Chemical Engineering Research and Design 223 (2025) 253–262

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

An integrated approach to optimize and intensify furfural–HMF purification in biorefinery processes

Carlos Rodrigo Caceres-Barrera [a], Eduardo Sánchez-Ramírez [a], Maricruz Juárez-García [a], Heriberto Alcocer-García [b], César Ramírez-Márquez [c], Juan Gabriel Segovia-Hernández [a,*]

[a] Department of Chemical Engineering, Universidad de Guanajuato, Campus Guanajuato, Guanajuato 36050, Mexico
[b] Department of Civil and Environmental Engineering, Universidad de Guanajuato, Campus Guanajuato, Guanajuato 36000, Mexico
[c] Chemical Engineering Department, Universidad Michoacana de San Nicolas de Hidalgo, Avenida Francisco J. Múgica, SN, Building V1, Ciudad Universitaria, Morelia, Michoacán 58060, Mexico

ARTICLE INFO

Keywords:
Energy reduction
Thermally coupled distillation columns
Biorefineries
Process intensification
Multi-objective optimization

ABSTRACT

Achieving sustainable production in biorefineries is essential to reduce dependence on fossil resources and to mitigate environmental impacts. Energy inefficiency in the purification stages of a biorefinery is one of the main challenges impeding the sustainability of these processes and their widespread use due to economic and environmental costs. This study aims to improve the sustainability indicators of a corn-stover biorefinery through a process intensification and an optimization approach. The proposed case study focuses on the purification section of hydroxymethylfurfural and furfural in a biorefinery whose main goal is to mitigate the energy consumption in the distillation process through the design and optimization of four intensified distillation options. These options include an indirect thermally coupled sequence, a side stripper, a fully thermally coupled Petlyuk column, and a single column with a lateral product stream. Each configuration is assessed with the objective to minimize the Total Annual Cost, Eco-Indicator 99, and energy consumption. Process modeling is conducted using Aspen Plus while the optimization is performed using Differential Evolution with Tabu List. Results demonstrate that optimal thermally coupled configurations achieve reductions of 13.2 % in Total Annual Cost, 19.1 % in Eco-Indicator 99, and 27.9 % in energy consumption compared to other conventional designs, while the side-stripper configuration yields savings of up to 8.9 %, 13.8 %, and 14.7 %, respectively. This work represents a significant advancement in promoting sustainable biorefinery operations.

1. Introduction

Energy consumption from fossil fuels is one of the main drivers of today's environmental challenges, accounting for about two-thirds of global greenhouse gas (GHG) emissions. Despite ongoing efforts to decarbonize, fossil fuels still represent over 80 % of the global energy supply. This dependence not only accelerates climate change but also underscores the urgency of improving energy efficiency. Achieving the Paris Agreement's 1.5 °C target requires rapid reductions in fossil fuel use combined with a substantial increase in efficiency across all sectors (World Economic Forum, 2025). The International Energy Agency highlights efficiency as the "first fuel" of the clean energy transition, estimating that doubling efficiency gains to 4 % annually by 2030 is essential to remain on track for net-zero (IEA, 2025).

The industrial sector is one of the world's largest energy consumers accounting for roughly one-third of global energy consumption, with the chemical industry alone responsible for nearly 30 % of industrial energy use (Saygin et al., 2011). Distillation is particularly significant, representing one of the most energy-intensive separation processes worldwide (Halvorsen and Skogestad, 2011). Energy costs are also economically burdensome, typically contributing 30–50 % of operating costs in petroleum refineries and similar heavy industries (Kiss et al., 2019). Thus, reducing energy consumption yields dual benefits: lower GHG emissions and improved profitability (Morrow et al., 2015; Zhang, 2019). In light of these drivers, improving energy efficiency in industrial processes has become a key priority under both sustainability and cost-reduction mandates. Many industrial processes are now being redesigned or retrofitted to use less energy. This includes measures like better heat integration (recovering and reusing waste heat), upgrading to more efficient equipment, electrifying processes where feasible, and

* Corresponding author.
E-mail address: gsegovia@ugto.mx (J.G. Segovia-Hernández).

https://doi.org/10.1016/j.cherd.2025.10.002
Received 12 August 2025; Received in revised form 29 September 2025; Accepted 3 October 2025
Available online 4 October 2025

adopting innovative process technologies(Thiel and Stark, 2021; Wei et al., 2019)

Biorefineries, which convert biomass into fuels and chemicals, are positioned as a sustainable alternative to fossil-based industries (De Jong et al., 2009; Cardona Alzate et al., 2020). In principle, using biomass resources can mitigate environmental impacts by reducing net carbon emissions (since biomass absorbs CO_2 during growth) and decreasing reliance on depleting fossil reserves. To truly fulfill their sustainability potential, biorefineries must be efficient in all the stages, integrating the three pillars of sustainability (environmental, economic, and social considerations) into biorefinery design and operation(De Jong et al., 2009; Martin, 2021). However, biorefineries face challenges due to the dilute and complex nature of biomass-derived streams, which makes product separation highly energy intensive (Huang and Ramaswamy, 2013; Martín and Grossmann, 2013). In fact, purification stages in biorefineries can account for 50–80 % of production costs, largely because of distillation and related separations (Worrell and Galitsky, 2005; Kiss et al., 2016). This disproportionate share of costs and emissions threatens the overall sustainability of biorefineries, making energy efficiency in downstream operations a central challenge (Cardona Alzate et al., 2020).

To address these issues and unlock the full economic and environmental potential of biorefineries, it is necessary to adopt innovative design philosophies that go beyond conventional approaches. In this context, Process Intensification (PI) emerges as a key enabler, offering tools and strategies to reconfigure traditional operations and achieve substantial reductions in energy consumption, costs, and environmental impacts (Kong et al., 2022; Segovia-Hernández and Bonilla-Petriciolet, 2016). Among the various PI approaches, Thermally Coupled Distillation Sequences (TCDS) stand out for their ability to integrate heat transfer between columns, thus reducing the unnecessary heating and cooling requirements (Hernández and Jiménez, 1999; Long and Lee, 2014). Fully thermally coupled Petlyuk columns (PA) and their Dividing Wall Column (DWC) counterparts can achieve up to 30 % energy savings (Segovia-Hernández and Bonilla-Petriciolet, 2016). Despite these benefits, implementation barriers remain, such as limited scale-up knowledge, process safety concerns, and complex controllability due to stronger variable interactions (Kim et al., 2017; Nikačević et al., 2012)

Numerous studies have validated the advantages of TCDS in petrochemical and natural gas processes. For example, (Zin et al., 2021) reported 39.2 % energy savings in a natural gas fractionation train using a PA, while (Kong et al., 2024) achieved up to 23.3 % TAC reduction in FCC processes by optimizing side-rectifier and side-stripper configurations. (Li et al., 2023) developed a systematic methodology for TCDS design, demonstrating 21 % operating cost savings in natural gas separations. Similarly, (Sánchez-Ramírez et al., 2022) integrated TCDS in a multi-objective optimization (MOO) framework for methyl-ethyl ketone purification. In the context of biorefinery processes, (Alcocer-García et al., 2024, 2019) have reported the use of intensified distillation designs that include TCDS for levulinic acid, incorporating a MOO. In these works, the use of DWC configuration presented economic savings mainly due to the reduced energy consumption. In the work of (Sánchez-Ramírez et al., 2017a, 2017b) was explored the use of DWC to purify biobutanol integrating a MOO obtaining significant savings in the TAC.

Regarding furan-based compounds, several studies have examined the design and, in some cases, the optimization of TCDS to achieve substantial energy savings. For instance, (Nhien et al., 2019, 2016) investigated intensified purification sections to produce furfuryl alcohol, and FF, respectively. These works primarily implement DWC and perform the optimization considering the TAC. As a result, they achieved important total cost savings. Additionally, Contreras-Zarazúa et al. (2021) explored the design and optimization of different intensified alternatives, including thermal coupling and divided-wall columns (DWC) for furfural purification, with an emphasis on reducing the inherent risk of the process. Some studies have confined their scope to process design without considering optimization. For instance, Kougioumtzis et al. (2018) proposed a process design for obtaining HMF from biomass, whereas Bangalore Ashok et al. (2022) reported the design of a process for the simultaneous production of γ-valerolactone, methyltetrahydrofuran, and HMF. In addition, previous work has shown that the conventional distillation configuration for FF and HMF contributes to approximately 32 % of the total energy consumption of the entire biorefinery process (Caceres-Barrera et al., 2024). This highlights the importance of implementing more energy-efficient separation strategies, such as TCDS, which could significantly improve the sustainability of these systems. Table 1 summarizes the mentioned studies. To the best of the authors' knowledge, an intensified distillation sequence that has been simultaneously designed and optimized for the recovery of both FF and HMF has not yet been reported in the literature.

Therefore, the objective and novelty of this work lies in the integration of PI into the design and a MOO of alternative separation sequences for the purification zone of HMF and FF within a multiproduct biorefinery. To achieve this, various TCDS, employed as PI strategies, are proposed and evaluated as alternatives to the conventional configuration previously reported (Caceres-Barrera et al., 2024). These alternatives include an indirect thermally coupled sequence, a side-stripper sequence, a PA, and a single column with a lateral product stream. Rigorous Aspen Plus simulations combined with optimization using the Differential Evolution with Tabu List (DETL) algorithm are used for this purpose. The optimization simultaneously considers energy consumption, TAC, and environmental impact (measured using Eco-Indicator 99), assessing which alternatives significantly reduce energy consumption and improve sustainability metrics. This study also examines trade-offs among objectives functions considered and the influence of key design variables of the purification columns. The results confirm the advantages of implementing PI and MOO strategies to improve the sustainability of the purification zone in biorefineries.

The rest of the paper is organized as follows: Section 2 presents the design of TCDS. Section 3 discusses the sustainability indicators and Section 4 details the formulation of the optimization problem. Later, the results of optimization of the different alternatives are discussed. The concluding remarks of the work are presented at the end.

2. Design of purification alternatives

This section presents the design of TCDS as intensified alternatives to improve the overall sustainability of the process (see Fig. 1). In the biorefinery process, biomass undergoes pretreatment to release the sugars glucose and xylose from the cellulose and hemicellulose fractions, respectively. Subsequently, in the dehydration reactor, HCl acts as a catalyst, converting glucose into HMF and xylose into furfural (FF), with

Table 1
Studies reporting process design, optimization, or integrated design–optimization strategies for the purification of furan-based compounds.

Reference	Description of the Process	Energy consumption (MJ/kg)	Comments
(Contreras-Zarazúa et al., 2019)	Purification of furfural from a aqueous solution	11.41	Design and optimization
(Nhien et al., 2016)	Purification of furfural from a aqueous solution	11.53	Design and optimization
(Nhien et al., 2019)	Production of furfuryl alcohol from furfural aqueous	92.65	Design of the process
(Kougioumtzis et al., 2018)	Production of HMF of biomass	125.00	Design of the process
(Bangalore Ashok et al., 2022)	Production of HMF and FF from biomass	22.40	Design of the process

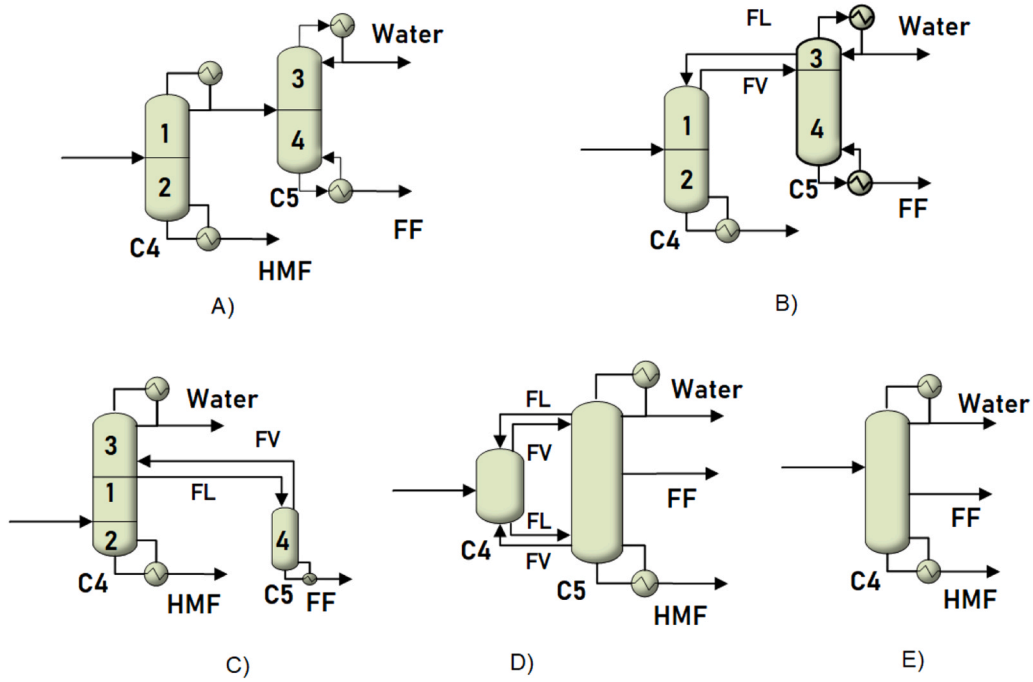

Fig. 1. Evaluated Alternatives to the CS for the Purification of FF and HMF. A) Base case, CS, B) the IS, C) the SS, D) the PA and E) LP. The sections in alternatives A, B and C are shown for add clarity.

humins formed as a byproduct in both reactions. Because humins are insoluble, they are purged from the reactor outlet. The remaining stream is sent to a flash unit to remove HCl, generating the mixture that must be purified. This stream is a ternary mixture composed of 74.10 mol% water, 14.45 mol% FF, 11.06 mol% HMF and traces of acetic acid, methanol and HCl. This corresponds to 32.28 wt% water, 33.57 wt% FF, and 33.73 wt% HMF and the traces. This composition represents the optimal scenario previously reported by Caceres-Barrera et al. (2024). In this case, the indirect sequence was chosen as the most suitable base case because it allows the elimination of HMF in the first column (C4) as the bottom product. Given that HMF is mutagenic, carcinogenic, and toxic (Islam et al., 2014), its early removal aligns with a widely recognized heuristic in process design: toxic or hazardous compounds should be separated first to minimize their circulation through the system. In the second column (C5), furfural is obtained as the bottom product and water as the top product, ensuring that the design remains both practical and consistent with industrial safety and sustainability criteria. For this mixture, there exists an azeotrope between water and furfural (90.6 mol % water,9.4 mol% furfural). However, the feed composition lies above the azeotropic composition of furfural. Product purities above 98 wt% are required for both FF and hydroxymethylfurfural. All alternatives were simulated in Aspen Plus using the RADFRAC rigorous distillation model. In this study, phase equilibria were modeled with the NRTL method augmented by the Hayden–O'Connell correction (NRTL–HOC). This choice is motivated by: (i) the pronounced non-ideality of aqueous–aldehyde mixtures, in which hydrogen bonding and strong dipolar interactions must be captured accurately, and (ii) the well-known heterogeneous azeotropy of the water–furfural pair, which requires a framework capable of describing liquid–liquid (LLE) and vapor–liquid (VLE) equilibria in a unified manner. The HOC contribution was included to account for association phenomena in the vapor phase (e.g., dimerization and solvation). Extensive VLE/LLE data exist for water–furfural, including a heterogeneous, minimum-boiling azeotrope at ~35.5 wt% furfural and ~98 °C at 1 atm, and NRTL–HOC reproduces this behavior accurately. For systems involving HMF, experimental data are scarce; nonetheless, the selected model satisfactorily predicts the behavior of the ternary mixtures examined here, as illustrated in Figures S3–S4 of the Supporting Information.

The thermally Coupled Distillation Sequences (TCDS) considered in this work are described below. In general terms, thermal coupling consists of eliminating a condenser or a reboiler and replacing it with material streams that provide the required heat transfer. The first configuration, the Thermally Coupled Indirect Sequence (IS), is shown in Fig. 1B. Energy savings are achieved by removing the condenser of column C4. In this arrangement, the vapor stream from the top of C4 is directed to C5, while the liquid flow required in C4 is supplied from the second column. The second alternative, the Side-Stripper Arrangement (SS) (Fig. 1C), is obtained by rearranging the four sections of the previous configuration. In this configuration, the second column consists only of the stripping section, so no condenser is required, which results in energy savings. A third option is the Fully Thermally Coupled Arrangement (PA), also known as the Petlyuk column (Fig. 1D). In this configuration, the most volatile compound is not completely separated in the first column as in previous cases. Instead, the intermediate component is distributed within top and bottom streams of the first column to ensure a good match between the composition of the interconnecting streams and the stage compositions in the second column. This design improves efficiency and achieves further energy savings. Finally, the conventional two-column sequence can be replaced by a single column with a lateral product stream (LP), as depicted in Fig. 1E. This is not actually a thermally coupling, however, only one reboiler and one condenser are employed to separate the ternary mixture. Depending on the feed composition, this configuration may offer higher energy efficiency than the base case.

3. Sustainability assessment

To ensure the sustainability of the biorefinery, it is essential to employ indicators that assess process performance. Indeed, numerous sustainability indicators have been reported. Additionally, these indicators are used as objective functions to optimize. The Sustainable Development Goals (SDGs) are the cornerstone of the United Nations' 2030 Agenda, a global framework that outlines a pathway to sustainability, providing specific and measurable objectives(Wackernagel et al., 2017). This study selected several indicators closely aligned with the SDGs. Specifically, an economic indicator (TAC), an environmental indicator (EI-99), and total process energy consumption were chosen. Their relationship with specific SDGs is detailed in Table 2.

4. Optimization procedure

This section outlines the chosen optimization method, describes the optimization objectives used, and defines the MOO problem being addressed.

4.1. DETL method

Since this work involves a MOO problem, solutions that achieve a balanced trade-off among the different objective functions are needed. To identify the optimal balance between these functions, and due to the high nonlinearity and nonconvexity of the equations involved, the stochastic global method, DETL, developed by (Srinivas and Rangaiah, 2007a)was chosen. In the DETL, the conventional differential evolution method is based on a population-based search method that mimics natural evolution (Storn and Price, 1997). This method is combined with the Tabu search which is a random search method that has the characteristic of remembering the search sites previously visited as well as improving its computational efficiency (Glover et al., 1995). The DETL method utilizes initialization mutation, crossover, and selection(Ahmad et al., 2022; Romero-García et al., 2020) with their main advantage being a faster convergence to the neighborhood global optimum compared to other stochastic methods(Contreras-Zarazúa et al., 2019).

Implementation of the DETL method implies interacting with Microsoft Excel. The proposed decision variables are sent to Aspen Plus which evaluates them and returns the simulation results (the energy and mass balance of the process) back to Excel. In Excel, these results are used to calculate the values for objective functions. The new values for decision variables are then generated according to the DETL method. This iterative process ceases from fulfilling the total number of individuals set. The optimization parameters employed in this study: an initial population of 120 individuals, 400 generations, a tabu list of 60 individuals, a tabu radius of 0.0001, a crossover factor of 0.9, and a mutation factor of 0.3, were adopted from previous works where their tuning had already been validated. In particular, (Srinivas and Rangaiah, 2007b) reported near optimal tunning parameters when testing the DETL method on a range of benchmark functions, including so-called "difficult" cases characterized by hundreds or thousands of local minima, where the likelihood of being trapped in suboptimal solutions is high.Moreover, these same parameters have been successfully applied in multi-objective optimization (MOO) studies of highly nonlinear and nonconvex biorefinery systems (e.g., (Alcocer-García et al., 2019; Contreras-Zarazúa et al., 2019; Quiroz-Ramírez et al., 2018a). Their repeated use across similar problem domains provides confidence that the chosen settings are robust and well-suited to address the nonlinearity and nonconvexity of the present system. For this reason, a dedicated sensitivity analysis of the optimization parameters was not performed here.

Table 2
Sustainability indicators selected and their relationship with SDGs 8.

Type of indicator	Name of indicator	Related to SDGs
Economic	Total annualized cost	Goal 1 (No Poverty) Goal 8 (Decent Work and Economic Growth) Goal 10 (Reduced Inequalities).
Environmental	Eco-indicator 99	Goal 7 (Affordable and Clean Energy) Goal 12 (Responsible Consumption and Production), Goal 13 (Climate Action) and Goal 11 (Sustainable Cities and Communities)
Energetic	Total energy consumption	Goal 12 (Responsible Consumption and Production), Goal 13 (Climate Action) and Goal 15 (Life on Land)

4.2. Objective functions

4.2.1. TAC

The process's economic evaluation was carried out using the TAC. This includes the capital cost (C_{TM}), representing the investment in process equipment, and the utility costs (C_{UT}), encompassing cooling, heating, and electricity. It is used as a payback period for ten-year-old equipment based on recent studies(Ma et al., 2023; Severino et al., 2021), assuming a 10 % annual depreciation rate. The TAC is calculated using Eq. 1.

The capital cost is calculated using the method introduced by (Guthrie, 1969), with the equations reported by (Turton et al., 2008). The required utilities are derived from the energy balance and calculated using the costs reported by Turton.

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

4.2.2. Eco-indicator 99 (EI-99)

It is an environmental index used to quantify either the environmental load of a process or a product, and it is based on a life cycle analysis (LCA) (Quiroz-Ramírez et al., 2018a). The EI-99 considers three major areas of environmental damage, known as damage categories: human health, ecosystem quality, and resource depletion corresponding to 11 impact categories. Compared to Global Warming Potential (GWP), which only considers climate change impacts, or ecotoxicity indicators, which focus solely on toxic effects in ecosystems, the EI-99 index offers a more holistic perspective. Indeed, ecotoxicity and climate change are two of the impact categories in the EI-99. In this study, the LCA includes the same system boundaries defined by (Caceres-Barrera et al., 2024), which include the impacts associated with four factors: biomass use, steel consumption for equipment construction, and both the use of steam and electricity in the employment of natural gas. For the calculation of biomass-related environmental impacts, we adopted the factors reported by (Contreras-Zarazúa et al., 2021)Specifically, for corn stover, a value of 11.34 points/ton was used, which accounts for the environmental burdens associated with harvesting and collection. It is important to note that transportation impacts of these materials were not included in this factor. A similar approach has been employed in other studies, e.g., (Quiroz-Ramírez et al., 2018a) and (Santibañez-Aguilar et al., 2014).

Eq. 2 represents the general equation to calculate the EI-99, where $\boldsymbol{w}$ is a weighting damage factor, $\boldsymbol{c_i}$ is the value of impact for category $\boldsymbol{i}$, and "***as***," "***asl***," "***ael***," and "***ab***" represent the quantities of steam, steel, electricity, and biomass used in the process, respectively. This approach has been successfully applied to previous works (Contreras-Zarazúa et al., 2019; Quiroz-Ramírez et al., 2018b). The values to weigh factors and impact categories were taken from those reported by (Goedkoop and Spriensma, 2001)and are shown in Table 1 of the supporting information. The functional unit is expressed in eco-points, where one point represents one-thousandth of the average environmental burden of a European citizen.

$$EI99 = \sum_i \omega c_i as + \sum_i \omega c_i asl + \sum_i \omega c_i ael + \sum_i \omega c_i ab \tag{2}$$

4.2.3. Energy consumption

Although the energy consumption process is partially included in the TAC calculation. Energy consumption is considered as a separate objective function to explicitly address trade-offs that the TAC alone may not adequately capture. While the TAC includes the economic implications of energy consumption, it does not directly quantify energy efficiency or account for the environmental impacts associated with energy use. In the work of (Caceres-Barrera et al., 2024), the same objective functions were used, and they revealed that there is a nonlinear relationship between the TAC and energy consumption. Thus, treating energy consumption as a distinct objective function enables a more comprehensive optimization framework. The total annual energy requirement (MJ/year) was calculated by summing the heating duties (reboilers) and cooling duties (condensers) of all distillation columns, as reported directly by Aspen Plus. An operating time of 8500 h/year was assumed. No additional electrical energy demands (e.g., pumps or auxiliary equipment) were included in this calculation.

4.3. Optimization problem

The different scenarios were evaluated considering the minimization of the multi-objective function shown in Eq. (3).

$$\mathrm{Min}(\mathrm{TAC}, \mathrm{EI99}, \mathrm{Energy}) = \mathrm{f}(\mathrm{N},\ \mathrm{Nf},\ \mathrm{RR},\ \mathrm{D},\ \mathrm{d}, \mathrm{Fi}, \mathrm{Fs}) \quad (3)$$

Subject to: $y_iP_c \geq x_iP_c,\ w_iF_c \geq u_iF_c$

The optimization problem is then constrained by ensuring that the purities (y_iP_c) are at least as high as x_iP_c and that the recovery flows of the products (w_iF_c) are greater than or equal to u_iF_c. From Eq. 3, 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, additionally Fi and Fs are the values for the flow and location of interconnection streams. The minimum purity targets for 5- HMF and FF were set at 98 % (wt%), aligning with the typical purity levels for conventional FF processes (Kougioumtzis et al., 2018; Wiranarongkorn et al., 2021). This level of purity is sufficient for the subsequent applications of these products.

4.4. Decision variables

The decision variables for each alternative represent the degrees of freedom for the specific arrangement; for example, the Petlyuk configuration has the greatest number of decision variables, including additional constraints regarding the location of the flows. The decision variables for each alternative and their ranges are presented in Table 3. Before the optimization process, a sensitivity analysis was carried out to determine appropriate ranges for the decision variables. The initial ranges were systematically tested in Aspen to identify values that caused convergence failures or yielded physically unrealistic outcomes. These limits were then refined and aligned with recommendations from the literature on industrial-scale equipment ((Douglas, 1988; Gorák and Olujic, 2014; Turton et al., 2008). The final ranges adopted therefore ensure both computational feasibility and engineering relevance, encompassing realistic operating conditions while allowing exploration of the decision space for optimization. Since many combinations of decision variables can lead to non-converged simulations, the Aspen pathway was utilized to identify and exclude these cases from the results. The PA convergence, for example, is particularly sensitive to the range of interconnection flows.

5. Results

This section presents the key optimization results for the designs obtained after thermally coupling columns C4 and C5 to purify HMF and FF respectively. All designs meet the specified purity requirements, achieving a minimum of 98 % w/w for HMF and FF. The water stream obtained contains only small amounts of furfural (below 1.7 %) together with traces of acetic acid, methanol, and HCl. Given its composition, this stream can be recycled to the process, for instance, by diluting the HCl stream prior to the dehydration reactor, thereby reducing freshwater consumption and enhancing process sustainability. The results are summarized in Figs. 2 and 3, where pairs of objective functions are represented using Pareto fronts to facilitate visualization. It is important to highlight that the objective function values reflect the overall process performance. All Pareto fronts were generated after 48,000 iterations, at which point the decision variable vector exhibited no further significant improvements, confirming the convergence of the DETL algorithm. This ensures that the results presented correspond to the optimal solutions obtained through the optimization process. The supporting information includes the evolution of Pareto front through generations. All optimizations were carried out on a computer with AMD Ryzen 5–1600 @3.2 GHz, and 16 GB of RAM. Each optimization required a computational time of around 350 h.

Fig. 2 shows the trade-off between TAC and the EI-99 index, where processes with lower economic costs exhibit higher environmental burdens. This behavior arises from the operating conditions of distillation columns: higher reflux ratios reduce column size and capital cost,

Table 3
Range of decision variables for each alternative. Where CS (conventional sequence, base case), IS (indirect thermally coupled sequence), SS (side-stripper), PA (Petlyuk column), LP (lateral stream product).

Scheme / **Variable**	**CS**	**IS**	**SS**	**PA**	**LP**
Number of stages, C4	15–100	15–100	15–100	15–100	15–100
Feed stage, C4	3–99	3–99	3–99	3–99	3–99
Diameter, C4,m	0.5–1.7	0.5–1.7	0.5–1.7	0.5–1.7	0.5–1.7
Flow rate,C4, kmolh^{-1}	Bottoms 11–11.9	Bottoms 11–11.9	Bottoms 11–11.9	NA	Bottoms 11–11.9
Reflux ratio, C4, kmolkmol^{-1}	0.05–50	NA	0.05–50	NA	0.05–50
LF output stage	NA	NA	3–99	NA	NA
Liquid flow,C4 kgh^{-1}	NA	NA	200–1600	NA	NA
Number of stages, C5	15–100	15–100	15–100	15–100	NA
Feed stage, C5	3–99	3–99	NA	NA	NA
Diameter, C5,m	0.5–1.7	0.5–1.7	0.5–1.7	0.5–1.7	NA
Flow rate,C5, kmolh^{-1}	Bottoms 14–15.44	Bottoms 13–15.44	Bottoms 15.39–15.4	Distillate 1450–1480	NA
Reflux ratio, C5, kmolkmol^{-1}	0.05–50	0.05–50	NA	0.05–50	NA
VF output stage	NA	NA	NA	3–99	NA
LF output stage	NA	NA	NA	3–99	NA
VF output rate	NA	NA	NA	200–1600	NA
LF output rate, kgh^{-1}	NA	10–1000	NA	10–1000	NA
Lateral product stage	NA	NA	NA	3–99	3–99
Lateral product rate	NA	NA	NA	1463–1463.5	1430–1480
Total of variables	**10**	**10**	**10**	**13**	**7**

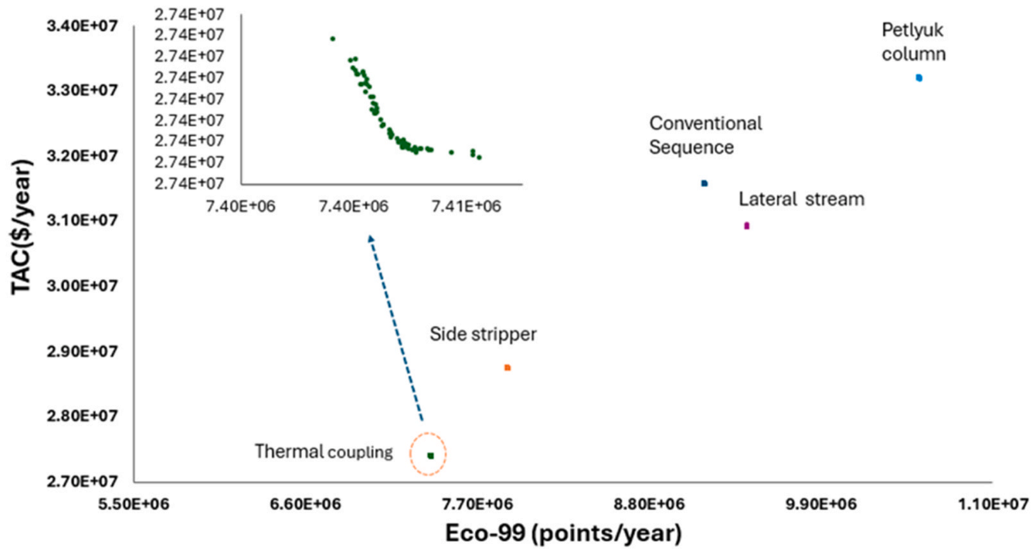

Fig. 2. Pareto front between objective functions: the TAC and the EI-99 for conventional and TCDS.

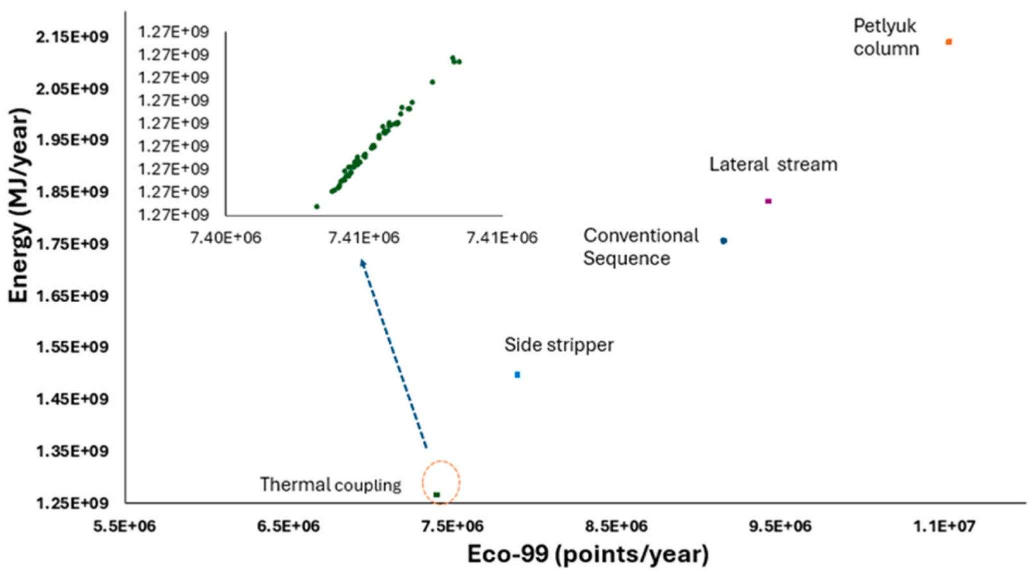

Fig. 3. Interaction between objective functions: Energy and the EI-99 for conventional and TCDS.

lowering the TAC, but at the expense of greater reboiler duties and steam consumption. The resulting increase in utility demand amplifies energy use and environmental impacts, leading to a nonlinear relationship between economic and environmental objectives, consistent with previous studies (Alcocer-García et al., 2019) and (Caceres-Barrera et al., 2024). Additionally, Fig. 3 demonstrates a direct correlation between energy consumption and the EI-99, which is attributable to the significant impact of steam required to heat both objective functions. This result is consistent with previous studies, where the fossil fuel category significantly influenced the Eco-Indicator (Alcocer-García et al., 2019; Romero-García et al., 2020). The supporting information includes a breakdown of the Eco-Indicator 99 results, confirming that steam usage contributes the most significantly to the overall environmental impact, while the impact associated with steel is nearly negligible as reported by previous works(Alcocer-García et al., 2019; Contreras-Zarazúa et al., 2022).

The first two thermally coupled configurations significantly contribute to reducing the total cost, the environmental impact, and the energy consumption of the overall process. Table 5 shows that IS sequence achieves a 13.2 % reduction in the TAC which is equivalent to USD 4.17 million/year, along with decreases of 19.1 % in the EI-99 and 27.9 % in energy consumption compared to CS, which is the conventional scheme. This translates into an energy reduction demand from

Table 4
Comparision between this work and related work of Bangalore et al., 2022.

Reference	(Bangalore et al., 2022)	This work
Energy consumption (MJ/kg)	22.4	36.37
Product purity, wt%	95 % FF, 100 % HMF	98 % FF, 98 %HMF
Raw material	Spruce tree	Corn stover
Composition raw material	44 %cellulose, 23,3 % xylose,27.5 % lignin,1,3 % acetate, 1.6 % ash,2.3 % others	44.48 % cellulose, 33.63 % hemicellulose, 22.37 % lignin
Reactor conditions	160 C,15.16 bar	160 C,15.16 bar

Table 5
Values for objective functions, for overall biorefinery, for conventional case and for TCDS. Where CS (conventional sequence, base case), IS (indirect thermally coupled sequence), SS (side-stripper), PA (Petlyuk column), LP (lateral stream product).

Objective Function Sequence	TAC (dollars/year)	EI-99 (points/year)	Energy (MJ/year)
CS	3.157×10^7	9.156×10^6	1.756×10^9
IS	2.740×10^7	7.404×10^6	1.266×10^9
IS Saving	−13.2 %	−19.1 %	−27.9 %
SS	2.875×10^7	7.897×10^6	1.497×10^9
SS Saving	−8.9 %	−13.8 %	−14.7 %
PA	3.320×10^7	1.052×10^7	2.14×10^9
PA Saving	5.1 %	14.9 %	21.9 %
LP	3.093×10^7	9.426×10^6	1.831×10^9
LP Saving	−2.1 %	3.0 %	4.3 %

50.45 MJ/kg in the base case to 36.37 MJ/kg for the IS sequence, which is slightly higher than the 22.4 MJ/kg reported by (Bangalore Ashok et al., 2022) for a biorefinery producing methyl tetrahydrofuran, gamma-valerolactone, and HMF. The main differences between the processes are shown in the Table 4. They include the composition of biomass and the higher purities for FF resulting in higher energy requirements.

For the SS sequence, the savings amount to 8.9 % in the TAC, equivalent to USD 2.82 million/year, 13.8 % in the EI-99, and 14.7 % in energy consumption, leading to a reduction in energy demand of 43.01 MJ/kg of product. These improvements highlight the superior efficiency of these thermally integrated configurations compared to the conventional setup since eliminating a condenser or reboiler minimizes energy consumption.

On the other hand, a PA sequence resulted in increases across all objective functions, with an increase of 5.1 % in the TAC, 14.9 % in the EI-99, and 21.9 % in energy consumption. even after systematically exploring a wide range of operating variables. The main factor driving this unfavorable behavior was the very high reflux ratio (18.4–18.5) required to meet the specified purity targets, which in turn significantly increased reboiler duty. This effect was further exacerbated by the large vapor throughput of approximately 12,600 kg/h. The sensitivity of Petlyuk systems to feed composition was established in the classical work of (Tedder and Rudd, 1978), who demonstrated that the prefractionator design (thermodynamically equivalent to the Petlyuk) achieves energy savings only under favorable feed conditions. Their analysis introduced the Ease of Separation Index (ESI), defined in terms of vapor–liquid equilibrium constants. They showed that Petlyuk configurations are advantageous when the ESI exceeds 1.6, the feed contains 40–80 % of the intermediate component, and the light and heavy components are present in nearly equal proportions. For the ternary mixture analyzed in this work (HMF/FF/water), the calculated ESI is below 1.6, placing the system outside the favorable region identified by Tedder and Rudd. Consequently, the indirect thermally coupled sequence (IS) provides superior energy efficiency, in full agreement with the aforementioned findings. This interpretation is further reinforced by subsequent studies, including (Agrawal and Fidkowski, 1998) and (Dung and Thai, 2018), which confirmed that the benefits of Petlyuk arrangements are strongly dependent on both feed composition and relative volatilities. Taken together, these findings demonstrate that the poor performance of the Petlyuk configuration in this case is not attributable to suboptimal operating parameters or restricted optimization ranges, but rather to intrinsic thermodynamic constraints imposed by the composition of the HMF/FF/water mixture.

The LP sequence achieves a modest reduction of 2.1 % in the TAC although the sequence increases 3.0 % in the EI-99 and 4.3 % in energy consumption. The limited economic savings, mainly in capital costs, stem from the use of a single distillation column instead of two. However, this configuration leads to higher utility costs, as previous studies have shown that achieving product purity for three components in a single-column setup requires a significantly higher vapor flow rate (Tedder and Rudd, 1978). It is well established that steam consumption is a major contributor to the EI-99 index, and it is closely linked to energy demand (Alcocer-García et al., 2019). In this case, the increased steam requirement directly translates to a higher environmental impact.

To better analyze the energy consumption associated with each distillation configuration, the reboiler duties of columns C4 and C5 were plotted for the different alternatives, as shown in Fig. 4 (see configurations in Fig. 1). In the CS, IS, and SS sequences, column C4 is responsible for separating HMF as the bottom product, while column C5 is responsible for separating FF as the bottom product. In the CS configuration, the low energy efficiency arises from the fact the more volatile components, water and FF, are withdrawn from the bottom of C4 and condensed. While significant energy must be supplied to C5 to vaporize this mixture and recover water as the top product, the IS sequence, conversely, demonstrates to have the best energy performance. Here, the vapor stream from the top of C4 is directly fed into C5 without intermediate condensation, allowing better utilization of the thermal energy already introduced in C4. This reduces significantly the overall reboiler duty. It can be seen in the SS configuration that the reboiler duty in C5 is negligible compared to that of C4, as the second column functions only as a stripping section. This arrangement, nevertheless, results in a higher reboiler duty in C4 compared to the total duty required in the IS configuration. On the other hand, in the PA and LP configurations, FF and HMF are recovered as middle and bottom products, respectively, within a single column with C5 for the case of PA and C4 for the case of LP. The high energy consumption observed in the Petlyuk (PA) column is attributed as commented before to the high operational reflux ratio identified by the optimizer, which is strongly influenced by the feed composition. For the LP configuration, the increased energy requirement is mainly associated with the increment in reboiler duty needed to achieve the desired purities within a single column.

Table 6 presents the key design variables of the optimized configurations by offering an insight into how column design affects energy efficiency and economic performance. Among the evaluated configurations, the IS sequence emerges as the most favorable option as it achieves a substantial reduction in column diameters regarding a base case of 40 % for C4 and 11.5 % for C5, and with a 10-stage reduction in C4, leading to lower capital costs. More importantly, IS sequence presents a significant reduction in energy consumption, primarily driven by a lower reflux ratio in column C5 of 2.83 as opposed to the 10.18 in the conventional configuration. The decrease in internal liquid recirculation substantially reduces the thermal load in both reboilers, with reboiler duty decreasing by 4.66 % in column C4 and 76.5 % in column C5 compared to the base case. Given that previous studies have identified steam consumption as the dominant factor influencing the Eco-Indicator

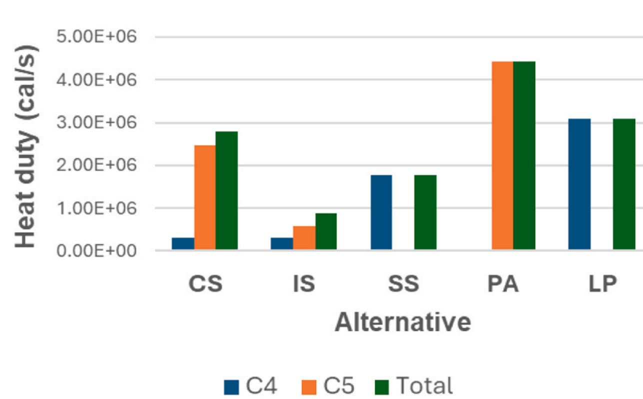

Fig. 4. Reboiler heat duty required by columns C4 and C5 in each configuration. (For reference of the columns see Fig. 1).

Table 6
Decision values for optimal scenarios, and energy requirements for columns for each alternative where CS (conventional sequence, base case), IS (indirect thermally coupled sequence), SS (side-stripper), PA (Petlyuk column), LP (lateral stream product).

Variable Name	CS	IS	SS	PA	LP
Number of stages, C4	42	32	73	18	64
Feed stage, C4	27	4	44	17	63
Diameter, C4, m	1.16	0.7	0.54	0.72	0.5
Flow rate, C4, kmolh^{-1}	Bottoms 11.89	Bottoms 11.89	Bottoms 11.89	NA	Bottoms 11.89
Reflux ratio, C4 kmolkmol^{-1}	0.09	NA	7	NA	13
LF output stage	NA	NA	43	NA	NA
Liquid flow,C4 kgh^{-1}	NA	NA	1540	NA	NA
Reboiler duty C4, cal/s	318637	303776	1.784×10^6	0	3.095×10^6
Condenser duty C4, cal/s	−279991	0	-1.746×10^6	0	-3.053×10^6
Number of stages, C5	59	75	9	65	NA
Feed stage, C5	34	73	NA	NA	NA
Diameter, C5, m	0.72	0.637	0.5	0.57	NA
Flow rate, C5, kmolh^{-1}	Bottoms 15.40	Bottoms 15.40	Bottoms 15.40	Bottoms 15.4	NA
Reflux ratio, C5, kmolkmol^{-1}	10.18	2.83	NA	18.95	NA
VF output stage	NA	NA	NA	46	NA
LF output stage	NA	NA	NA	52	NA
LF output rate, kgh^{-1}	NA	NA	NA	643.25	NA
LF7 output rate, kgh^{-1}	NA	72	NA	106.72	NA
Lateral product stage	NA	NA	NA	55	60
Lateral product rate,kgh^{-1}	NA	NA	NA	1463.03	1479.56
Reboiler duty C5, cal/s	2.47×10^6	578543	92.6	4.42×10^6	NA
Condenser duty C5, cal/s	-2.47×10^6	−839551	0	-4.38×10^6	NA

for distillation processes (Quiroz-Ramírez et al., 2018b), the superior energy efficiency of IS sequence translates into a significant reduction in environmental impact, making it the most sustainable configuration among those evaluated.

In SS sequence, the optimization led to significantly more compact column designs, with diameter reductions of 53 % for C4 and 30 % for C5. However, these improvements come at the cost of an increased number of stages in column C4, which rises by 31 stages relative to the base case. Meanwhile, in the SS sequence column C5 operates as a side-stripper with only nine stages, replacing the 75-stage column in the conventional setup. This modification leads to substantial capital cost savings. The increased number of stages in column C4, combined with a higher reflux ratio compared to the conventional configuration, ensures that enough vapor is generated for effective separation, thus allowing the elimination of the reboiler in C5. Consequently, the total reboiler duty is reduced by 36 % relative to the base case, highlighting the improved energy efficiency of this configuration.

Conversely, an optimal design for the PA sequence comprises an 18-stage prefractionator coupled with a 65-stage main column (C5). Although both columns exhibit diameter reductions of 38 % for C4 and 21 % for C5, which leads to lower capital expenditures, this configuration exhibits the highest energy demand among all alternatives as the reboiler duty for C5 reaches 4.42×10^6 cal/s. This excessive energy consumption is mainly due to the high reflux ratio required for effective separation of 18.95 compared to 10.18 in the base case, which significantly increases utility costs and adversely impacts environmental performance. Despite being a thermally integrated system, the PA does not offer energy savings in this case, largely because the reflux ratio remains high. As previous studies have shown, the energy-saving potential of a Petlyuk configuration depends heavily on the composition of the feed mixture (Dung and Thai, 2018; Tedder and Rudd, 1978). In this case, since the feed is rich in the most volatile component, the expected benefits of the PA are not achieved.

The LP sequence achieves cost savings by consolidating the separation process into a single 64-stage column, compared to the base case, which utilizes two columns with 42 and 59 stages, respectively. This design simplification reduces capital costs, further enhanced by a significant reduction of 0.5 m in the column diameter. However, despite these economic advantages, LP sequence exhibits a total thermal load of 3.095×10^6 cal/s, exceeding the 2.789×10^6 cal/s required in the conventional setup. This increased energy demand arises from the necessity to maintain a high reflux ratio (13), which exceeds the values observed for the individual columns in the base case (0.09 and 10.18, respectively). Although the LP sequence achieves a lower TAC, it comes at the expense of higher energy consumption and greater environmental impact, highlighting the trade-off between cost efficiency and sustainability.

6. Conclusions

This study presents an integral approach for the design and the MOO of intensified distillation sequences in order to purify FF and HMF within a multiproduct biorefinery. By incorporating PI strategies, specifically through thermal integration, this work demonstrates how efficient distillation alternatives can not only reduce energy consumption but also enhance both the economic and environmental performance of biorefinery operations.

This work shows that some intensified alternatives achieve substantial improvement regarding the conventional design. Among the evaluated configurations, the IS and the SS, both representative TCDS technologies, achieved substantial energy savings of 27.9 % and 14.7 %, respectively. These reductions translated directly into improved sustainability metrics, with the IS showing the most balanced performance. The IS had a decrease of 13.2 % in the TAC and a decrease of 19.1 % in the EI-99. The SS had a decrease of 8.9 % in the TAC and a decrease of 13.8 % in the EI-99.

On the other hand, some alternatives did not yield better results than the base case due to their higher operational demands. The PA sequence, for example, increased its reflux ratios leading to a 21.9 % rise in energy consumption. Similarly, the single-column configuration with a lateral product stream offered only marginal economic benefits (2.1 % in TAC reduction) but incurred in higher energy use and environmental impact. A major insight from the analysis of design variables is the critical influence of the reflux ratio, which consistently emerged as the parameter with the greatest impact in optimizing energy and cost performance. In contrast, variations in column diameter and stage number yielded relatively minor improvements.

The DETL algorithm was successfully applied to the MOO considering the different sustainability indicators by demonstrating the value of advanced stochastic techniques in the design of intensified separation processes. Overall, the findings highlight the effectiveness of TCDS as a powerful PI tool as they reinforce the importance to integrate sustainability metrics in the process design. This work contributes to the development of more competitive and sustainable biorefineries, facilitating the transition of chemical production from fossil-based to renewable resources.

This study is limited by its focus on corn-stover-based systems and by the absence of dynamic analyses of operational stability, recognizing that intensified processes generally pose greater challenges for monitoring and control than conventional configurations. Future research should broaden the methodology to include other biomass feedstocks, enabling a more comprehensive assessment of the applicability and robustness of the proposed intensified designs across diverse biorefinery contexts. Additionally, incorporating advanced control strategies—such as model predictive control and fault-tolerant frameworks—will be crucial to ensure reliable long-term operation under disturbances and variable operating conditions. Moreover, attention should be directed toward addressing the practical challenges associated with scale-up, process controllability, and seamless integration with upstream and downstream biorefinery units. These aspects are vital to bridge the gap between simulation-based conceptual designs and their industrial implementation, thereby enhancing both the technical feasibility and sustainability of future large-scale applications.

CRediT authorship contribution statement

Carlos Rodrigo Caceres-Barrera: Writing – original draft, Software, Methodology, Investigation, Conceptualization. **Eduardo Sánchez-Ramírez:** Writing – review & editing, Validation, Supervision, Software, Investigation. **Juan Gabriel Segovia-Hernández:** Writing – review & editing, Validation, Supervision, Software, Investigation. **Maricruz Juárez-García:** Writing – review & editing, Validation **Heriberto Alcocer-García:** Writing – review & editing, Software, Validation. **César Ramírez-Márquez:** Writing – review & editing.

Supporting information

Evolution of Pareto front through generations for IS sequence. Breakdown Eco-indicator 99 for conventional sequence. Unit indicators used to measure the EI-99. Experimental and predicted data for LVE using NRTL-HOC in Aspen for water and furfural. Experimental and predicted data using NRTL-HOC in Aspen for LLE for water+ HMF+ MIBK.

Declaration of Competing Intetrest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Authors acknowledge the support provided by SECIHTI, and Uni versidad de Guanajuato.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cherd.2025.10.002.

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Glossary

CS: Conventional separation scheme
DETL: Differential Evolution with Tabu List
EI-99: Eco-indicator 99
FF: Furfural
HMF: Hydroxymethylfurfural
IS: indirect thermally coupled sequence
LF: Interconnecting liquid flow Petlyuk column
LLE: liquid-liquid equilibrium
LP: single column lateral product arrangement
MOO: multi-objective optimization
PA: Petlyuk arrangement
SS: side stripper arrangement
TAC: total annualized cost
TCDS: thermally coupled distillation sequences
VF: Interconnecting vapor flow Petlyuk column
VLE: vapor-liquid equilibrium