assumptions

Parameter	Value/method	Parameter	Value/method
IRR	0.10	Corn stover	\$51.60 per tonne
Duration	20 years	Sulfuric acid	\$89.72 per tonne
Depreciation	MACRS7	Ammonia	\$448.60 per tonne
The tax rate applied to the taxable income	0.35	Cellulase	\$212.00 per tonne
Operating days	350.4	CSL	\$56.82 per tonne
LANG factor	3	Caustic	\$74.80 per tonne
Startup months	3	Denaturant	\$756.00 per tonne
The fraction of FOC during the startup phase	1	FGD_lime	\$199.40 per tonne
Sale fraction during the startup	0.5	Boiler chemicals	\$4995.90 per tonne
The finance interest rate	0.08	Cooling tower chemicals	\$3000.00 per tonne
The finance year	10	Labor cost	\$2.5 million
The fraction of the project's total capital expenditure	0.4	Field expenses	0.10
The ratio between working capital and FCI	0.05	Steam power depreciation	MACRS20

Table 3 Average price data for lignin-derived chemicals[45]

Product	Average price
Vanillic acid	22 \$ per kg
Vanillin	25 \$ per kg
Syringic acid	30 \$ per kg
Syringaldehyde	25 \$ per kg
Acetosyringone	45 \$ per kg
Phenol	10 \$ per kg

2.5. Sensitivity analysis

The capacity of TEA to assess the effects of numerous factors on process economics through sensitivity analysis is one of its primary characteristics. Sensitivity analysis is gradually altering the values of important parameters and assessing how they affect process profitability.[47] Important considerations in the area of EC lignin conversion include the cost of the catalyst, the price of the finished product, and the availability of lignin. Decision-makers may observe how changes in each parameter influence the process' overall profitability by adjusting these parameters within a reasonable range.

Process economics also depends significantly on catalyst costs. Sensitivity analysis enables decision-makers to evaluate how changes in catalyst costs will affect the overall profitability of the process. This research aids in locating cost-cutting opportunities and investigating potential catalyst alternatives. Sensitivity analysis also takes into account the impact of product pricing on process profitability. Decision-makers can gauge how sensitive the economics of the process is to market conditions by varying the cost of the final goods derived through lignin conversion. Understanding the possible risks brought on by market volatility and creating methods to reduce them, such as diversifying the product line or focusing on certain markets, are made easier with the aid of this knowledge. For this study, we varied parameters by a common value of 20% to understand their impacts on the chemicals' MSP.

2.6. LCA approach

Estimating the lifecycle greenhouse gas (GHG) emission impacts of adding the EC system to the ethanol biorefinery is the objective of the life cycle assessment (LCA). This research follows the guidelines of the ISO 14040 (2006) series.[24] First, we establish the LCA scope, system boundary, and functional unit. The system boundary encompasses the biorefinery location.

Crop production, power generation, and other downstream and upstream activities are considered outside the scope of this analysis. The functional unit is 1 MJ of ethanol.

The LCA is implemented in the GREET.NET software developed by Argonne National Laboratory (ANL).[48] We modified the existing corn to ethanol GREET.NET model to incorporate the material and energy flow changes from the EC system addition.

The model includes all the steps from crop production to ethanol biorefinery products. Only the ethanol production step is modified for the purpose of this study. The inventory table is provided in Table 4. It is worth mentioning that some compounds are not available in the database in Greet software, and we replaced them with the closest compatible substitutes based on their most common industrial use such as sugar and methanol substitute. The industrial applications considered are alcohol (methanol) or solvent substitutes and food (sugar) additives. After modifying the existing cornstover to ethanol pathway in GREET, the original emission factor was reduced from 415 to 348.

Then, allocation methods are employed in attributional LCA to define how the environmental impacts are distributed among multiple by-products. There are four main types of allocation methods: displacement, energy, mass, and economic allocation. These methods significantly impact the estimated environmental benefits of EC lignin chemicals because they have very different energy density and economic value than ethanol. The displacement is broadly considered the best approach to properly account for the LCA impacts, but we investigated all methods to understand the range of possible estimates. Following is a detailed description of each method.

2.6.1. Displacement method. Under the displacement approach, which is sometimes referred to as the "substitution method" or the "system boundary expansion method", the goods that are to be replaced by non-fuel products are first identified. The ISO standards advocate system expansion or

Table 4 Emissions factors from the consumption of materials in the corn stover to ethanol pathway existed and in GREET.NET

GHG emission source	Emission factor (g CO_2 per kg)
Corn stover	43.8
Sulfuric acid	44.1
Ammonia	2840
Corn steep Liquor	1720
Diammonium phosphate	1740
Sodium hydroxide	2120
Calcium oxide	1280
Glucose	791
Electricity (export credit)	−130
Plasma power	1.98
Chemicals	Emission factor (g CO_2 per kg) (export credit)
Vanillic acid	−496
Vanillin	−798
Syringic acid	−798
Syringaldehyde	−798
Acetosyringone	−496
Phenol	−496
Ethanol	Emission factor (g CO_2 per kg)
Corn stover ethanol (no by-products)	415
Corn stover ethanol with by-products	348

displacement method, wherein the impacts of co-products as if created in a reference system are considered as environmental impact credits. Credits are deducted from the overall energy consumption as well as emission loads of the process involved in producing biofuel to arrive at the anticipated energy usage and emissions burdens. The displacement approach usually captures the true consequences of producing several products from a single pathway.[49]

2.6.2. Energy allocation. By using Energy allocation, the energy consumption and emission loads associated with a particular fuel production pathway are distributed among goods based on the shares of their energy output. Every product has an output of energy that is calculated by multiplying the total quantity of the product(s) made up by the energy content of the product, which is typically the product's heating content. This approach can be applied in situations when the majority of the products or all of them have been utilized for their energy content.[49]

2.6.3. Mass allocation. According to their particular mass production shares, all products in a given biofuel pathway have their energy usage as well as emission loads divided among them. The underlying premise of this allocation scheme is that the mass process is correlated with emissions and utilization of energy. Both general LCA models as well as LCAs of consumer products frequently employ this technique.[49]

2.6.4. Economic allocation. This approach divides up the energy and emission loads according to the relative economic revenue of each product. The economic revenue of a given product is calculated using the product cost as well as the product yield of a particular pathway.

Using this approach would be widely recommended by economists. This approach is used in several LCA purposes of general equilibrium designs. It assumes that decisions and actions are motivated by economic factors and that responsibilities should be distributed in a way that maximizes those advantages. The unique advantage of this approach is that it standardizes all products on a single basis (economic values).[49]

3. Results

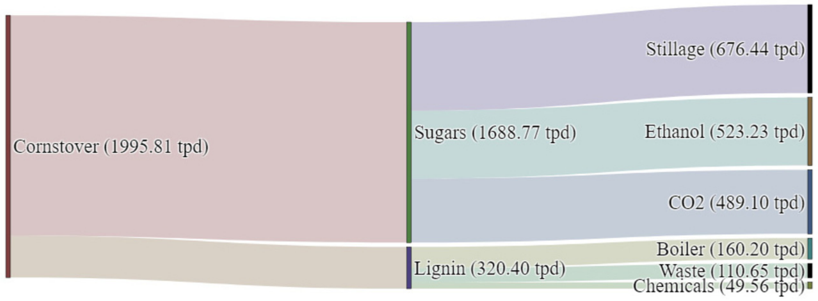
3.1. Mass and energy balance

The Sankey diagrams (Fig. 4(a) and (b)) provide a visual representation of the mass as well as energy balance in the ethanol production design, showing how the input of corn stover has been transformed into ethanol, chemicals, CO_2, and waste. Fig. 4(a) is a simplified representation of the mass balance for the given inputs and outputs. The mass balance is consistent as the sum of all the output streams matches the input stream. In the model, 84.63% of the input biomass (1995.81 tpd) was converted into 1688.77 tpd of sugars, with 31% of sugars producing 523.23 tpd of ethanol. A boiler process utilizes 8.03% of the input biomass to generate 160.20 tpd of energy. From the EC process, around 2.4% of the input biomass yields 49.56 tpd of chemicals. Fig. 4(b), shows how the input energy is distributed and transformed throughout the process. The input energy is 1484.95 GJ h^{-1}. The ethanol production process consumes about 44.15% of the input energy. The boiler operation uses 11.2% of the input energy to provide heat and steam. Finally, around 3.5% of the input energy is used for the EC production of chemicals. The energy balance highlights the energy distribution and utilization efficiency throughout the entire ethanol and chemical production process. Furthermore, Fig. 5 displays the stream states determined by BioSTEAM and provides a more thorough flow diagram of the process for the lignin conversion.

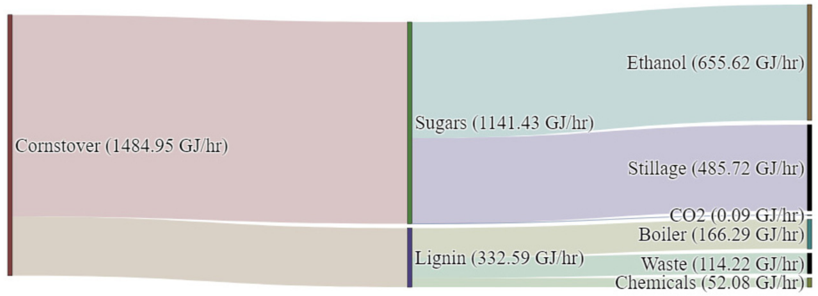
3.2. TEA

3.2.1. Capital costs. The installed cost chart (Fig. 6) provides a comprehensive overview of the expenses linked to various equipment within the model. Notably, the EC reactor emerges as the most substantial investment, amounting to a substantial $216.38 million. Following is the boiler turbogenerator (BT) in the amount of $57 million. Due to the complexity and high cost of the EC pump and BT and their essential role across the system, high expenses are anticipated. Following closely behind is the wastewater treatment system (WWTC), commanding an installation cost of $44.6 million, crucial for maintaining process efficiency and ensuring product quality during ethanol manufacturing. With a cost of $30.27 million, the pretreatment reactor system is another critical component. Moreover, the wastewater treatment, pressure filters, pre-saccharification system, and molecular sieve exhibit notable costs in the model, showcasing their significance in the process.

3.2.2. Operating costs. The operating cost chart, as depicted in Fig. 7, outlines the significant components contri-

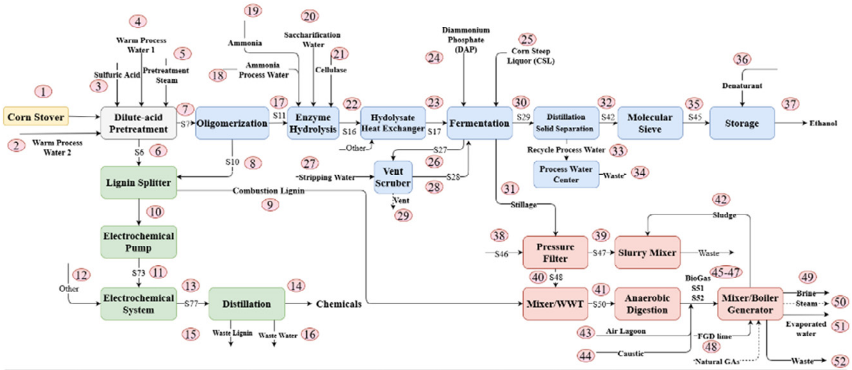


(a) Mass balance



(b) Energy balance

Fig. 4 (a) Mass balance and (b) Energy balance for converting corn stover to sugars followed by ethanol, and lignin conversion to chemicals.



Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
T(K)	298.15	368.15	294.15	368.15	541.15	403.15	403.15	373.3	373.15	393.85	393.85	298.15	380.02
P(bar)	1.013	4.762	5.471	4.762	13.172	2.689	2.689	1.013	1.013	1.013	1.215	1.013	1.013
m	2501.5	3685	46.22	561.95	962.6	858.1	6899.2	350.8	604.5	604.5	604.5	60.1	848.8
E*%	1	0	0	0	0	0.22	0.766	0	0.112	0.112	0.112	0	0.2
Stream	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**
T(K)	380.02	380.02	380.02	373.28	368.15	298.15	298.15	298.15	371.7	321.15	298.15	298.15	304.5
P(bar)	1.013	1.013	1.013	1.013	4.762	1.215	1.013	1.013	1.013	1.013	1.013	1.013	1.013
m	50.05	111.25	747.51	6548.34	2141.1	31.22	0	304.14	9024.8	9026.8	3.32	27.1	500.41
E*%	0.03	0.08	0.13	0.76	0	0.01	0	0.01	0.77	0.77	0	0	0.01
Stream	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**
T(K)	298.15	298.15	304.5	386.14	314.6	340.0	386.85	386.85	339.26	298.15	339.26	320.15	314.62
P(bar)	1.013	1.013	1.013	2.127	6.079	1.621	1.621	1.621	1.013	1.013	1.013	3.951	3.951
m	633.37	644.68	489.1	1026.3	8174.1	511.88	514.41	514.41	511.88	11.35	523.23	0.024	409.64
E*%	0	0	6.02	0.42	0.35	0.43	4.25	4.25	0.44	0	0.44	0	0.1
Stream	**40**	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**	**51**	**52**
T(K)	314.62	318.33	307.77	298.15	298.15	307.59	307.59	308.15	298.15	307.63	307.6	298.15	307.63
P(bar)	3.951	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
m	7764.5	8368.9	680.60	295.73	82.97	499.16	7188.9	680.84	8.94	237.92	499.16	731.1	6571.8
E*%	0.25	0.37	0.1	0	0	0.2	0.06	0.1	0	0.04	0.2	0	0

* Heating value as a percent of biomass input

Fig. 5 Process diagram and material stream table for the corn stover to ethanol and EC lignin chemicals biorefinery.

buting to the total operating costs. The operating cost breakdown highlights two primary components: fixed expenses and variable costs. Fixed expenses encompass depreciation at $0.58 per kilogram of chemicals, reflecting the gradual reduction in asset value over time, alongside Operations and Maintenance (O&M) costs at $0.71 per kg of chemicals, crucial for machinery

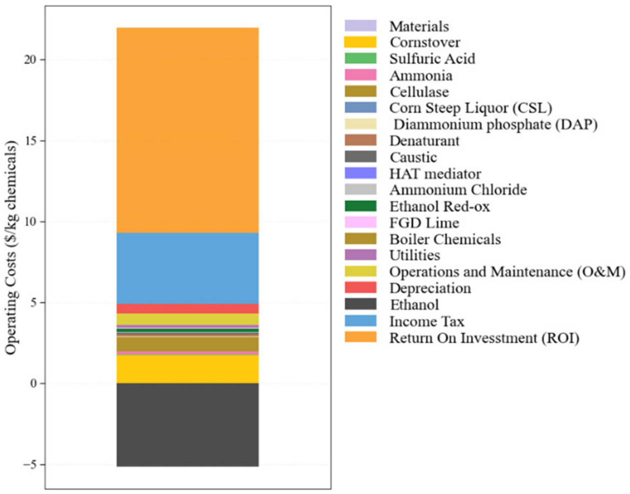


Fig. 6 Corn stover to ethanol and EC chemicals capital costs (MM$).

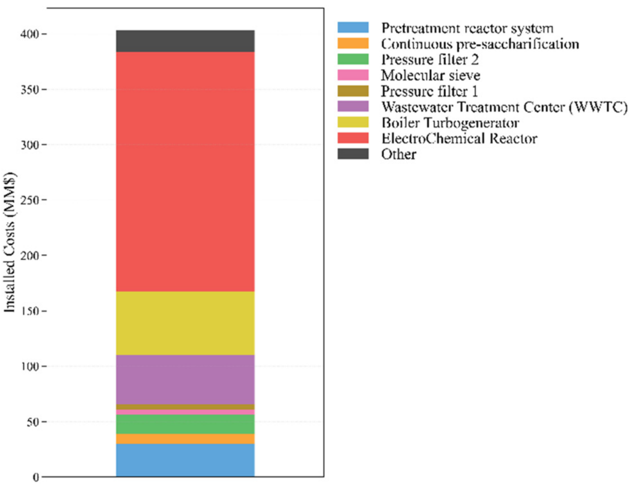


Fig. 7 Corn stover to ethanol and EC chemicals operational expenses ($ per kg of chemicals).

upkeep. In contrast, variable costs vary with production levels and comprise significant contributors such as cornstover at $1.73 per kg, cellulase at $0.86 per kg, and income tax at $4.37 per kg of chemicals. These expenses underscore the criticality of raw materials and essential chemicals, representing a substantial portion of the overall operating expenses. As previously mentioned, while market prices are not currently available for the HAT mediator, the assumption for its price is considered conservative, and it contributes less than $0.02 per kg of chemicals of the operation cost. Moreover, the revenue from the sale of ethanol is responsible for the negative value. Additionally, the ROI (Return on Investment) value of 12.71 shows that the project creates a positive return.

3.2.3. Profitability. The investigation aimed to ascertain the MSP of the EC lignin chemicals. We estimated a baseline bulk chemicals MSP of $16.86 per kg. This is competitive relative to the average vanillin market price of $25 per kg. However, the MSP does not account for potential downstream purification steps required by certain market applications. The MSP may underestimate the value of some lignin-derived chemicals.

For this study, we followed the common techno-economic analysis approach of valorizing chemical groups based on industrial prices.[25] In previous studies, we evaluated separation costs for lignin-derived chemical mixtures.[26] However, there is limited data available on the separation and recovery of the electrochemical products. Therefore, we decided to limit the scope to the chemical mixtures pending future experimental data that can validate their recovery. We believe this approach provides supporting evidence for continued research and development of this pathway.

A detailed separation analysis will be needed to improve our understanding of the value of individual chemicals derived from lignin EC conversion.

3.3. Sensitivity analysis

An assessment of sensitivity has been conducted on the TEA major parameters (Fig. 8a) that highlight crucial aspects impacting the MSP in a ±20% variation scenario. Understanding these is pivotal for strategic decision-making and cost optimization. Among these, operating days emerged as a significant influencer, directly impacting the MSP. Capital cost also demonstrated substantial sensitivity, signifying potential savings through efficient management of capital expenses or exploring cost-effective alternatives. Furthermore, lignin split fraction significantly affects the overall profitability, emphasizing the potential impact of enhancing lignin fractionation on the system's profitability. Variations in ethanol production underscored opportunities for enhancing chemical production efficiency. The feedstock price variable emphasized the importance of effective cost control. Other factors, like cellulase, ammonia, and labor cost, demonstrated lower sensitivities. Although they might not have a substantial impact on the MSP, it is vital to guarantee their sustainable and economical source throughout the production process.

Fig. 8(b) examines the impact of varying mediator performance metrics on the MSP within the framework of improving the process intensification. Each metric is evaluated to assess its influence on the MSP. Among the parameters examined, oxidation yield, conversion, and reduction yield emerged as significant influencers on MSP. A decrease of 20% from the base case in these metrics resulted in potential reductions in MSP, indicating the importance of optimizing mediator performance to enhance process efficiency and minimize costs. Conversely, optimistic scenarios, with a 20% increase from the base case, suggest potential improvements in MSP, emphasizing the potential cost-saving benefits of enhancing mediator performance. Other metrics, such as faradaic efficiency, HAT replacement, voltage, and mmol, demonstrated slight variations in sensitivity, indicating their secondary influence on MSP. These results underscore the importance of focusing on key performance metrics, particularly oxidation yield, conversion, and reduction yield, in the design of improved HAT

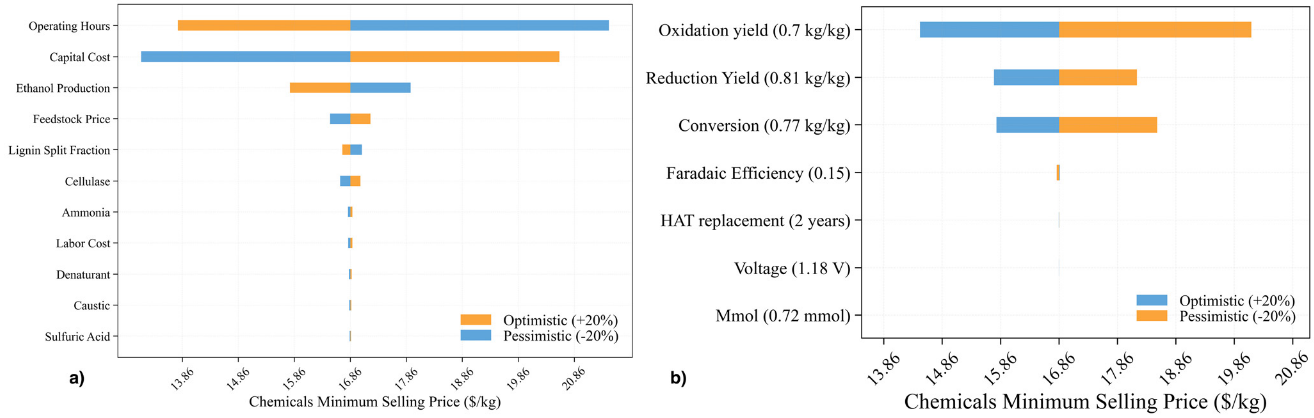


Fig. 8 Sensitivity analysis by applying ±20% (a) to the TEA's base case values for the significant parameters, (b) to the mediator performance metrics, including yield, conversion, reduction, faradaic efficiency, and potential.

mediators to achieve optimal cost-efficiency in chemical production processes.

3.4. LCA

The GWP of Corn Stover Ethanol with EC Lignin Chemicals was analyzed with four associated allocation methods: mass allocation, energy allocation, economic allocation, and displacement method. Fig. 9 shows the GWP ranges from 12.84 to 22.06 grams of CO_2eq per MJ of ethanol. The economic allocation yields the lowest GWP because of the high economic value of the chemicals. Using economic allocation leads to the GWP being reduced by around 46%, while this number changes to around 10% when employing energy allocation. The most widely used approach, the displacement method, results in a GWP of 21.5 grams of CO_2eq per MJ of ethanol. Corn stover and various chemicals contribute the most to the GWP. Electricity provides a small GWP credit relative to the chemicals. EC power has a negligible impact because it is mostly based on the by-product electricity from the facility. These numbers are comparable to the 25 grams of CO_2eq per MJ reported by Canter *et al.*[50]

These results suggest that lignin EC conversion to chemicals is a viable strategy to improve the profitability and environmental benefits of corn stover to ethanol biorefineries. However, there are a few limitations to consider. The background data employed in this study is based on laboratory experiments, and their scale-up may result in performance and composition differences. The separation and purification of individual chemicals could be challenging and require additional capital investment, result in material losses, and increase energy costs. The model chemical compounds require more detailed characterization and thermodynamic data to

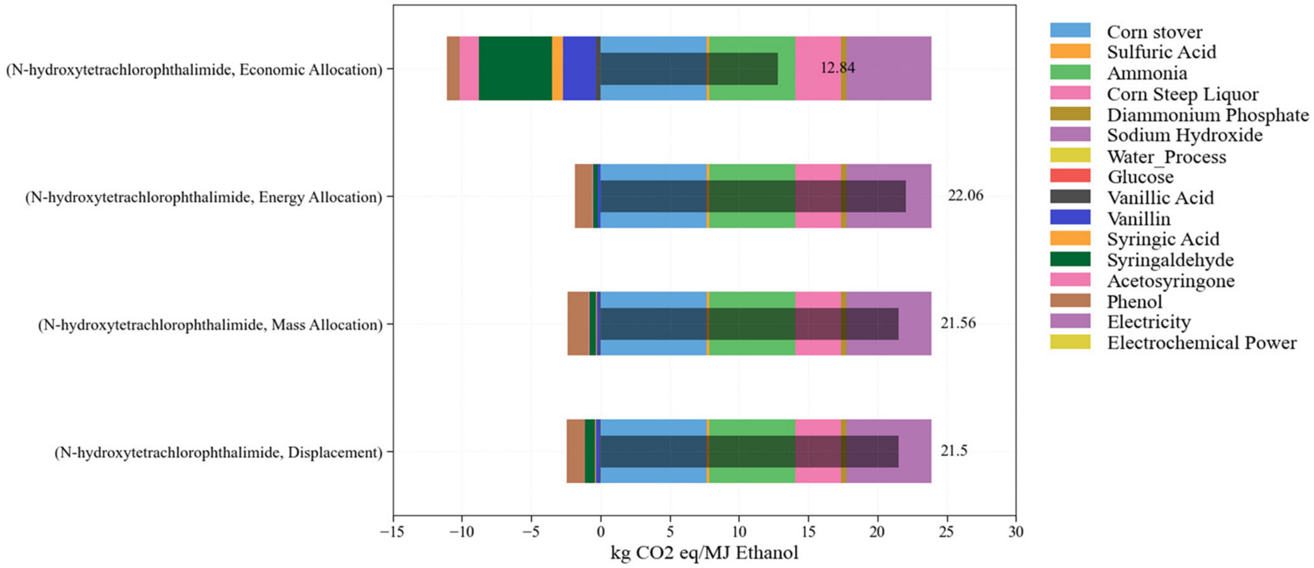


Fig. 9 LCA GHG emission comparison of allocation methods (economic, energy, mass, and displacement).

better represent the real chemicals identified in the experiments. Future work could evaluate these limitations as additional separation test data becomes available.

4. Conclusion

A comprehensive biorefinery process was investigated in this work, demonstrating the conversion of corn stover biomass into ethanol as the main product and other co-products utilizing HAT mediators for electrocatalytic oxidation, then depolymerizing oxidized lignin into monomers by chemo-catalytic reduction. This procedure includes several stages, such as biomass pretreatment, enzymatic hydrolysis, fermentation, distillation, EC approaches for lignin valorization, and effective waste management and heat recovery.

We found that approximately 49.56 metric tons per day (tpd) of chemicals could be produced by about a 2000 tonne per day (tpd) biorefinery. With ethanol production accounting for about 44.15% of input energy (1484.95 GJ h^{-1}), it is evident from the energy balance that this process consumes the most energy. In addition, the generation of chemicals using EC technology uses about 3.5% of the input energy. Financial analyses highlighted both operating and installed costs, indicating a positive return on investment and underlining the economic feasibility of the proposed model. Based on an operating cost analysis, the average chemical cost is estimated at $16.86 per kilogram.

Sensitivity analysis showed that increasing the lignin fraction going to EC conversion could further increase the profitability of the facility, but the biorefinery may need to find an alternative energy source, resulting in additional environmental impacts. Through systematic adjustments representing both pessimistic and optimistic scenarios, the analysis elucidates the potential cost implications associated with alterations in mediator performance. These results underscore the sensitivity of MSP to changes in mediator performance, highlighting the importance of optimizing mediator characteristics to achieve desired outcomes in yield, conversion, and efficiency while mitigating potential cost implications.

The LCA estimated the GWP to range from 12.84 to 22.06 grams of CO_2eq per MJ of ethanol, depending on the allocation method. Economic allocation yields the lowest GWP due to the high economic value of the chemicals. The displacement method, which is the most common method, yields a GWP of 21.5 grams of CO_2eq per MJ. All GWP values are lower than the estimate for a conventional corn stover to ethanol biorefinery.

These findings could significantly impact the economic viability of biorefineries by demonstrating the potential for higher-value product streams from lignin. Factors such as policy incentives for bio-based products, market demand for sustainable chemicals, and advancements in electrochemical technologies could influence the adoption of our proposed technology.

Further investigations are essential to elucidate how variations in product formulations influence the commercial prospects of this technology. This exploration seeks to optimize the technology's potential advantages, both in terms of sustainability and economic viability, potentially revolutionizing biorefinery practices. Assessing scalability, performance over extended periods, and compatibility with existing infrastructure will be pivotal for evaluating its feasibility for widespread adoption.

Author contributions

Ebrahimpourboura: investigation (TEA, LCA), writing – original draft. Mosalpuri: investigation (electrochemical TEA). Yang: investigation (experimental), writing – original draft. Ponukumati (experimental). Stephenson: conceptualization, supervision. Foston: conceptualization, supervision, writing – review & editing. Thimsen: funding acquisition, writing – review & editing. Mba Wright: conceptualization, supervision, writing – review & editing.

Data availability

Data for this study was conducted using publicly available code available at **https://github.com/BioSTEAMDevelopmentGroup/Bioindustrial-Park**.

Conflicts of interest

The authors have no conflicts of interest to declare.

Acknowledgements

The authors acknowledge the financial support of the National Science Foundation (ECO-CBET 2033714).

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