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Optimization of Separation Processes in Multiproduct Biorefinery Design to Produce Furan-Based Compounds and Their Derivatives Using Performance Indicators

Carlos Rodrigo Caceres-Barrera, Eduardo Sánchez-Ramírez, Maricruz Juárez-García, Heriberto Alcocer-García, and Juan Gabriel Segovia-Hernández*

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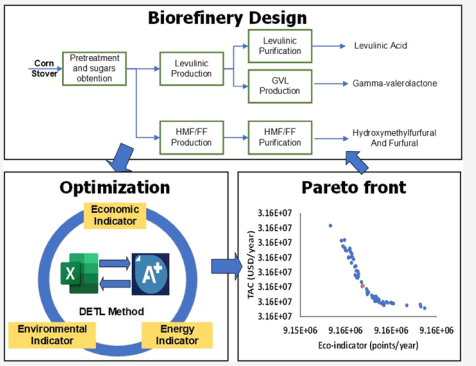
ABSTRACT: The current dependence on fossil fuels to produce fuels and chemicals leads to resource depletion and environmental pollution. A promising alternative is to convert lignocellulosic biomass into high-value products through biorefineries, as biofuel production remains unprofitable. This study designs and optimizes a multiproduct biorefinery using corn stover, with sections for pretreatment, levulinic acid and γ-valerolactone production, and furfural and hydroxymethylfurfural production. Product flows are determined by sugar sent to each section and its direct impact on process performance. Three preset scenarios and one open search for optimal design were explored, all optimized with sustainability indicators. Scenario four was the optimum, producing primarily hydroxymethylfurfural with a total annual cost of 2.73 × 10^7 USD/year, an environmental impact of 5.62 × 10^6 points/year, and an energy requirement of 1.26 × 10^9 MJ/year. In this work was obtained the design of a biorefinery for producing all target compounds with optimal cost-effectiveness, minimal environmental impact, and low energy consumption.



1. INTRODUCTION

The prevailing global economic system has driven a significant demand for raw materials and energy, which cannot be sustainably met by nonrenewable sources. For instance, 4% of oil is allocated to the production of plastics and chemicals, and additionally, global energy production primarily depends on fossil fuels.[1] This scenario presents challenges related to rising prices, uncertain availability, health concerns, and environmental degradation due to greenhouse gas emissions.[2] In fact, CO_2 emissions contribute to 60% of global warming effects, with global emissions reaching 37.1 GT in 2019.[3] Therefore, a transition to more sustainable practices is imperative.

To address these issues, we propose implementing strategies based on circular economy and waste valorization according to the principles of the UN's 2030 Agenda. One of these approaches involves the use of biomass, a renewable and low-cost raw material, to produce high-value-added products.[4] In fact, there is a great availability of this lignocellulosic materials (LCM), with 998 million tons produced globally each year, including 76 million tons in Mexico.[5] The traditional disposal methods for this waste, such as burning, release 8.68 billion tons of CO_2 worldwide annually, including 34.15 million tons in Mexico.[5] Then, it is possible to implement more sustainable processes using biorefineries, where LCM can be broken down into simple sugars and subsequently converted into chemicals, fuels, and energy.[2] Due to its capacity to transform biomass into chemicals, fuels, and energy through a multistage process, biorefineries are expected to eventually replace traditional oil refineries. According to the Organization for Economic Cooperation and Development (OECD), by 2030, 30% of all chemicals should be produced from biological materials.[6] These schemes significantly contribute to the achievement of some Sustainable Development Goals (SDGs) included in the UN's Agenda 2030 specifically Goal 7 (Affordable and Clean Energy) and Goal 12 (Responsible Consumption and Production)[7]

Despite the clear advantages of biorefineries, their economic feasibility remains a significant challenge. At the scale of this work, which is focused on plant design, one of the primary issues is the low concentration of desired products in the reactor effluents. This results in a process that is both highly energy-intensive and costly. Additionally, since many of these technologies are still in the development stage, the levels of efficiency and scalability required to make them competitive with conventional processes are yet to be achieved. Moreover, it is essential to critically evaluate whether biorefineries truly

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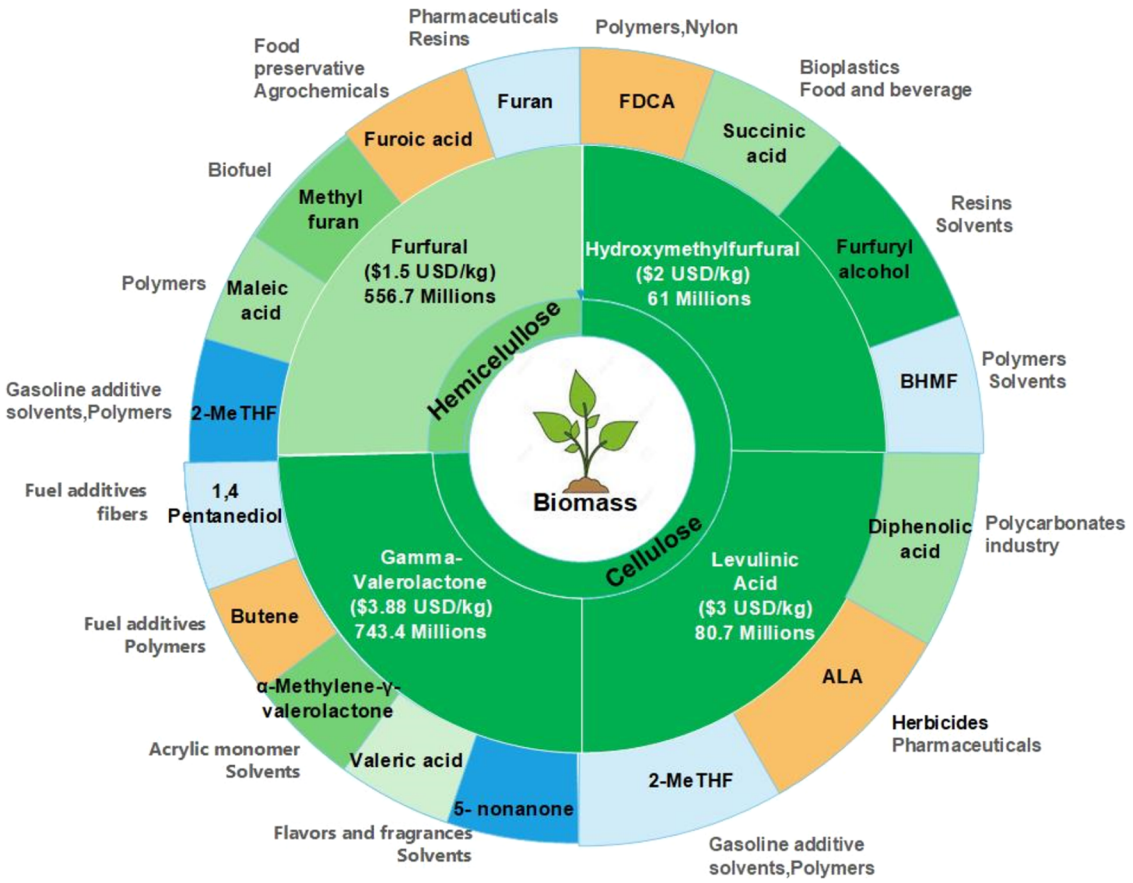

Figure 1. Global market, main derivatives, and applications of the product portfolio of this work.[10−14] Prices of compounds are also reported.[15−18] Abbreviations used: ALA, amino levulinic acid; 2-MeTHF, 2-methyltetrahydrofuran; FDCA: 2,5-furan dicarboxylic acid; BHMF, 2,5-bi(hydroxymethyl)furan.

offer a lower environmental impact compared with traditional processes. While they utilize renewable feedstocks, biorefineries can still impose substantial environmental burdens. These arise from the high energy and water demands of the processes as well as the potential ecological impacts associated with large-scale biomass utilization. Therefore, a comprehensive assessment of both economic and environmental aspects is crucial to fully understand the viability and sustainability of biorefineries.

The current trend for biorefineries is to seek the production of high-value-added chemicals, either independently or in conjunction with biofuels. Due to the production of biofuels like bioethanol and biodiesel being still unprofitable.[8,9] In fact, a wide set of chemical compounds can be produced from biomass. Then, two criteria were used to select the products: first, a literature review of bioproducts capable of replacing traditional compounds and serving as platform chemicals. Second, they were selected based on their global demand statistics. The selected compounds for this work are levulinic acid (LA), gammavalerolactone (GVL), hydroxymethylfurfural (HMF), and furfural (FF). The global markets for the selected compounds, the main derivatives, and their applications are shown in Figure 1.

Ensuring the sustainability of the biorefinery involves evaluating its performance using relevant indicators adjusted to specific objectives and contexts.[19,20] These indicators can include assessing environmental, social, exergetic, energetic, and technoeconomic performance. To address these different dimensions, a wide range of evaluation methods is available. Many recent studies have focused on analyzing the sustainability of biocompounds and bioenergy systems. For instance, Khounani et al.[21] reported about the LCA of furfural production from wood. They analyzed the impact of catalyst selection and identified that one of the primary contributors to life cycle assessment (LCA) is the use of electricity generated from fossil fuel resources. Pateromichelakis et al.[15] reported a biorefinery that produces LA, FF, GVL, and aromatics, they carried out the simulation, technoeconomic, and LCA studies without optimization. Santibañez-Aguilar et al. conducted the multiobjective optimization (MOO) of the supply chain for bioethanol and biodiesel production, considering economic, environmental, and social indicators. In the work of Huynh and Ierapetritou, stochastic programming was used to integrate biorefinery design with carbon pricing policies, evaluating economic and environmental metrics. In this study, the annualized total cost (TAC) serves as the economic indicator, while the eco-indicator 99 (EI-99) is used for environmental assessment; additionally, the total energy requirement for the process is considered. Then, finding the most sustainable plant design involves minimizing these indicators, which results in a challenging task due to the complexity of the mathematical model, which includes nonlinear and nonconvex kinetic and thermodynamic models. This complexity generates an optimization problem necessitating a suitable solution strategy, for which a stochastic approach was selected, namely, the Differential Evolution with Tabu List (DETL) method.[22]

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The literature review highlights several studies that address either commercial-scale design or integrated design and optimization of biorefineries for the four target compounds examined in this work. For HMF production, Chang et al.[23] developed a process for producing HMF from glucose, integrating enzymatic and catalytic reactions with a simulated-moving-bed (SMB) separation technique. This method aligns with the high-fructose corn syrup production process, enabling scalable HMF production while maximizing resource efficiency and potentially reducing costs. Kougioumtzis et al.[24] reported experimental data for a two-step reaction sequence to produce HMF from biomass, which was incorporated into an Aspen Plus process model for precise mass and energy balance simulations. This model provided key scale-up parameters for transitioning from laboratory to industrial-scale production. Wiranarongkorn et al.[25] conducted a technoeconomic analysis of an integrated biorefinery system for the coproduction of furfural (FF) and HMF, alongside energy generation from bagasse. They assessed economic feasibility by varying biomass allocation between biorefinery and energy production. Advanced heat integration minimized utility energy consumption and enhanced energy efficiency. Regarding GVL production studies, López-Aguado et al.[26] reported a liquid-phase process for producing GVL from LA using catalytic hydrogenation and conducted a technoeconomic analysis of the process, covering reaction and purification stages. Ashok et al.[17] presented a biorefinery for the simultaneous production of GVL, 2-methyltetrahydrofuran (2-MTHF), and HMF from lignocellulosic biomass, performing process simulation and technoeconomic analysis, including energy integration. Their results indicated the profitability of the biorefinery. Kapanji et al.[27] reported a lignocellulosic biomass biorefinery to produce LA, FF, GVL, and electricity simultaneously, performing process simulation and technoeconomic analysis with a favorable internal rate of return values.

In the literature on levulinic acid (LA) production, Alonso et al.[28] reported the conversion of cellulose and corn stover to LA, followed by its conversion to GVL using solid catalysts in both reactions. Alcocer-García et al.[29] conducted a multiobjective optimization (MOO) of LA production, considering economic and environmental objectives. Giuliano et al.[30] proposed a biorefinery for producing LA, along with succinic acid and ethanol, using a single-objective mathematical programming approach. Finally, regarding studies on furfural biorefineries, studies by Nhien et al.[31] combined heat integration and process intensification elements to reduce cost and environmental impact in recovering furfural from biomass. Almeida et al.[32] optimized experimental data for obtaining furfural from sugarcane bagasse and hemicellulose hydrolysate, followed by process simulation, achieving positive profitability results. Mazar et al.[33] reported a biorefinery producing furfural with lignin and acetic acid recovery, carrying out process scale-up and technoeconomic analysis. Moreover, Contreras-Zarazúa et al.[34] proposed the synthesis, design, and MOO of FF production from biomass.

As observed in the literature review, the reported works fall into one of the three categories. They utilized simplified methods for the design of equipment, produce a single product, or perform optimization with a single objective. To the best of our knowledge, no research has rigorously simulated and conducted Multiobjective Optimization (MOO) based on sustainability metrics for a multiproduct biorefinery producing a portfolio comprising LA, GVL, FF, and HMF.

In this work was carried out the design and optimization of a biorefinery for the simultaneous production of LA, GVL, FF, and HMF using corn stover as the raw material. The process was rigorously simulated using Aspen Plus. The design is formed by three main sections: pretreatment, production, and purification of LA and GVL, and production, and purification of FF and HMF. We explored four scenarios to evaluate the simultaneous production of all compounds. These scenarios differ in the way the production of a specific compound prevails. Every single scenario was optimized using a multiobjective approach considering as objective functions: TAC, EI-99, and energy consumption of the process and using the stochastic method DETL. The study explores whether it is possible to synthesize all the compounds at the same time and, if so, in what proportions. It also examines the most sustainable plant configuration for achieving this. This pioneering research in biorefinery design and optimization for simultaneous high-value product manufacturing marks a significant advancement toward sustainable practices.

2. PROCESS MODELING

In the development of a multiproduct biorefinery, rigorous process modeling is crucial to achieve an optimized design that balances economic, environmental, and energy considerations. This section presents the detailed modeling approach employed for the biorefinery, focusing on the conversion of Mexican lignocellulosic biomass into levulinic acid (LA), γ-valerolactone (GVL), hydroxymethylfurfural (HMF), and furfural (FF). Utilizing Aspen Plus V 8.8 simulation software, we integrated the NRTL-HOC thermodynamic model to accurately represent the physical properties and reactions within the system. The process model covers the complete biorefinery workflow, starting with biomass pretreatment and hydrolysis and up to the separation and purification of target compounds. The approach integrates the DETL optimization method to tackle the complex, nonlinear, and nonconvex characteristics of the process model, ensuring a comprehensive and robust analysis of the biorefinery's performance.

2.1. Raw Materials. Corn stover was selected as the raw material because it is an abundant residue in Mexico and does not compete with food production. It's availability is 48.2×10^9 kg/year, with an average composition (in % w/w) of 44.38% cellulose, 33.63% hemicellulose, and 22.37% lignin.[34] This variability can influence the availability of fermentable sugars and, in turn, may impact the economic and technical feasibility of the process. This assumption simplifies the analysis and is standard practice in early-stage studies such as this work. The design of the biorefinery is based on a feed rate of 15,000 kg/h, equivalent to 127,500 tons/year. The selection of this quantity represents 10% of the corn stover available in Guanajuato in 2019.[6]

2.2. Simulation. The simulation was carried out using Aspen Plus version 8.8. The components of biomass: cellulose, hemicellulose, and lignin were defined using thermodynamic properties reported previously.[35] It was considered that cellulose consists only of glucan and hemicellulose only composed by xylan, an approach successfully used in previous works.[36,37] It used the NRTL-HOC model, which accurately predicts the equilibrium of mixtures of polar compounds and vapor phase dimerization in mixtures containing carboxylic acids.[38]

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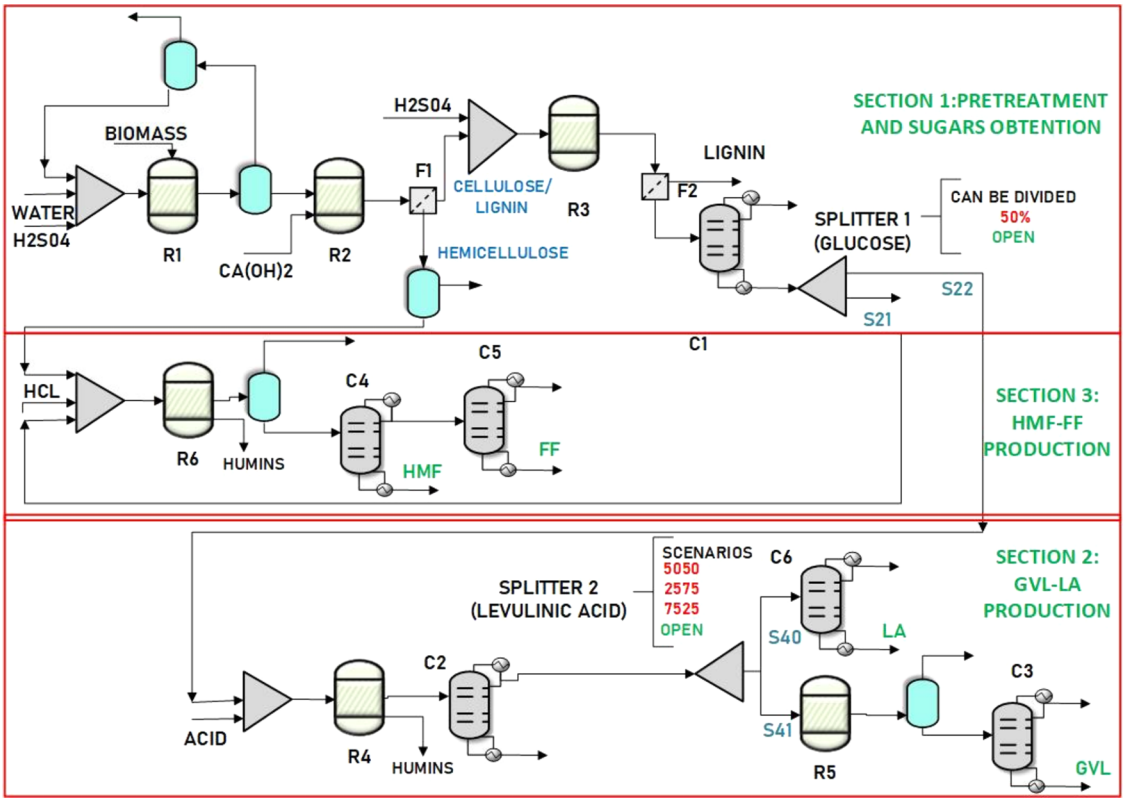

Figure 2. Diagram for the process and proposed scenarios identifying the three main sections.

The plant design was initially carried out using the shortcut methods for the distillation columns (DSTWU model from Aspen). Subsequently, with the values obtained from this stage, a rigorous model of the columns was developed using the RADFRAC model. Heuristic rules were applied for other variables such as the column diameter. All of the reactors are designed using the stoichiometric reactor model from Aspen. As a result, we based our reactor configuration on the best-reported yields and conditions available in the literature, which represent the optimal conditions from previous studies. These fixed yields were assumed to be reasonable approximations of the achievable outputs under ideal operating conditions. It is important to note that this study should be viewed as a preliminary analysis of the overall feasibility of the biorefinery. Once a simulation was obtained that met the desired purities and recovery rates, the designs were optimized.

2.3. Process Description. According to Conde-Mejía et al.[36] a biorefinery design consists of three main zones: pretreatment, where biomass polymers are degraded into simpler sugars; reaction zones, where the sugars are converted into various products; and separation zones, where products are purified to meet commercial standards. See Figure 2 as described below.

2.3.1. Section 1: Pretreatment Stage. The initial stage is the pretreatment, with the objective of breaking down the complex structure of LCM allowing obtain the corresponding monomers for subsequent processing. Among the different pretreatment methods, dilute acid pretreatment was chosen for its ability to achieve shorter residence times and high hemicellulose conversion rates.[39] Biomass is combined with a diluted solution of sulfuric acid; however, this implies corrosion and the need to neutralize the acid solution.

The pretreatment reactor, designated as R1, operates under the conditions specified by Contreras-Zarazúa et al.[34] These conditions include a water-to-biomass ratio of 7:3 and an acid-to-water ratio of 7.7 kg of sulfuric acid per 1000 kg of water. The reactor operated at a temperature of 158 °C and a pressure of 5.5 bar. Equations 1 and 2 represent the conversion of hemicellulose in xylose and cellulose in glucose with conversion values of 90 and 9.9% respectively. Equation 3 is the transformation of xylose to FF in which conversion is 9%. Equation 4 corresponds to the obtention of acetic acid from xylose, and eq 5 corresponds to the obtention of methanol from xylose both with a conversion of 8%. Finally, eq 6 represents the retention of soluble lignin with a yield of 5%.

$$C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5 \quad (1)$$

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6 \quad (2)$$

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + H_2O \quad (3)$$

$$2C_5H_{10}O_5 \rightarrow 5C_2H_4O_2 \quad (4)$$

$$C_5H_{10}O_5 \rightarrow 4.68CH_4O \quad (5)$$

$$C_{10}H_{13.9}O_{1.3} \rightarrow (C_{10}H_{13.9}O_{1.3})sol \quad (6)$$

Following pretreatment, it is essential to neutralize the reactor effluent with calcium hydroxide. This neutralization occurs in reactor R2, which operates at 25 °C and 1 atm, following the reaction outlined in eq 7.[34] Next, the liquid stream, mainly consisting of hemicellulose and approximately 10% xylose, must be separated from the solid phase containing cellulose and lignin through filtration.

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O \quad (7)$$

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Table 1. Summary of the Conditions Used for the Design of Reactors

reactor	temperature (°C)	pressure (bar)	eq	conversion	reference
R2	25	1	7	100	Contreras-Zarazúa et al.[34]
R3	200	15.86	8	100	Ashok et al.[17]
R4	200	15.86	9	75	Ashok et al.[17]
R5	200	1	10	99	Hengne et al.[44]
			11	100	Hengne et al.[44]
R6	160	15.16	12	50	Ashok et al.[17]
			13	80	

The cellulose−lignin mixture is fed along with sulfuric acid to the hydrolysis reactor R3, where cellulose's glycosidic bonds are broken, converting it into glucose.[40] Operating conditions are 200 °C and 15.86 bar and the conversion is 100% and were taken of Ashok et al.,[17] the only reaction is showed in eq 8.

$$(C_6H_{10}O_5)_n + H_2O \rightarrow C_6H_{12}O_6 \quad (8)$$

In the next step, both soluble and insoluble lignin are filtered from the R3 effluent and can be used for energy generation or even to produce aromatic compounds.[41] The C1 distillation column is designed to recover most of the sulfuric acid in the distillate stream, and glucose and xylose are obtained from the bottom stream. The glucose-rich bottom stream can be directed toward the production of LA and GVL or used for synthesizing HMF.

2.3.2. Section 2: LA and GVL Reaction and Purification Zone. As mentioned, a portion of the C1 column bottoms is directed to hydrolysis reactor R4 to generate LA and formic acid (FA). This process operates at 200 °C and 15.86 bar, using sulfuric acid as a catalyst, as reported by Ashok et al.[17] The reaction, shown in eq 9, converts 75% of the glucose into LA, FA, and water, while the remaining 25% is converted into humins. These dark-colored compounds are degradation products that appear after the hydrolysis of glucose.[42]

$$C_6H_{12}O_6 \rightarrow C_5H_8O_3 + CH_2O_2 + H_2O \quad (9)$$

The effluent from R4 enters column C2 which is used for sulfuric acid recovery as the bottom product while LA and FA acids are obtained in the distillate. The distillate stream of C2 can be divided into two parts: one portion is routed to distillation column C6 to obtain pure LA, while the other fraction is directed to reactor R5 to produce GVL. R5 is a hydrogenation reactor where FA decomposes into H_2 and CO_2, for this reason external hydrogen addition is unnecessary, while LA is converted to GVL.[43] Operating conditions for R5 are 200 °C and 1 bar and the reactions performed are represented by eqs 10 and 11.[17] Equation 10 represents the transformation of FA into H_2 and CO_2 with a yield of 99% and eq 11 is the hydrogenation of LA to obtain GVL and water with a yield of 100%. The purification of GVL, involves a flash separation at 80 °C and 1 bar to remove CO_2, followed by obtention of pure GVL as the bottom product in the distillation column C3.

$$CH_2O_2 \rightarrow H_2 + CO_2 \quad (10)$$

$$C_5H_8O_3 + H_2 \rightarrow C_5H_8O_2 + H_2O \quad (11)$$

2.3.3. Section 3: FF and HMF Reaction and Purification. The remaining portions of glucose and xylose arising from column C1 are directed to reactor R6, operating at 160 °C and 15.16 bar.[17] Hemicellulose is converted into FF and glucose is converted in HMF, both reactions of dehydration are catalyzed by hydrochloric acid.[15] The production of 5-hydroxymethylfurfural (HMF) from glucose is not a straightforward process due to the formation of several byproducts (as formic acid and levulinic acid, as well as insoluble humins and soluble polymeric species) that can significantly affect both the yield and the downstream recovery processes. In this work, we simplified the modeling of the reaction by focusing on the primary conversion of glucose to HMF and treating the formation of humins as the major byproduct. Specifically, we assumed in eq 12 a 50% yield for HMF and attributed the remaining 50% of the glucose to humins formation. Equation 13 represents the production of FF with a conversion of 80%, the remaining yield in both equations corresponds to the formation of humins The exclusion of these byproducts in our model was primarily to maintain simplicity in the initial feasibility analysis, where the goal was to optimize the core production process of HMF. The formation of humins, being an insoluble and nonvolatile species, was considered as a separate purge stream from the reactor.

$$C_6H_{12}O_6 \rightarrow C_6H_6O_3 + 3H_2O \quad (12)$$

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O \quad (13)$$

The effluent of reactor R6 is directed to a flash separator operating at 1 bar and adiabatic conditions to recover HCl. Purification of HMF and FF is accomplished as bottom products of columns C4 and C5, respectively, yielding high-purity products. The summary of data for design of reactors for the process is reported in Table 1.

2.4. Proposed Scenarios. To evaluate the simultaneous production of the four key compounds: LA, GVL, FF and HMF, multiple scenarios were devised. Initially, the bottoms stream of column C1, rich in glucose, was divided using splitter 1: one part was sent to the LA reactor R4 (stream S22), and the other to the HMF reactor R6 (stream 21). Subsequently, the distillate stream from column C2, predominantly containing LA, had two potential pathways using splitter 2: purification in column C6 (stream 40) or redirection to reactor R5 for GVL production (stream 41). To generate scenarios 1−3, splitter 1 was fixed at 50%, while the ratios for splitter 2 were set at proportions of 50/50, 25/75, and 75/25, as detailed in Table 2 and Figure 2. Scenario 4 was generated when the ranges of splitters 1 and 2 were left unrestricted, allowing the algorithm to identify the optimal scenario. Subsequently, designs were conceptualized and optimizations were executed for each scenario, systematically exploring diverse configurations to meet the objective functions. Figure 2 illustrates the plant schematic for the various scenarios.

From Table 2, we observe that scenario 1 (50/50) evenly directs the flows toward the production of both compounds: LA and GVL. In scenario 2 (25/75), GVL is preferably produced, while in scenario 3 (75/25), LA is preferentially

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Table 2. Different Scenarios According to Division of Streams

scenario	percentage of splitter 1 send to section 2	percentage sends to column C6 (splitter 2)	percentage sends to reactor R5 (splitter 2)
1 (50/50)	50	50	50
2 (25/75)	50	25	75
3 (75/25)	50	75	25
4 (optimized)	open	open	open

produced. Scenario four enables the optimization algorithm to search across the entire range of splitters to find the solution that minimizes all objective functions.

2.5. Key Performance Indicators. *2.5.1. Selection of Indicators.* Measuring sustainability requires evaluating processes from multiple perspectives, and a wide array of metrics is available for this purpose. In this paper, the selection of indicators aligns with the Sustainable Development Goals (SDGs) to create a comprehensive framework. Specifically, we use an economic metric (Total Annual Cost, TAC), energy assessment, and environmental Eco-indicator 99 (EI-99). These indicators serve as objective functions for the optimization problem, ensuring a holistic approach. TAC is essential within a sustainability framework, enabling organizations to understand the economic implications of their actions and contribute to SDGs such as Goal 1 (No Poverty), Goal 8 (Decent Work and Economic Growth), and Goal 10 (Reduced Inequalities). Energy consumption analysis supports Goal 7 (Affordable and Clean Energy) and Goal 12 (Responsible Consumption and Production), with the type of energy source also affecting Goal 13 (Climate Action) and Goal 11 (Sustainable Cities and Communities). EI-99, a life cycle assessment (LCA) tool, evaluates environmental impacts across categories like human health and ecosystem quality, directly contributing to Goals 12, 13, and 15 (Life on Land) by promoting sustainable practices and quantifying impacts like global warming potential.

While these selected methods provide a strong foundation, they are not the only available approaches for sustainability assessment. Recent works by Aghbashlo et al. proposed combining LCA with exergy analysis (exergoenvironmental analysis) for deeper insights into environmental impacts. This combined method, particularly useful for bioenergy and bioproduct systems, accounts for the environmental footprint of all process flows and components.[45,46] Regarding environmental metrics, EI-99 is not the only one; it exists, for example, the Social Cost of Carbon (SCC), which focuses on the economic valuation of CO_2 and its associated externalities. For example, Patrón and Ricardez included SCC to estimate the environmental impact in postcombustion CO_2 capture.[47] However, unlike SCC, EI-99 captures impacts related to not only carbon emissions but also other environmental issues, including toxic emissions, land use, and water pollution. Moreover, EI-99 evaluates effects on human health and ecosystems, while SCC generally assesses impacts from an economic perspective. There are also metrics similar to EI-99, such as ReCiPe, TRACI, and ILCD, which provide alternative approaches to environmental impact assessment.[48] Each of these methods offers unique perspectives on sustainability and could complement the analysis. Finally, while social indicators are essential for a comprehensive sustainability evaluation, they fall outside the scope of this work; however, they present an interesting avenue for future research.

2.5.2. Economic Indicator. The TAC corresponds to the annualized cost of all process equipment (capital cost) plus the cost of plant services (steam, cooling water, electricity).[49] Where the capital cost is calculated using the modular cost technique used for estimating the preliminary cost of new chemical plants. This approach was introduced by Guthrie et al.[50] The equations published by Turton et al.[49] were used for this purpose and TAC is calculated using the eq 14, where C_{TM} is the cost of the equipment, n is the payback period of investment (10 years) and C_{UT} is the external utilities cost.

$$\mathrm{TAC} = \frac{\sum_{i=1}^{n} C_{\mathrm{TM},i}}{n} + \sum_{j=1}^{n} C_{\mathrm{UT},j} \tag{14}$$

The energy requirements for the equipment are derived from the simulation in Aspen Plus. Unit costs of steam, cooling water, and electricity services, as reported by Turton are employed.[49] The plant operates for 8500 h/year.

2.5.3. Return of Investment (ROI). Additionally, an auxiliary calculus was used to measure the return on investment as a profitability indicator. This metric accounts for the varying market prices of the product portfolio. It is calculated by dividing the net benefit by the total investment in the process, following the methodology established by Jimenez-Gutierrez.[51]

2.5.4. Eco-Indicator 99. The Eco-indicator 99 (EI-99) tool assesses environmental impacts using LCA and focuses on three damage categories: human health, ecosystem quality, and natural resources and 10 impact categories.[52] The human health category considers climate change and respiratory issues. The ecosystem quality category evaluates effects on species diversity including ecotoxicity and eutrophication. The natural resources category accounts for future energy requirements for resource extraction and considers land use for agriculture and bulk materials.

In this work, the environmental impact was considered due to 4 factors as shown in Figure 3. First, the impact for use of biomass regarding mainly to land use, transportation, and other impacts. In this sense the previously reported value of 11.34 points/ton of corn stover was used. It's worth mentioning that all the scenarios use the same quantity of biomass. The impact of chemicals such as acids and bases, can be ignored due to their small quantities, which do not significantly affect the EI-99 value. Also, for the equipments used in the process, the

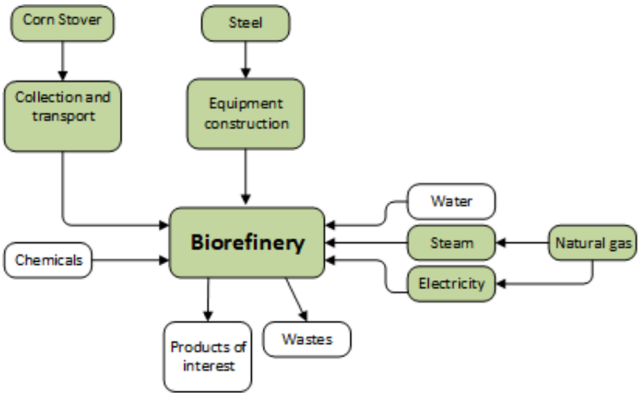

Figure 3. Process tree of environmental assessment of a biorefinery. White boxes are not included in the assessment.

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impact of three factors were considered: the steel used for the equipment, the electricity required for pumping water for cooling, and the generation of steam for heating.[53] EI-99 is calculated using eq 15, where subindices b correspond to the liberation of chemical substances and d correspond to the damage category. Then β_b is the amount of chemical b released to the environment per united of reference, $\alpha_{b,k}$ is the damage in category k per unit of chemical b, δ_d is a weighting factor for damage in category d, and ω_d is a factor for normalization.[29] In Table S1, the values for each impact category are shown, they were taken from Goedkoop et al.[52] The result is expressed in eco-points, with one point representing 1000th of the annual environmental burden of an average European citizen.

$$\mathrm{EI99} = \sum_{b} \sum_{d} \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \tag{15}$$

2.5.5. Total Energy Consumption. In this study, the overall process energy requirements were included as an additional objective function. Reducing energy consumption contributes to a more sustainable process for two key reasons. First, it results in economic savings and enhances profitability. Second, heating energy is typically sourced from boiler steam, which is generated from fossil fuels, contributing to atmospheric pollutant emissions. Consequently, decreasing energy consumption reduces the environmental impact by mitigating greenhouse gas emissions. The total energy is calculated by summing the cooling and heating requirements for the entire process on an annual basis. These data are obtained from the simulation results in Aspen Plus, assuming a yearly operation of 8500 h.

3. OPTIMIZATION PROCEDURE

This section provides an overview of the optimization method selected and the optimization objectives employed, and delineates the MOO problem addressed.

3.1. DETL Method. MOO problems aim to identify a set of variables that satisfy given constraints while optimizing multiple objective functions, achieving a balanced trade-off among them.[54] The equations within the biorefinery model exhibit substantial nonlinearity and high nonconvexity, according to Ponce-Ortega et al.[55] these models render deterministic approaches impractical. Therefore, stochastic methods are preferred, and among the various options, evolutionary algorithms are particularly notable. Specifically, the DETL method was selected.[22]

DETL is a stochastic search technique designed for solving complex nonlinear and nonconvex problems. It combines traditional differential evolution with tabu search to improve efficiency by avoiding repeated search points.[56] The method operates by evolving a set of solutions (population) through mutation and crossover steps, selecting the best individuals to proceed to the next generation.[57] Different studies have shown DETL's effectiveness in solving multiobjective optimization (MOO) problems. For instance, Sánchez-Ramírez et al.[56] show its application in the design of the biobutanol purification process. Additionally, Contreras-Zarazúa et al.[53] and Alcocer-García et al.[29] utilized DETL to optimize FF and LA purification processes, respectively. This supports the selection of the method.

3.2. Interaction between Software. The implementation of DETL involves an interaction between Microsoft Excel and Aspen Plus using the Component Object Model (COM) technology. The decision variable vector is transmitted from Excel to Aspen Plus, where the process variables are evaluated. Postsimulation, the resulting vector is sent back to Excel, where the objective function is evaluated, and new decision variable values are generated.

3.3. DETL Parameters. The parameters used were an initial generation of 120 individuals, 400 generations, a tabu list of 60 individuals, a tabu radius of 0.0001, and values of 0.9 for the crossover factor and 0.3 for the mutation factor. Instead the tuning of these parameters can highly influence the performance, and no tuning was considered. The parameters used in this work were taken from previous works where successful results were obtained.[38,56]

3.4. Decision Variables. The decision variables are in all scenarios the design variables for the distillation columns (C1−C6) of the biorefinery and additionally in scenario four the ranges of the splitters. These variables are defined within an operating range and are shown in Table 3.[55] The values of mass flows for connection between the equipment were determined using the mass balance of the process.

Table 3. Decision Variables for Optimization

variable name	range of variable	variable type
range splitter 1, %	5−95	continuous
range splitter 2, %	5−95	continuous
number of stages, C1 to C6	20−100	discrete
feed stage, C1 to C6	3−99	discrete
column diameter, C1 to C6, m	0.5−1.7	continuous
molar reflux ratio C1	0.02−0.5	continuous
molar reflux ratio C2	1.2−2.2	continuous
molar reflux ratio C3	0.02−0.12	continuous
molar reflux ratio C4	0.1−0.5	continuous
mass reflux ratio C5	10−15	continuous
molar reflux ratio C6	0.01−0.3	continuous
distillate flow C1, kmol/h	130−144	continuous
distillate flow C2, kmol/h	33−41	continuous
distillate flow C3, kmol/h	8−10	continuous
distillate flow C4, kmol/h	85−105	continuous
distillate flow C5, kg/h	1400−1700	continuous
distillate flow C6 kmol/h	10−14	continuous

3.5. Objective Functions and Constraints. The objective functions center on economic and environmental metrics, notably the TAC, EI-99, and total energy requirements for the process. These metrics ensure the attainment of a sustainable design for the biorefinery. For the different scenarios the minimization of the multiobjective function was performed as shown in eq 16.

$$\mathrm{Min}(\mathrm{TAC}, \mathrm{EI99}, \mathrm{Energy}) = f(N, \mathrm{Nf}, \mathrm{RR}, D, d) \tag{16}$$

Subject to $y_i P_c \geq x_i P_c$, $w_i F_c \geq u_i F_c$

This means that the optimization problem is constrained by ensuring that the purities ($y_i P_c$) are at least as high as $x_i P_c$ and that the recovery flows of the products ($w_i F_c$) are greater than or equal to $u_i F_c$. From eq 16, N is the number of stages for the distillation columns, Nf is the feed stage, RR is the reflux ratio, D is the distillate flow rate, and d is the column diameter. The total number of decision variables was 30 for scenarios 1−3 and 32 for scenario 4. The minimum purity targets were set at 98% (wt %) for 5-hydroxymethylfurfural, 98.5% for GVL, and 99% for FF and LA. These purities ensure the subsequent commercialization.

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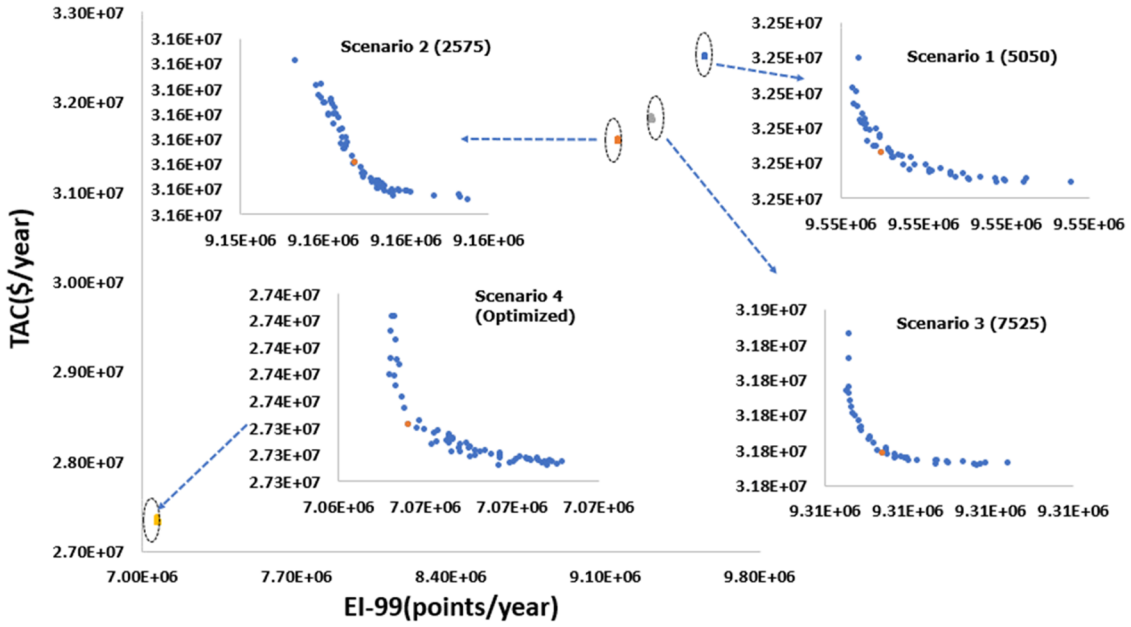

Figure 4. Pareto front between objective functions: TAC and EI-99.

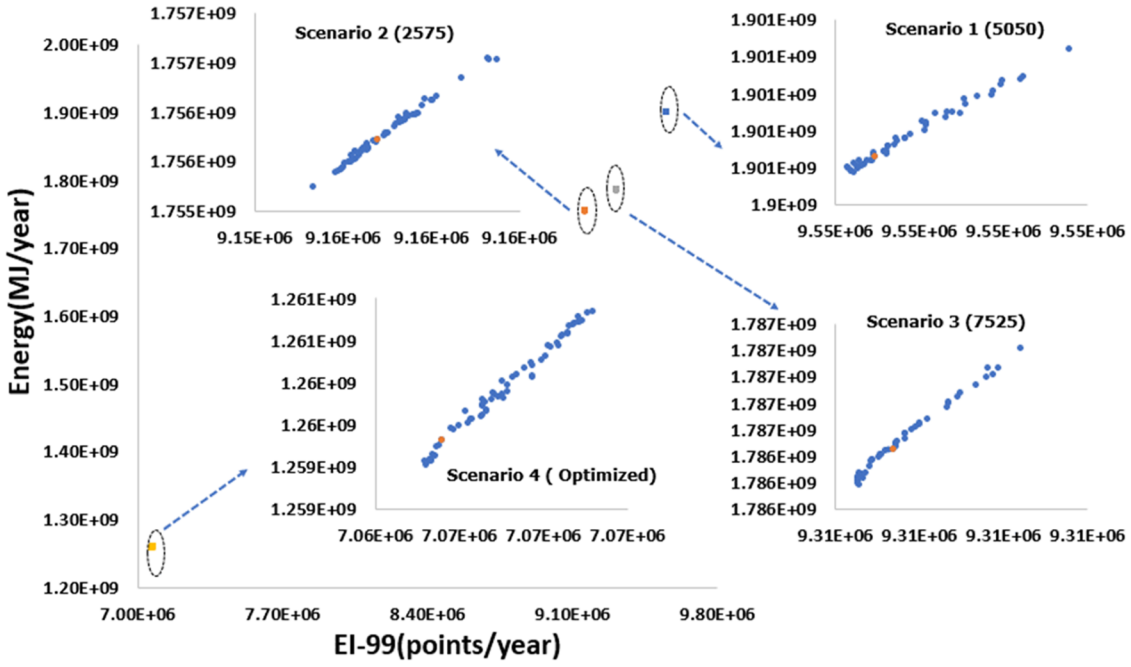

Figure 5. Pareto front between objective functions: Energy and EI-99.

4. RESULTS AND DISCUSSION

This section presents the results of the multiobjective optimization process. All of the obtained designs meet the required product compositions and recovery rates. The design variables and objective functions calculated for the biorefinery design prior to optimization are shown in Tables S2 and S3. Notably, the optimized designs demonstrate significant improvements over this baseline configuration. To facilitate visualization, Pareto fronts are used to illustrate the relationships between pairs of objective functions. The utopia point methodology, an ideal solution strategically positioned at the extremity of the Pareto front, was employed to identify the optimal solution, where improving one objective implies deteriorating the other.[58] Figures 4, 5, and S1 depict the behavior of the objective functions postoptimization. All Pareto fronts were derived after 48,000 iterations, as the vector of decision variables no longer yielded significant improvements beyond this point, indicating that the DETL algorithm had reached convergence. Consequently, the results presented here correspond to the best solution obtained.

Figure 4 illustrates the Pareto fronts of TAC vs EI-99 for each scenario (see Table 2). To enhance visualization, the Pareto diagrams for each scenario are zoomed in. The clear rivalry between these two objective functions is evident. For example, the case with the lowest eco-indicator value corresponds to the highest TAC value, and vice versa, therefore the most economical process is the one that pollutes the most, while achieving the lowest environmental impact

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Table 4. Decision Variable Values for the Optimal Case of Each Scenario

	parameter	scenario 1 (50/50)	scenario 2 (25/75)	scenario 3 (75/25)	scenario 4 (optimized)
	range splitter 1, %	50	50	50	33
	range splitter 2, %	50	25	75	51
column 1	number of stages	34	30	42	31
	feed stage	21	9	29	9
	reflux ratio	0.029	0.044	0.031	0.043
	distillate rate (kmol/h)	135.83	136.39	134.99	136.38
	column diameter (m)	1.06	1.29	1.055	1.23
column 2	number of stages	56	50	48	55
	feed stage	35	38	18	16
	reflux ratio	1.40	1.26	1.43	0.314
	distillate rate (kmol/h)	38.44	37.84	39.3	25
	column diameter (m)	0.91	0.61	0.89	0.74
column 3	number of stages	50	41	52	39
	feed stage	22	27	29	22
	reflux ratio	0.09	0.10	0.08	0.04
	distillate rate (kmol/h)	9.89	14.76	5.00	7.30
	column diameter (m)	0.73	0.79	0.88	0.99
column 4	number of stages	47	42	43	42
	feed stage	23	27	24	16
	reflux ratio	0.10	0.09	0.20	0.014
	distillate rate (kmol/h)	95.27	94.94	95.65	102.33
	column diameter (m)	0.77	1.16	0.61	0.94
column 5	number of stages	67	59	63	64
	feed stage	42	34	47	48
	mass reflux ratio	10.00	10.18	10.76	2.49
	distillate rate (kg/h)	1458.88*	1555.64*	1462.15*	1712.32
	column diameter (m)	0.74	0.72	0.98	1.44
column 6	number of stages	56	63	73	73
	feed stage	35	35	24	13
	reflux ratio	0.15	0.12	0.098	0.14
	distillate rate (kmol/h)	12.88	6.49	19.55	8.48
	column diameter (m)	0.54	0.68	0.61	0.53

necessitates an increase in the TAC. This competitive relationship between these variables was reported by Alcocer-García et al.[29] where was implemented the MOO of the purification zone for LA. However, Romero-García et al.[58] report a direct relationship between TAC and EI-99 for MOO of reaction of FF, indicating that the behavior is specific to the process studied.

From Figure 4, it can be observed that scenario 4, that is a scenario that optimizes the range for splitters 1 and 2, exhibits the lowest costs with values ranging from 2.733×10^7 to 2.738×10^7 dollars/year. The results show that in splitter 1, 33% of the glucose flow is directed toward LA and GVL production, while the remaining 67% is sent to HMF production, and in splitter 2, the flow is divided almost evenly, with about 50% directed toward LA and GVL production. Additionally, it is evident that Scenario 1 (50/50) presents the highest values for the total annual cost objective function, ranging from 3.250×10^7 to 3.252×10^7 dollars/year, which represent an increment of 19% regarding to scenario 4. Scenarios 3 and 2 represent increments of TAC of 16.4 and 15.6%, respectively, regarding scenario 4. In terms of EI-99, the minimum environmental impact is observed in scenario 4, with values ranging from 7.066×10^6 to 7.076×10^6 points/year. Scenarios 2, 3, and 1 display increases of 29.5, 31.7, and 35.16%, respectively, compared scenario 4. These results can be explained by the fact that scenario 4 has a minimum steam requirement for heating. Has been reported reboiler duty of columns have the largest impacts in both objective functions (TAC and EI-99).[59] In scenario 4, most of the glucose flow is directed toward HMF production, rather than LA and GVL. HMF is the product with the lowest boiling point among these three. Therefore, their production requires less energy.

Figure 5 shows the direct relation between energy consumption and EI-99, graphically it can be seen that the higher the energy consumption, the EI-99 also increases and vice versa. This is explained by analyzing the impact categories used in the eco-indicator to assess the environmental impact of the distillation columns; the eco-indicator calculation comprises three components: the steel used for equipment construction, the electricity used in the process, and the amount of steam used, this last component has the greatest impact on the final EI-99 value.[29] This is consistent with results obtained from LCA of other processes, where fossil fuels were the category with the greatest environmental impact.[29,58] Several researchers have noted that reducing the high-energy consumption in the purification area is one of the current targets for increasing the efficiency of biorefineries.[60]

From Figure 5 it can be observed that scenario 4 has the lowest energy requirements with values between 1.259×10^9 to 1.260×10^9 MJ/year, while the requirements for scenario 2 represent a 39.42% increase compared to scenario 4 and in the case of scenarios 3 and 1 representing an increment of 41.84 and 50,85% compared to scenario 4. From the results obtained,

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Table 5. Production of the compounds of interest and values for objective functions for optimal designs

parameter	scenario 1 (50/50)	scenario 2 (25/75)	scenario 3 (75/25)	scenario 4 (open)
LA production (kg/h)	723.44	344.59	1124.34	470.9
GVL production (kg/h)	612.57	895.75	312.17	295.86
HMF production (kg/h)	1507.63	1490.05	1533.72	1852.45
FF production (kg/h)	1467.43	1364.20	1461.63	1352
TAC (dollars/year)	3.250×10^7	3.157×10^7	3.180×10^7	2.73×10^7
EI-99 (points/year)	9.551×10^6	9.156×10^6	9.309×10^6	7.066×10^6
energy (MJ/year)	1.901×10^9	1.756×10^9	1.786×10^9	1.26×10^9
ROI (%)	5.81	5.45	6.04	3.88

it is observed that scenarios where most of the glucose flow to produce LA and GVL are the most energy demanding.

Additionally, Figure S1 shows the Pareto between TAC and energy to showcase the nontrivial relationship between these objectives. The lifetime energy costs are indeed considered in the total annualized cost (TAC), which is part of the economic indicator. However, energy consumption should still be treated as a separate optimization objective because, while energy costs contribute to the TAC, they do not fully capture the broader design trade-offs associated with energy consumption.

Regarding Table 4, it is important to highlight that splitter fractions indeed exhibit a more pronounced effect on the process performance compared to other variables. Splitters play a fundamental role in determining the mass and energy distribution across different units in the biorefinery. In summary, while the initial approach fixed the splitter fractions to arbitrary values to maintain feasibility and control in the early stages, the subsequent optimization allowed these fractions to vary freely, and the results clearly demonstrate the critical influence of splitter settings on the overall process performance. Table 4 presents the design parameters for the optimal configurations selected in the four scenarios. A detailed examination of these findings reveals several distinct observations. One important observation is that reflux ratios in the columns tend to be conservative, typically below one, except for column C2. This approach reduces internal flows and energy demand but necessitates a greater number of stages. Scenarios 1 and 3 demonstrate the highest Total Annual Cost (TAC) primarily due to their increased number of stages; however, there is relatively minor variation in the total stages and column diameters across scenarios. These findings suggest that the plant is flexible and efficient in producing all compounds and capable of adjustments to meet diverse requirements while maintaining operational efficiency. The variability in distillate rates reflects differences in the input and output flows specific to each scenario.

Moreover, the variable with the most significant impact on TAC and the ecological indicator is the reboiler duty, these have been reported previously by other authors.[29] Specifically, Scenario 1, which involves the production of a high quantity of LA (the compound with the highest boiling point), entails a high reboiler duty, leading to a high TAC. It is important to note that while all xylose is converted to FF, glucose can be converted into HMF, LA, or GVL, each requiring different amounts of energy for their respective purification processes. The results indicate that Scenario 4, which produces the highest quantity of HMF (boiling point: 114 °C), has the lowest energy requirements among the scenarios. In contrast, the purification of LA in column C6 (boiling point: 246 °C) requires the most energy, and similarly, the purification of GVL (boiling point: 208 °C) also demands a significant amount of energy. These findings underscore the critical role of energy requirements in the overall cost and environmental impact of the process, highlighting the need for strategic planning in the design and operation of the columns.

While analyzing the different scenarios, it was observed that the varying flows of levulinic acid (LA) and formic acid significantly impacted the separation process in column C6. Figure S3, along with a detailed analysis, illustrates the composition profiles for C6, where LA is purified These profiles offer key insights into how variations in feed composition and operating conditions influence the internal distribution within the column and its ability to achieve the desired purities. For more details, refer to the Supporting Information.

The variations in the design parameters presented in Table 4 can be explained from a phenomenological perspective. The adjustments in the split fractions lead to significant changes in the flow rates throughout various sections of the biorefinery. When the split fractions are modified, the corresponding flow rates for the distillate and bottoms must also be recalibrated to maintain mass balance within the system. In addition to flow rate adjustments, the reflux ratio must also be recalibrated to ensure that the desired purities are achieved at both the top and bottom of the distillation column. Furthermore, the diameters of the columns are adjusted in response to these changes in flow rates and reflux ratios. This adaptation is essential to facilitate efficient operation under newly established conditions. A properly sized column diameter ensures adequate vapor−liquid contact and promotes effective mass transfer, which is vital for achieving the desired separation efficiencies. It is important to note that changes in the reflux ratio have a direct impact on the number of theoretical stages within the distillation column. The theoretical stages are indicative of the column's ability to achieve the required separation. Therefore, when the split ratio is altered, it necessitates a comprehensive modification of multiple interconnected variables, including flow rates, reflux ratios, and column diameters. This holistic approach ensures that the system operates efficiently and consistently meets the targeted purity levels for all products.

Table 5 illustrates objective function values for optimal designs across various scenarios, marked by red points in Figures 4 and 5. Based on this and the previous results, it was found that the optimal solution within scenario 4 (open search for splitters) showcases superior values across all objective functions. This scenario prioritizes the highest quantity of HMF across all of the scenarios. This result emphasizes Scenario 4 as the most sustainable design. Indeed, according to the results obtained, the cost of services accounts for 63% of the total annual cost of the plant. Additionally, Table 5 presents the calculations of the Return on Investment (ROI)

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for the optimal designs, using the methodology reported by Jimenez-Gutierrez.[51] The selling prices for the products are the same as those shown in Figure 1. As shown in Table 5, all of the optimal scenarios have positive ROI values, indicating economic feasibility. It is worth noting that although Scenario 4 shows the best performance across multiple objectives, it has the lowest ROI. The highest ROI is obtained for Scenario 3, which, however, ranks as the second worst in terms of the objective function values

5. CONCLUSIONS AND RECOMMENDATIONS

This study presents the design and multiobjective optimization of a multiproduct biorefinery for the simultaneous production of levulinic acid (LA), furfural (FF), 5-hydroxymethylfurfural (HMF), and γ-valerolactone (GVL) from corn stover-derived sugars. All of these products are key platform chemicals with broad applications across various sectors. These products can serve as sustainable alternatives to petroleum-derived chemicals, potentially accelerating the shift toward a greener chemical industry. The research explored four scenarios, each differing in the splitting of streams toward the preferential production of specific compounds to identify the most sustainable configuration. Scenario 4, which prioritized maximizing the production of HMF, emerged as the optimal design, achieving a minimal total annual cost (TAC), environmental impact (Eco-99), and energy consumption. The optimal values obtained are 2.73×10^7 USD/year for TAC, 7.066×10^6 points/year for Eco-99, and an energy requirement of 1.26×10^9 MJ/year.

The novelty of this work lies in its comprehensive approach to optimizing a biorefinery for the simultaneous production of multiple high-value products rather than focusing on a single one. This multiobjective optimization approach ensures a balanced consideration of economic viability, environmental impact, and energy efficiency, addressing the complexities and trade-offs inherent in biorefinery operations. The implementation of the DETL method was crucial to face the nonlinear and nonconvex nature of the optimization problem, ensuring robust and reliable results. Future work could explore hybrid deterministic-stochastic approaches, as reported by Liñán et al.[61] In this work, the coupling of a deterministic method with the stochastic DETL was obtained. Significant improvements in computational efficiency, speed, and convergence rates were observed. This suggests that a hybrid approach could enhance the overall performance of the optimization process, making it a valuable consideration for future research directions. However, this hybrid approach introduces more complexity and higher computational costs. On the other hand, to further improve the metrics of this work, it is useful to apply techniques of process intensification (PI), including the thermal coupling of columns or evaluating the feasibility of replacing two units (reaction and separation) into a single piece of equipment, as has been widely studied.

One of the most significant insights into this work is the inherent flexibility of the biorefinery to adjust the production ratio of each compound in response to market demand. This adaptability allows the facility to optimize its profitability by dynamically shifting the production focus between different chemical products. The findings of this work highlight the importance of balancing operational efficiency with market-driven economic strategies. For real-world applications, this means that biorefineries must be designed not only with technical optimization in mind but also with economic flexibility.

The current work has some limitations that were previously mentioned regarding the use of yield data for the reactors, the assumption of a fixed composition of biomass, and the simulation of humins. Future studies incorporating kinetic data, a more dynamic feedstock composition analysis, and detailed modeling of byproducts like humins will be essential to advancing from conceptual design to a more robust and scalable biorefinery process.

This study represents a pioneering effort in the field of biorefinery optimization, marking significant advancement toward sustainable industrial practices. By demonstrating the feasibility and benefits of a multiproduct biorefinery, this research opens the door for the development of more efficient and environmentally friendly alternatives to traditional oil-based production methods. The findings highlight the potential of biorefineries to contribute to a circular economy and support global sustainability goals, emphasizing the importance of continued innovation and optimization in this field.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.4c02646.

Pareto front between objective functions: TAC and Energy. Mass balance for the optimal design of scenario 4. Composition profiles for column C6.Unit indicators used to measure the EI-99. Variable designs for unoptimized design of the biorefinery. Objective functions for unoptimized design of the biorefinery. (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Juan Gabriel Segovia-Hernández − *Department of Chemical Engineering, Universidad de Guanajuato, Guanajuato 36050, Mexico;* orcid.org/0000-0003-4175-9809; Email: gsegovia@ugto.mx

Authors

Carlos Rodrigo Caceres-Barrera − *Department of Chemical Engineering, Universidad de Guanajuato, Guanajuato 36050, Mexico;* orcid.org/0009-0006-4772-6732

Eduardo Sánchez-Ramírez − *Department of Chemical Engineering, Universidad de Guanajuato, Guanajuato 36050, Mexico;* orcid.org/0000-0002-4326-4837

Maricruz Juárez-García − *Department of Chemical Engineering, Universidad de Guanajuato, Guanajuato 36050, Mexico*

Heriberto Alcocer-García − *Department of Civil and Environmental Engineering, Universidad de Guanajuato, Guanajuato 36000, Mexico*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.4c02646

Notes

The authors declare no competing financial interest.

■ GLOSSARY

DETL:differential evolution with Tabu list

EI-99:eco-indicator 99
FF:furfural
GVL:γ-valerolactone
HMF:hydroxymethylfurfural
LA:levulinic acid
LCM:lignocellulosic materials
MOO:multiobjective optimization
SDG:sustainable development goals
TAC:total annual cost

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