



Sequential Synthesis Methodology in the Design and Optimization of Sustainable Distillation Sequences for Levulinic Acid Purification

Heriberto Alcocer-García¹ · Juan Gabriel Segovia-Hernández² · Eduardo Sánchez-Ramírez² · Carlos Rodrigo Caceres-Barrera² · Salvador Hernández²

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Abstract

Levulinic acid is acknowledged as a significant high-value product derived from lignocellulosic biomass. Its acquisition involves acid hydrolysis, resulting in a challenging separation and purification process due to the formation of a dilute azeotropic mixture. This complexity renders separation costly and presents a hurdle for large-scale production. Various purification methods, including hybrid and intensified systems, have been proposed to address this issue. However, a systematic synthesis methodology incorporating multi-objective optimization considering economic and environmental factors has yet to be applied to this mixture. Hence, this study employs such a methodology to derive sustainable and thermodynamically feasible intensified designs. The optimization algorithm employed is differential evolution with a tabu list. Two objectives are considered: total annual cost as the economic criterion and the eco-indicator 99 as the environmental index. The intensified design, incorporating thermal coupling, presents the best results of the designs studied, with a total annual cost value of \$13.9 million and 4.21×10^9 environmental points per year. This represents an economic saving of \$4.6 million per year and reduces environmental impact by 1.15×10^9 points compared to the reference design, providing a sustainable alternative for purifying levulinic acid at a cost of \$0.261 per kilogram.

Keywords Intensified distillation · Bio-blocks · Energy reduction · Biomass

Introduction

Sustainability is crucial for meeting present needs while ensuring the welfare of future generations, addressing the adverse impacts of human activities on the environment through sustainable practices. These not only benefit the planet but also offer advantages to industries such as improved efficiency, reduced waste, cost savings, and greater competitiveness [1, 2]. In efforts to enhance process sustainability, viable alternatives to fossil-based products have emerged, promoting a shift towards renewable origins [3, 4]. One sustainable alternative involves using lignocellulosic biomass as a feedstock for chemical compounds, offering the potential to produce products that directly replace

derivatives of crude oil within a biorefinery framework. One such sustainable alternative is the utilization of lignocellulosic biomass as a feedstock for chemical compounds. Lignocellulosic biomass shares fundamental chemical elements (carbon, hydrogen, and oxygen) with crude oil, offering the potential to produce products within a biorefinery framework that serve as direct replacements for both chemically identical and functionally similar derivatives of crude oil [5]. Biorefinery industries are expected to revitalize rural areas by becoming dispersed industrial complexes of various sizes, integrating multiple bioindustries to utilize all lignocellulosic biomass components and reduce reliance on imported fossil fuels [6]. Despite significant interest in biofuels, economic challenges hinder their production. Overcoming these obstacles involves establishing biorefineries that can produce both value-added products (chemicals) and biofuels from biomass resources in an integrated and efficient manner, leading to additional economic and environmental benefits [7]. Among these bioproducts, levulinic acid stands out for its diverse applications and high added value [8, 9].

✉ Heriberto Alcocer-García
h.alcocer@ugto.mx

¹ Department of Civil and Environmental Engineering, Universidad de Guanajuato, Guanajuato, Mexico

² Department of Chemical Engineering, Universidad de Guanajuato, Guanajuato, Mexico

The production of levulinic acid from lignocellulosic material involves various steps such as pretreatment, thermal and enzymatic hydrolysis, and acid hydrolysis, resulting in a mixture containing levulinic acid, furfural, formic acid, and water [9, 10]. However, the dilute nature of this mixture and the formation of azeotropes make its purification challenging, contributing to the energy-intensive and costly nature of the process [11–13]. According to Kiss et al. [14], separation costs can make up a substantial portion of the total cost, limiting the industrial scalability of levulinic acid production due to the high energy cost associated with water removal. Various hybrid technologies have been developed for purifying the mixture, combining liquid-liquid extraction columns with solvents like isobutyl-methyl-ketone [15, 16] and furfural [17, 18] to remove water. Further separation is achieved through distillation columns. Process intensification, aimed at sustainable processes, is proposed by Nhien et al. [18], incorporating a decanter and suggesting the use of a dividing wall column. Alcocer-García et al. [12] propose intensified schemes such as thermally coupled columns and finding economic and environmental savings. Although in the available literature there are already works that have dealt with the purification of levulinic acid, none of them propose an orderly synthesis methodology. This approach has the advantage of considering the whole range of separation possibilities. This results in an adequate selection of sustainable purification alternatives.

Therefore, this study proposes a sequential synthesis starting with conventional distillation columns for separating the quaternary mixture and then implementing process intensification using thermal couplings and section movement. Process intensification, based on theoretical studies, shows potential energy and cost savings of around 30% through configurations like dividing wall columns and Petlyuk columns [19–24]. The methodology is adjusted from Errico et al. [25], with designs undergoing thermodynamic feasibility analysis and multi-objective optimization. This modification helps to avoid the evaluation of thermodynamically infeasible designs or designs with limited potential for energy savings and environmental impact reduction. Designs are generated using differential evolution with a tabu list, optimizing total annual cost (TAC) and eco-indicator 99 (EI99) for economic and environmental impact. The objective of this multi-objective optimization is to derive designs that strike a harmonious balance between both objective functions and propose enhancements to process sustainability, aiming for unexplored designs with lower cost and environmental impact.

Methodology

This section delineates the methodological framework employed in this study. It commences with an exposition of the systematic synthesis methodology for designing

intensified schemes. Subsequently, a detailed account of the specific case study under examination is provided. Finally, the optimization process and the delineation of objective functions are elucidated.

Systematic Synthesis

This methodology is based on the work of Errico et al. [25] where the systematic synthesis of intensified schemes is proposed through four simple steps:

- Step 1: the simple column configurations

The procedure starts by drawing all the possible N -component separation; the number of simple column sequences (S_n) can be predicted with Eq. 1:

$$S_n = \frac{[2(N-1)]!}{N!(N-1)!} \quad (1)$$

- Step 2: the thermally coupled configurations (P_n) can be calculated using Eq. 2:

$$P_n = \frac{[2(N-1)]!}{N!(N-1)!} \left[\sum_{j=1}^{N-3} \frac{(N-2)!}{j!(N-2-j)!} + 1 \right] \quad (2)$$

Each thermally coupled configuration can be obtained from the corresponding simple column sequence by substituting one or more condenser/s and/or reboiler/s associated to no product streams with a bidirectional vapor–liquid connection. The use of thermal couplings is suggested since their use in distillation systems favors energy savings [26].

- Step 3: the thermodynamically equivalent configurations

From the thermally coupled configurations, the thermodynamically equivalent designs can be generated through moving a column section associated to a condenser and/or a reboiler that provides the common reflux flow rate, or the vapor boil up between two consecutive columns. Following this procedure, the elimination of a condenser or a reboiler associated with a submixture from a simple column in a distillation sequence makes the rectifying or the stripping section of the subsequent column movable. For this reason, the number of movable sections is equal to the number of thermal couplings in the considered sequence [27]. A configuration in this subspace has the same energy requirement as the corresponding thermally coupled structure. Nevertheless, the capital cost saving can be achieved by a better liquid and vapor flow rate redistribution between the sections. Moreover, a better controllability of the system can be obtained [28]. For an n -component mixture, the number of

thermodynamically equivalent structures (TES) of a given sequence can be predicted utilizing Eq. 3, where NTC is the number of thermal couplings:

$$\text{TES} = 2^{\text{NTC}} \quad (3)$$

- Step 4: generation of the intensified structures with less than $N-1$ columns

Now, from the thermodynamically equivalent structures, it is possible to generate the new subspace of systems with less than $N-1$ columns. The methodology is simple and consists in the elimination of the side columns having only one column section. The number of intensified structures (NIS) can be predicted using Eq. 4, where NS is the number of single-section columns in the thermodynamically equivalent structure:

$$\text{NIS} = 2^{\text{NS}} - 1 \quad (4)$$

In each design stage, a certain number of schemes are generated to be evaluated, as reported by Errico et al. [25] for a quaternary mixture implementing Eqs. 1–4: 5 simple column configurations, 15 thermally coupled configurations, 25 thermodynamically equivalent configurations, and 31 systems with less than $N-1$ columns would be generated, adding up to a total of 76 different configurations. An illustrative figure of the number of designs generated is shown in Fig. S1 in the supplementary material. Considering that it is intended to carry out a feasibility analysis and a multi-objective optimization for each configuration, this would represent an overwhelming task. For this reason, a selective strategy like to the Branch and Bound method was adopted.

This approach involves iteratively partitioning the space of feasible solutions into smaller subsets, extracting the best result from each subset while eliminating the other individuals and their subsequent partitions [29].

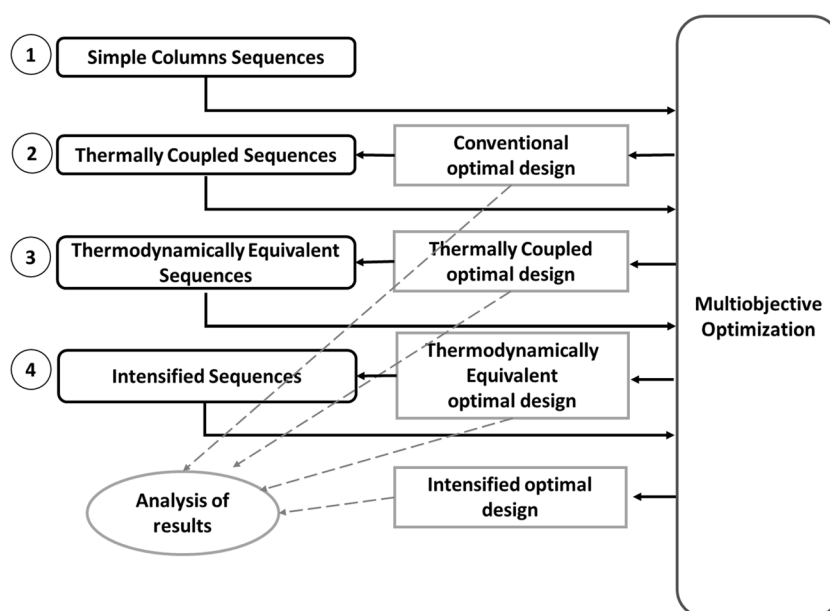
In other words, once the results of the conventional designs are obtained, thermally coupled designs were proposed, starting with the design that presents the best results. In a sequential manner, based on the best thermally coupled design, section movement was proposed, obtaining thermodynamically equivalent configurations and the intensified structures with less than $N-1$ columns. The systematic synthesis methodology is described in Fig. 1.

Case of the Study

The annual production of levulinic acid considered for this study is 5×10^7 kg/year for all proposed designs. The feed used for the mixture to be purified is 90000 kg/h, with a mass composition of 86% water, 7% levulinic acid, 4% furfural, and 3% formic acid, operating at a temperature of 298.15 K and a pressure of 202.65 kPa. This feed was selected based on previous works [12, 18] and to have a point of comparison. All proposed schemes were simulated using Aspen Plus V8.8, and physical and thermodynamic properties were calculated using the NRTL-HOC thermodynamic model.

In this study, various hybrid designs are explored, combining a liquid-liquid extraction column using furfural as an extracting agent followed by a train of distillation columns. These designs were assessed through a rigorous multi-objective optimization strategy incorporating economic and environmental indices. Mass and heat integration is employed as an intensification strategy using thermal couplings and section movements in the distillation section. Additionally, with

Fig. 1 Systematic synthesis methodology



the intention of exploring indicator behavior concerning the distribution of mixture flows, conventional alternatives for the separation of the quaternary mixture are investigated, and a systematic synthesis is conducted starting from the best designs. In this study, conventional schemes refer to those that do not have process intensification through thermal couplings, wall-column integration, and section movement. They merely feature a single liquid-liquid extraction column followed by basic distillation columns (equipped with condensers and reboilers).

In this case, the first subset comprises the conventional designs. Therefore, five different conventional separation schemes are proposed. This is because quaternary mixtures present five arrangements for their separation: direct (CS2), indirect (CS3), direct-indirect (CS4), indirect-direct (CS1), and symmetrical (CS5) [30] (see Fig. 2). It is crucial to emphasize that each design incorporates the liquid-liquid extraction column. The CS1 design is taken as a reference point for all the designs examined, which was derived from the research of Alcocer-García et al. [12], shown in Fig. S2 in supplementary material. In that study, multi-objective optimization was applied to the same mixture using similar criteria to those used in this study.

Optimization Procedure

To assess all alternatives developed within a framework of sustainable processes, it is essential to establish specific metrics. These metrics should align with the definition of sustainable development as “development that meets the needs of the present without compromising the ability of future generations to meet their own needs” [3]. In process design, the inclusion of “green metrics” should be considered, aiming to align with the objectives of the UN 2030 agenda and contribute to processes that fulfill a broader goal than just environmental sustainability. Within these green metrics, it is crucial to highlight aspects related to the environment, economy, safety, and process control [31].

While control and safety aspects are important, in this work, we focus on their economic and environmental aspects as sustainability criteria. Therefore, the objective functions considered for this multi-objective optimization were total annualized cost (TAC) as an economic indicator and eco-indicator 99 (EI99) as an environmental indicator. TAC is proportional to heat, services, and column size. EI99 is used to quantify the environmental impact of

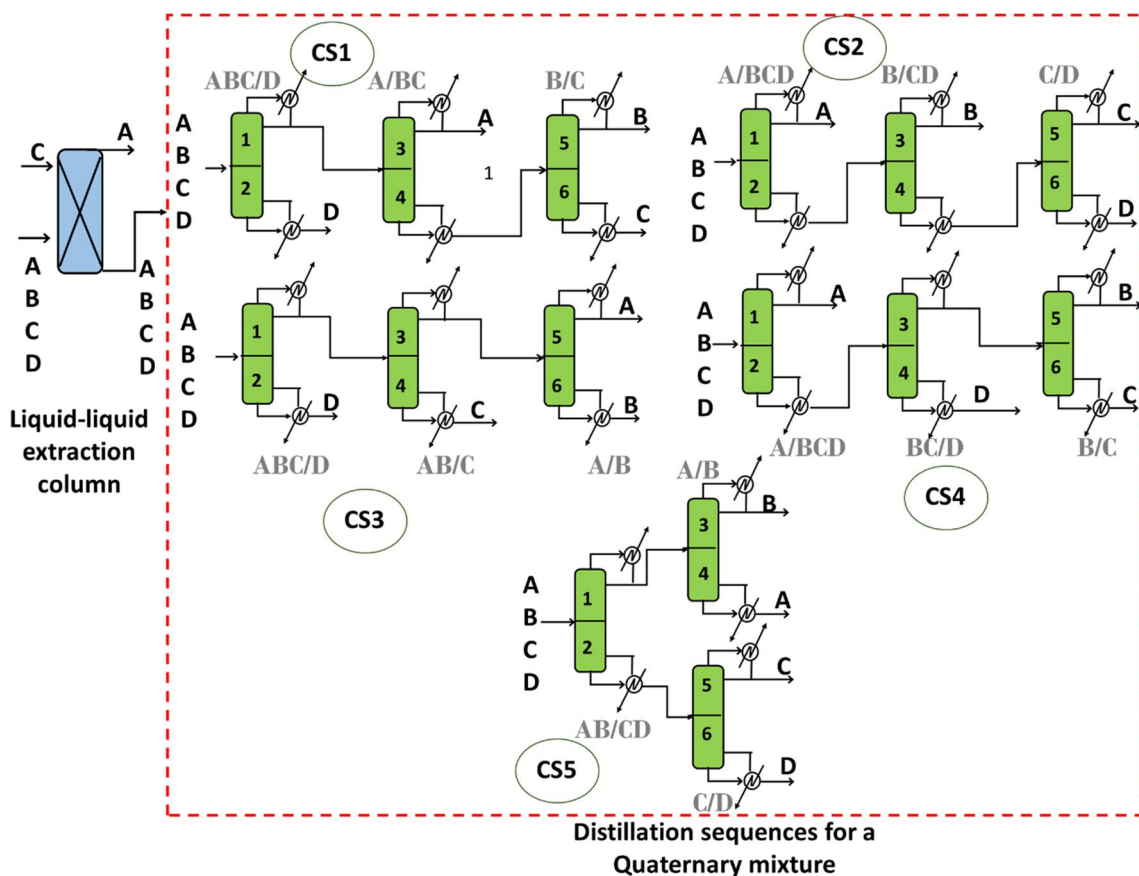


Fig. 2 Proposed conventional sequences for quaternary mixture: water (A), formic acid (B), furfural (C), and levulinic acid (D)

flow diagrams throughout the life cycle, including three main categories of damage: human health, ecosystem quality, and depletion of resources.

The design of the various proposed alternatives involved minimizing the multi-objective function specified in Eq. 5:

$$\text{Min(TAC, EI99)} = f \left(\begin{array}{c} N_e, N_1, N_2, N_3, N_{f1}, N_{f2}, N_{f3}, RR_1, RR_2, RR_3, \\ D_1, D_2, D_3, B_2, F_{V2}, F_{L2}, F_{L3}, S_{O2}, S_{OF2}, \phi_e, \phi_1, \phi_2, \phi_3, S \end{array} \right) \quad (5)$$

Subject to: $y_j P_c \geq x_j P_c$ $w_j F_c \geq u_j F_c$

where N_e is the number of stages for the extractor, N is the number of stages for the distillation columns, N_f is the column feed stage, RR is the reflux ratio, D is the distillate flow rate, B is the bottom flow rate, S_O is the side outlet stage, S_{OF} is the side outlet flow, F_L is the interconnection liquid flow rate, F_V is the interconnection vapor flow rate, ϕ is the column diameter, and S is the solvent flow rate. Numerical subscripts are associated with the distillation column to which the design variable is associated. In addition, the optimization problem is restricted to the fact that the resulting purities $y_j P_c$ must be equal to or greater than $x_j P_c$ and the recovery flows of the $w_j F_c$ products must be greater than or equal to $u_j F_c$. The minimum purity targets for levulinic acid and formic acid were set at 98% (wt%) and 85%, respectively. These purities were considered due to the purity required for their industrial applications [32, 33]. The purity target for furfural was set at 99.9% (wt%), considering its potential use as an extracting agent [12, 18]. The minimum recovery rate for products is 6212.415 kg/h for levulinic acid, 101,270.174 kg/h for furfural, and 293.885 kg/h for formic acid. These values were proposed so as not to obtain lower recoveries or purities than those presented in the studies of Alcocer-García et al. [12] and Nhien et al. [18], where the same composition is used in the feed. It is important to note that each design contains between 15 and 18 of the design variables mentioned above in the multi-objective function. For example, Eq. 6 and Eq. 7 describe the optimization problem for CS1 and S11 designs, respectively:

$$\text{Min(TAC, EI99)} = f \left(\begin{array}{c} N_e, N_1, N_2, N_3, N_{f1}, N_{f2}, N_{f3}, RR_1, RR_2, RR_3, \\ D_1, D_2, D_3, \phi_e, \phi_1, \phi_2, \phi_3, S \end{array} \right) \quad (6)$$

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

$$\text{Min(TAC, EI99)} = f \left(\begin{array}{c} N_e, N_1, N_2, N_{f1}, N_{f2}, RR_1, RR_2, \\ D_1, D_2, S_{O2}, S_{OF2}, \phi_e, \phi_1, \phi_2, S \end{array} \right) \quad (7)$$

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

In Section 1 of the supplementary material, the variables to be optimized for each design studied were placed.

For the calculation of the total annual cost (TAC), the method published by Guthrie [34] was used with modifications proposed by Ulrich [35]. In this method, an estimation of process costs is carried out by separating each of

the involved units. Additionally, the equations published by Turton et al. [36] were employed to approximate process costs using Eq. 8:

$$\text{TAC} = \frac{\sum_{i=1}^n C_{TM,i}}{n} + \sum_{j=1}^n C_{ut,j} \quad (8)$$

where TAC is the total annual cost, C_{TM} is the capital cost of the plant, n is the payback period, and C_{ut} is the cost of the services, respectively. The payback period was considered 10 years. The equations and parameters for calculating the CTM were taken from the work of Alcocer-García et al. [12]. The values of the economic parameters were obtained from Turton et al. [36].

The eco-indicator 99 stands out as one of the best eco-indicators for quantifying environmental impact, as its evaluation is based on the life cycle [37, 38]. In the design stage of complex distillation schemes, the eco-indicator 99 has been incorporated, achieving intensified designs with a lower environmental impact compared to conventional designs [12, 39]. In the EI99 methodology, 11 impact categories are included, which are aggregated into three main damage categories: human health, ecosystem quality, and resource depletion. The quantification was conducted following the procedure proposed by Goedkoop and Spriensma [40] as reported in Eq. 9:

$$\text{EI99} = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (9)$$

where β_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused in category k per unit of chemical b released to the environment, δ_d is a weighting factor for damage in category d , and ω_d is the normalization factor for damage of category d . The scale is chosen in such a way that the value of 1 point is representative for one thousandth of the yearly environmental load of one average European inhabitant. In this work, for eco-indicator 99 calculation, the impact of three factors was considered the most important in the levulinic acid downstream processing: steam (used in column reboiler), electricity (used for pumping), and steel (to build distillation columns and accessories). The values for those three factors are summarized in the manual reported by Goedkoop and Spriensma [40] and also are shown in Table S1 in supplementary material.

All the sustainable metrics were evaluated in the early design stage through a multi-objective optimization. Multi-objective optimization (MOO) involves systematically and simultaneously optimizing a set of objective functions. Consequently, determining the optimum can be seen as identifying a favorable compromise among all the objective functions within the problem [41]. The selected method to optimize the studied processes is differential evolution with

Table 1 Range and type of variables used in the calculation of objective functions

Variable	Range of variable	Type of variable
Number of stages	5–99	Discrete
Feed stage	4–99	Discrete
Reflux ratio	0.01–350	Continuous
Distillate rate (kg/h)	280–102,000	Continuous
Side stream stage	4–99	Discrete
Diameter (m)	0.5–5	Continuous
Extractant flow (kg/h)	100,000–120,000	Continuous

tabu list (DETL). DETL is a stochastic global search technique that iteratively explores all feasible regions in search of the optimality zone [42]. The DETL has demonstrated several advantages over other optimization methods. Among the advantages exhibited by the method is the faster convergence in the optimality zone, requiring less computational effort and reducing the computational time needed to effectively solve nonlinear and non-convex problems. Additionally, DETL possesses the capability to memorize previously evaluated solutions, thus eliminating the need to reevaluate solutions already tested. This memory function contributes to a reduction in the computational time required to attain

the optimal solution. The differential evolution with tabu list method has been successfully applied to diverse problems in the chemical industry [43]. The DETL method comprises four fundamental steps based on the theory of biological evolution: (i) initialization, (ii) mutation, (iii) crossover, and (iv) selection. The parameters employed for DETL were adopted from Srinivas et al. [42].

The optimization method is implemented using a hybrid platform with Microsoft Excel and Aspen Plus. The design variables are transferred from Excel to Aspen Plus through DDE (Dynamic Data Exchange) using COM technology. After the simulation, Aspen Plus returns the results to Excel, where the objective function values are analyzed, and new values for decision variables are proposed. For the optimization of the processes analyzed in this study, the following parameters are used for the DETL method: an initial generation of 120 individuals, 417 generations, a taboo list encompassing 50% of the total individuals, a tabu radius set at 0.00001, and crossing and mutation fractions of 0.8 and 0.6, respectively. These parameter values were chosen based on previous similar works where the DETL method was applied to complex distillation schemes and demonstrated good convergence [12, 26, 39]. The tuning process involves conducting multiple tests with various numbers of individuals and generations to identify

Table 2 Design parameters and performance indexes for conventional schemes

	Parameter	CS1 [12]	CS2	CS4
C1	Number of stages	22	24	28
	Extractant (t/h)	106.722	106.154	106.018
	Diameter (m)	1.434	0.538	0.987
C2	Number of stages	28	24	17
	Feed stage	13	16	11
	Reflux (kg/kg)	0.076	0.025	0.026
	Reboiler duty (MW)	23.026	10.278	9.403
	Diameter (m)	3.642	0.653	1.276
C3	Number of stages	46	39	35
	Feed stage	34	32	9
	Reflux (kg/kg)	0.206	64.901	0.125
	Reboiler duty (MW)	4.465	3.311	13.935
C4	Diameter (m)	2.413	0.431	0.983
	Number of stages	60	39	56
	Feed stage	28	13	16
	Reflux (kg/kg)	54.199	0.11	43.9
	Reboiler duty (MW)	3.486	13.571	3.237
	Diameter (m)	2.000	0.512	1.662
	Levulinic acid (%w/w)	0.980	0.980	0.981
	Formic acid (%w/w)	0.851	0.850	0.857
	Furfural (%w/w)	0.999	0.999	0.999
	TAC (\$/y)	1.854E+07	1.562E+07	1.494E+07
	EI99 (points/y)	5.359E+09	4.699E+09	4.597E+09
	TAC saving		16%	19%
	EI99 saving		12%	14%

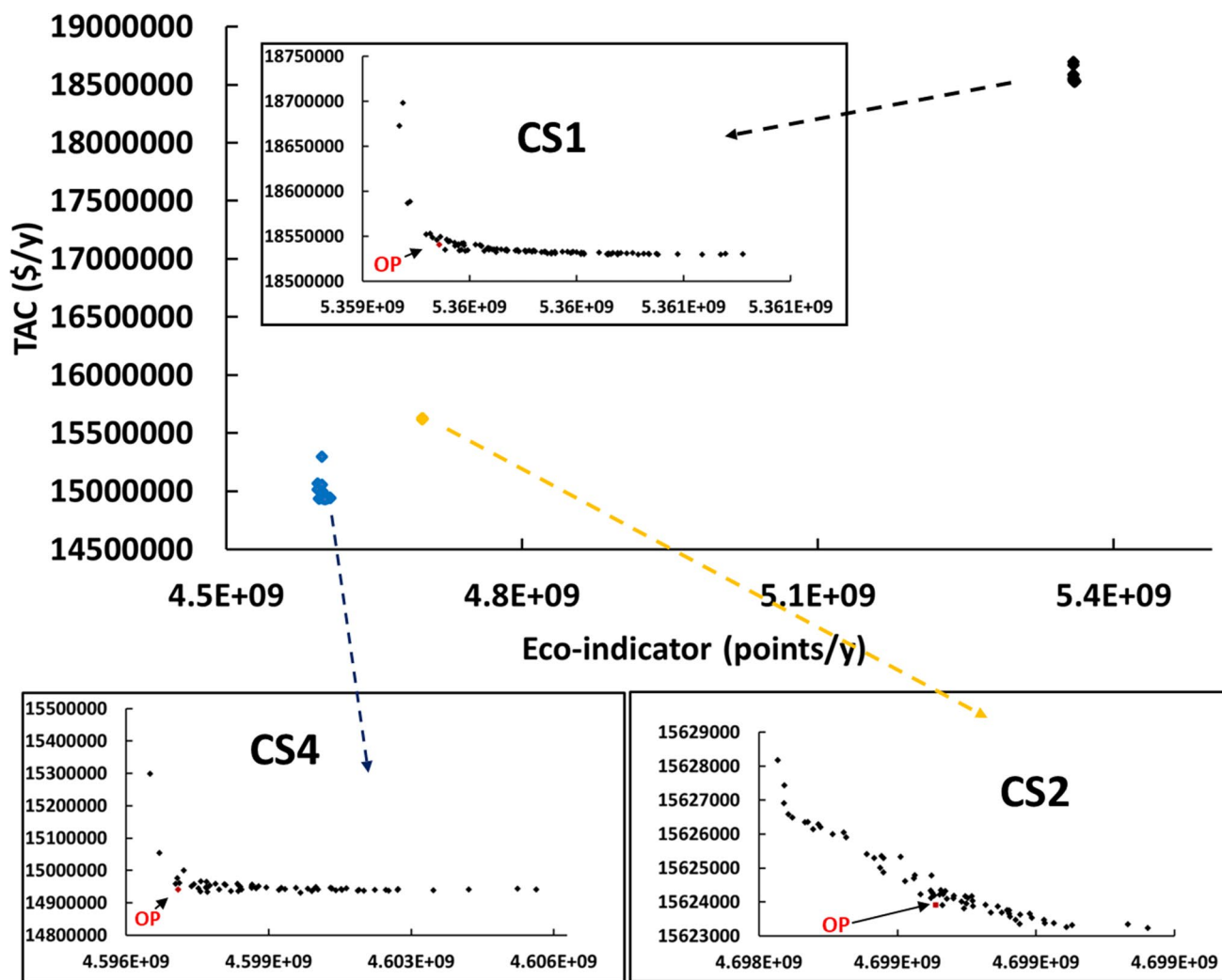


Fig. 3 Superposed Pareto chart of the optimized designs of conventional distillation configurations

the optimal parameters that yield the best convergence performance for DETL. Around 18 variables, continuous or discrete, were considered in this multi-objective optimization exercise. The flows and their respective purities of the compounds of interest were treated as constraints. Within the DETL algorithm, the non-convergence of designs that do not satisfy the energy and matter balances was penalized, with the aim of obtaining only designs that are thermodynamically feasible and facilitating the search for the method.

In the optimization process, Table 1 shows the form of variables used and the search range. The range of values for these parameters was not unrestricted; limits were set on variables such as reflux ratio, diameter, and number of stages, in accordance with the recommendations of Górak and Olujić [44] and Douglas [45]. The natural limits for the concentrations were considered between 0 and 1; the limits of interconnection flows of vapor and liquid were established through the

mass balance. Solvent flow was considered a variable to be optimized, considering a feed ratio between 1.1 and 1.3.

Results

This section presents the primary results derived from the simultaneous evaluation of the multi-objective function. The optimization effectively satisfies all constraints pertaining to purity and recovery. Prior to the optimization process, all designs underwent thorough modeling and simulation using Aspen Plus 8.8, utilizing the rigorous RADFRAC unit. Consequently, all process schemes were robustly formulated, considering the comprehensive set of MESH equations, which include mass balances, equilibrium relationships, summation constraints, and energy balance. Pareto fronts were generated after 50,000 evaluations, with each Pareto front showcasing the optimal design (OP), where both

Table 3 Design parameters and performance indexes for thermally coupled schemes

	Parameter	TCS1	TCS2	TCS3
C1	Number of stages	29	28	27
	Extractant (t/h)	106.061	106.064	106.015
	Diameter (m)	0.633	1.289	0.544
C2	Number of stages	17	17	23
	Feed stage	4.17	10	14.23
	Reflux (kg/kg)	-	0.034	-
	Reboiler duty (MW)	0	9.427	0
	Diameter (m)	1.389	0.758	0.832
C3	Number of stages	31	34	33
	Feed stage	12	15.1	13.1
	Reflux (kg/kg)	0.116	-	-
	Reboiler duty (MW)	23.169	14.077	28.712
	Diameter (m)	0.578	1.230	1.522
	Steam outlet stage	13	-	14
	Steam flow (kg/h)	75,669.886	-	78,029.651
C4	Number of stages	58	23	25
	Feed stage	32	21	23
	Reflux (kg/kg)	43.139	247.23	337.03
	Reboiler duty (MW)	3.2	0.848	1.138
	Diameter (m)	1.547	1.653	1.751
	Liquid outlet stage	-	20	22
	Liquid flow (kg/h)	-	14,336.512	59,254.342
	Levulinic acid (%w/w)	0.981	0.983	0.986
Formic acid (%w/w)	0.855	0.853	0.862	
Furfural (%w/w)	0.999	0.999	1	
TAC (\$/y)	1.64E+07	1.39E+07	1.90E+07	
EI99 (points/y)	4.56E+09	4.21E+09	5.16E+09	
TAC saving	12%	25%	-2%	
EI99 saving	15%	21%	4%	

objective functions are balanced, and their minimum values are achieved.

Conventional Sequence Results

An extensive analysis of the quaternary mixture was conducted. The ternary diagram representing furfural-water-formic acid at 101.325 kPa, using the NRTL-HOC thermodynamic model, is shown in Fig. S3 in the supplementary material, corroborating the presence of two azeotropes within the mixture. The water-furfural mixture exhibited a minimum boiling (unstable node) heterogeneous azeotrope with a mass composition of 64.54% water and 35.46% furfural at 370.94 K. Additionally, a maximum-boiling (saddle) homogeneous azeotrope was observed between formic acid and water, with an azeotropic temperature of 379.96 K and mass compositions of 24.75% water and 75.28% formic acid. The presence of the heterogeneous azeotrope and the limited flow of formic acid (B) rendered the separation of the mixture into AB/CD and AB/C unfeasible. Here, A

represents water, B denotes formic acid, C stands for furfural, and D represents levulinic acid. Consequently, achieving the desired purities and recoveries of all products in CS3 and CS5 designs was deemed impossible, leading to the exclusion of these designs from subsequent optimization and intensification efforts. Therefore, in the initial phase, conventional CS1, CS2, and CS4 designs were evaluated. The CS1 design is taken as a comparative point in all the designs studied. The results of the three designs are shown in Table 2 and Fig. 3.

The results show that both the CS2 and CS4 designs have better results than the CS1 design, because in both sequences, only the water is removed by the top of the first distillation column. Furthermore, in the CS1 design, water, furfural, and formic acid are also separated through the top, which affects the required temperature for separation, thereby influencing energy consumption and the overall cost of system services.

On the other hand, CS2 and CS4 designs, their energy consumption is very similar, with the CS4 design having the

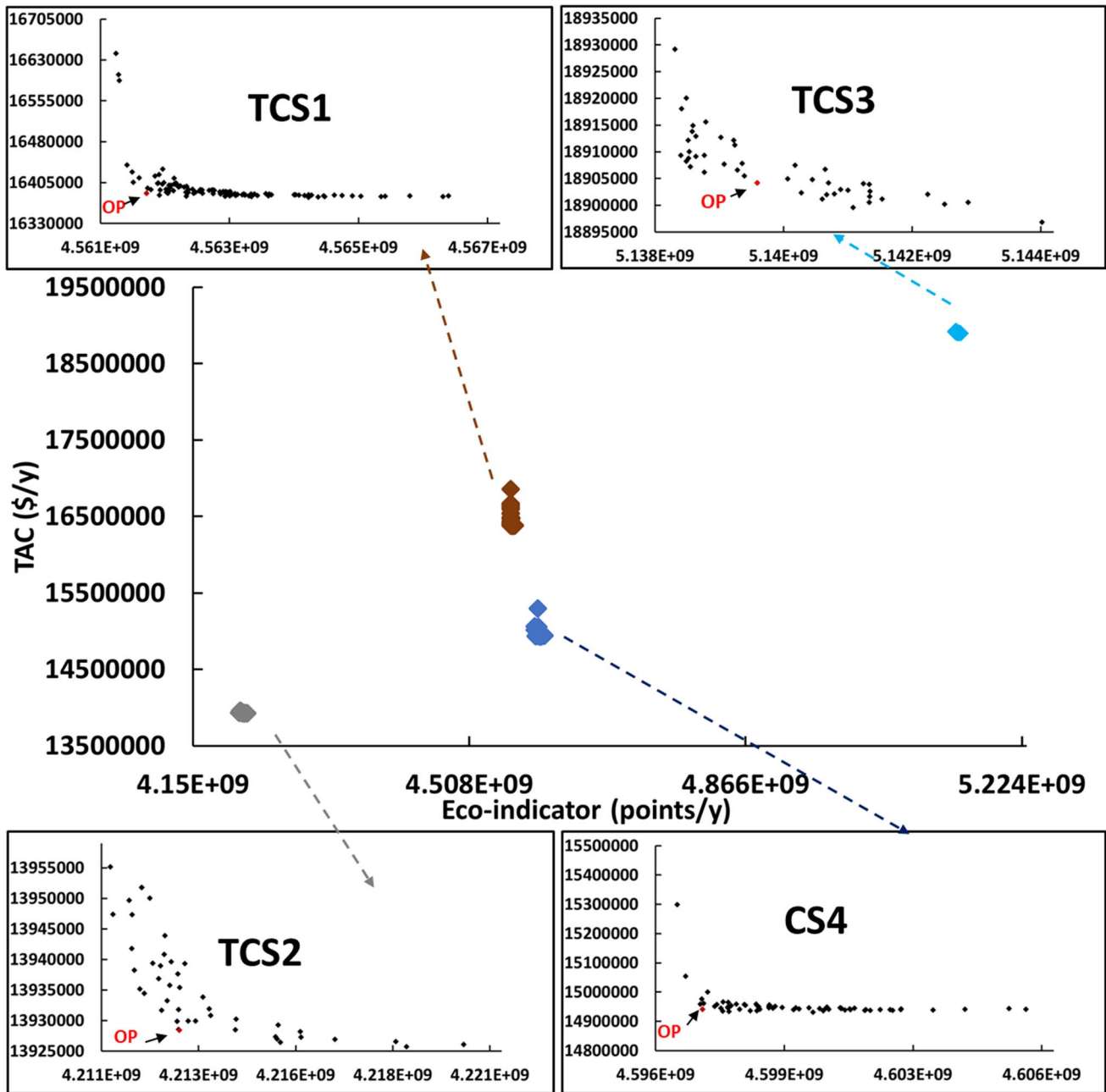


Fig. 4 Superposed Pareto chart of the optimized designs of thermally coupled distillation configurations

lowest consumption. The decrease in energy consumption of the CS4 design is because the column where the formic acid is purified has a lower reflux ratio than the column that performs the same function of the CS2 design. On the other hand, the first distillation column, which in both designs fulfills the function of separating water, in the CS4 design, is smaller, impacting a reduction in the energy consumption of that column compared to the CS2 design. Therefore, the CS4 design presents the best results, presenting a saving in TAC of 19% and EI99 of 14%, compared to the CS1 design.

Thermally Coupled Sequence Results

Starting from the topology of the CS4 design shown in Fig. 2, it is possible to generate a modified thermally coupling scheme if a heat exchanger (reboiler or condenser) directly connected to a non-product stream is replaced with a liquid/vapor stream. The first thermally coupled design TCS1 incorporates a thermal coupling at the bottom of the first distillation column, where the steam from the second distillation column is intended to satisfy the full energy

Table 4 Design parameters and performance indexes for intensified schemes

	Parameter	TES1	DWCS1	SII
C1	Number of stages	27	27	26
	Extractant (t/h)	106.031	106.031	106.024
	Diameter (m)	1.164	0.987	1.359
C2	Number of stages	24	24	19
	Feed stage	15	14	14
	Reflux (kg/kg)	0.041	0.031	0.402
	Reboiler duty (MW)	9.436	9.417	9.442
	Diameter (m)	1.138	1.324	0.836
	C3	Number of stages	41	41
Feed stage		26,15	26,15	18
Reflux (kg/kg)		239.790	239.805	353.25
Reboiler duty (MW)		14.230	14.25	20.722
Diameter (m)		1.488	0.678	1.139
Steam outlet stage		16	16	-
Steam flow (kg/h)		100,591.162	100,593.475	-
Side outlet				14
Side outlet flow (kg/h)				100,505.101
C4		Number of stages	8	9
	Feed stage	2	2	-
	Reboiler duty (MW)	1.41	1.41	-
	Diameter (m)	1.031	0.662	-
	Liquid outlet stage	1	1	-
	Liquid flow (kg/h)	110,210.787	110,210.788	-
Levulinic acid (%w/w)	0.981	0.981	0.981	
Formic acid (%w/w)	0.851	0.857	0.857	
Furfural (%w/w)	0.999	0.999	0.999	
TAC (\$/y)	1.43E+07	1.43E+07	1.77E+07	
EI99 (points/y)	4.35E+09	4.34E+09	5.22E+09	
TAC saving	23%	23%	5%	
EI99 saving	19%	19%	3%	

consumption of the first distillation column, as shown in Fig. S4 in the supplementary material.

The second thermally coupled design TCS2 incorporates a thermal coupling at the top of the second distillation column, where the liquid from the third distillation column performs the function of reflux ratio in the second distillation column. Simultaneously, the steam flow exiting the dome of the second distillation column aids in reducing the energy needed in the third distillation column, as shown in Fig. S5 in the supplementary material. For the latest thermally coupled design TCS3, the two previous thermal couplings were integrated, as shown in Fig. S6 in the supplementary material.

The results of the three thermally coupled designs are shown in Table 3 and Fig. 4. Before carrying out the analysis of the results, it would be expected that the design of the three proposed designs would present better values than the conventional starting design (CS4), due to the energy savings due to the integration of heat. However, the results show a different behavior that is worth analyzing.

In the TCS1 design, a small decrease in the overall thermal load is achieved compared to the CS4 design, due to the thermal coupling. The decrease is reflected in the EI99. However, it is notorious that it suffered an increase in the TAC, and this is because the temperature at the bottom of the second distillation column is higher than the first distillation column. Therefore, the cost associated with steam to meet energy consumption increases.

Finally, the TCS3 design presented a lower overall energy consumption than the CS1 design, which was reflected in the decrease of the EI99, but this was not better than that obtained by the other two thermally coupled designs or the CS4 design. Similar to the TCS1 design, elevated energy consumption in the second distillation column renders the process more expensive, resulting in the first proposed design yielding a higher total annual cost (TAC) than the comparative CS1 design. Therefore, the TCS2 design presents the best results of thermally coupled designs and outperforms

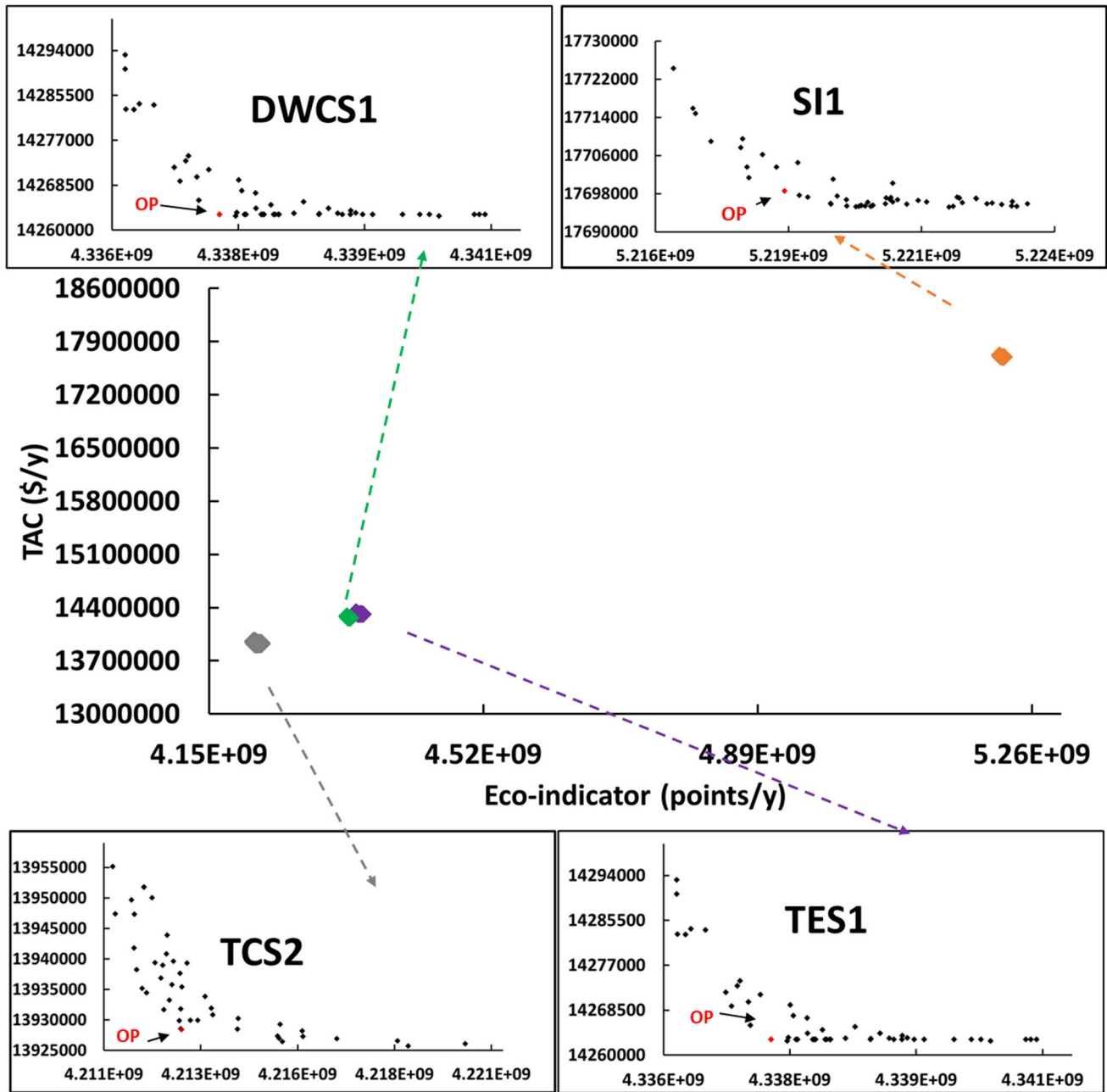


Fig. 5 Superposed Pareto chart of the optimized designs of intensified distillation configurations

the CS4 design, achieving a 25% TAC saving and a decrease in EI99 compared to the CS1 design, recalling that the CS4 design had achieved a decrease of 19% and 14%, respectively.

Intensified Design Results

Due to the significant cost escalation resulting from the thermal coupling of the first distillation column with the second column, as discussed earlier, the process intensification continued. Additionally, considering that the TCS2

design demonstrates superior values for the objective functions among the studied designs, the intensification proceeded through the movement of sections in this design. Through the thermal coupling, there are column sections where either a condenser or a reboiler provides a common reflux ratio/vapor boil up between adjacent columns [46]. With this consideration, it is possible to transpose column sections to generate thermally equivalent sequences. Note that the down scheme in Fig. S7 in the supplementary material was obtained from the corresponding thermally coupled sequence by moving Section 5 over Section 3. This

Table 5 Summary of results for all studied schemes

Scheme	TAC (\$/y)	EI99 (points/y)	TEC (MW)	TAC per kg of levulinic acid (\$/kg)	TEC per kg of levulinic acid (MW/kg)	EI99 per kg of levulinic acid (points/kg)	TAC saving	EI99 saving
CS1[12]	1.85E+07	5.36E+09	30.976	0.351	4.99E−03	101.486		
CS2	1.56E+07	4.70E+09	27.160	0.293	4.34E−03	88.273	16%	12%
CS4	1.49E+07	4.60E+09	26.575	0.282	4.26E−03	86.775	19%	14%
TCS1	1.64E+07	4.56E+09	26.369	0.308	4.21E−03	85.580	12%	15%
TCS2	1.39E+07	4.21E+09	24.352	0.261	3.88E−03	78.982	25%	21%
TCS3	1.90E+07	5.16E+09	29.850	0.356	4.75E−03	96.682	-2%	4%
TES1	1.43E+07	4.35E+09	26.369	0.268	4.20E−03	81.509	23%	19%
DWCS1	1.43E+07	4.34E+09	24.352	0.268	3.88E−03	81.320	23%	19%
SI1	1.77E+07	5.22E+09	29.850	0.332	4.75E−03	97.771	5%	3%

scheme is a thermodynamic equivalent scheme (TES1) of the thermally coupled TCS2 sequences in Fig. S5 in the supplementary material.

Up to this point, thermodynamic schemes featuring a side stripper/rectifier have been devised. Two distinct avenues can be pursued to enhance the process:

i) **DWC synthesis:** To create a dividing wall column, it is enough to integrate the single side section into the second distillation column. As depicted in the lower scheme of Fig. S8 in the supplementary material, a stripping section (column Section 6) is positioned within the column, resulting in a DWC (DWCS1) with two reboilers. In this arrangement, column 3 represents the shell of the dividing wall column. Consequently, any alteration in the number of stages significantly impacts the total annual cost (TAC) in comparison to other columns due to the steel cost of the column’s dividing wall. The stages of column 4 and the shell of column 3 constitute the dividing wall column. It is worth noting that the DWCS1 design differs from the proposals of Errico et al. [25],

as it was incorporated due to the potential cost savings associated with this type of column.

ii) **Elimination of column section:** Once again, beginning with the thermodynamic equivalent schemes, the methodology is rather straightforward; it is only necessary to eliminate column Section 6 and instead add a side stream. Consequently, the lower scheme in Fig. S9 in the supplementary material illustrates the intensified scheme (SI1).

The results of the three thermally coupled designs are shown in Table 4 and Fig. 5. The design parameters between TES1 and DWCS1 are very similar, as expected; the only difference between them is the column diameters. One would anticipate that the cost of DWCS1 would be much lower by reducing the steel cost. However, since column C3 represents the shell of the column and the generated wall is only nine stages; this cost reduction is small, as is the reduction in environmental impact.

On the other hand, in the SI1 design, the reflux ratio was significantly increased compared to the other designs. This is due to the large difference in product flows, and this increase

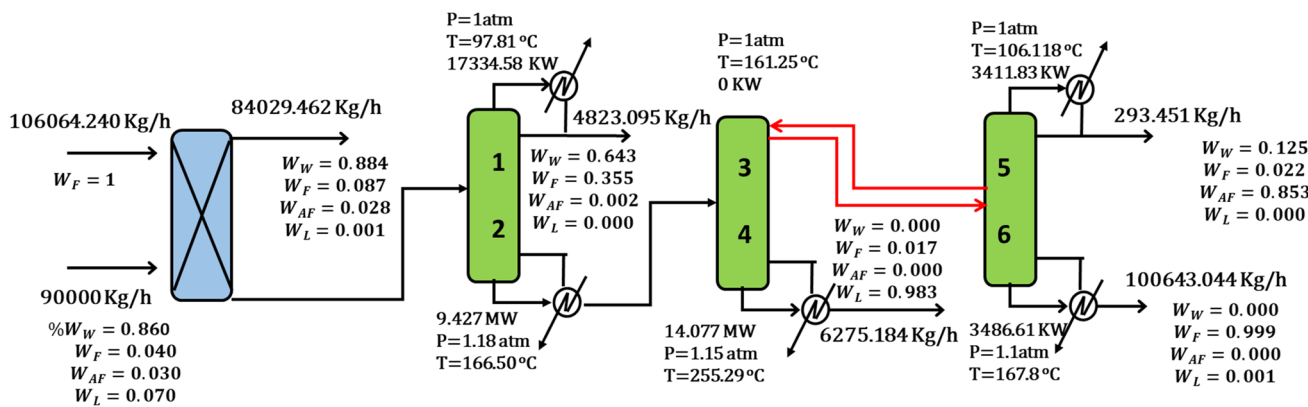


Fig. 6 Optimal configuration of TCS2 design

Table 6 Summary of results for all studied schemes

Scheme	TAC (\$/y)	Levulinic acid obtained (kg/h)	TAC per kg of levulinic acid (\$/kg)
TCS2	1.39E+07	6275	0.261
DWCS-D [12]	1.79E+07	6194	0.341
PS-TDWC-D [18]	1.37E+07	6187	0.261

in reflux had a negative impact on the thermal load, leading to an increase in the TAC and the EI99. Therefore, considering the intensified schemes, DWCS1 is the one that shows the best results with savings of 23% and 19% in TAC and EI99, respectively, compared to the CS1 design.

General Results

The synthesis route found where benefits and economic benefits were found is shown in Figs. S10 and S11. It can be observed that thanks to the systematic synthesis, the study of alternatives generated from designs CS3 and CS5, which would be thermodynamically infeasible, was avoided. And the alternatives with limited potential for economic savings and environmental impact reduction were also excluded. The best results are summarized in Table 5. To have a comparison regarding the total energy consumption (TEC), the energy requirements of each design were placed.

All designs evaluated in this study achieved savings between 5–25% and 3–21% in TAC and EI99, respectively, compared to the CS1 design, except for the TCS3 design, which, due to its high energy consumption, experienced a 2% increase in TAC. Six of the identified designs outperformed the best design by Alcocer-García et al. [12], thanks to the systematic synthesis employed in this study, leading to a reduction in both the cost associated with levulinic acid purification and its environmental impact. TCS2 design (Fig. 6) presents the best results, achieving a 25% TAC saving and a decrease 21% in EI99 compared to the CS1 design. Obtaining the following values per kilogram of levulinic acid produced purification cost of \$0.261, environmental impact of 78.982 points, and an energy expenditure of 3.88E – 03 MW, values below the conventional design used as a reference and the best design reported by Alcocer-García et al. [12].

The TSE1 and DWCS1 designs closely approach the TCS2 design, which was the top-performing alternative, making it important to consider these alternatives in a more robust analysis that incorporates other metrics such as control and safety to ensure the attainment of the most sustainable process.

Additionally, Table 6 shows a comparison between the best result obtained in this study (TCS2) and the best results reported in the Alcocer-García et al. [12] (DWCS-D) and Nhien et al.

[18] (PS-TDWC-D) where alternatives are presented to separate the same mixture studied as in this case study.

Obtaining that the TCS2 design presents better results in costs and environmental impact than the best design reported by Alcocer-García et al. [12] and similar values in terms of purification cost per kilogram of levulinic acid with respect to the best design found by Nhien et al. [18]. The TCS2 design represents a system with a single thermal coupling, and Nhien et al.'s [18] proposal is a complex system that includes a dividing wall column with a decanter included, which could reflect that the TCS2 design presents fewer detailed engineering complications, making it a better alternative.

Conclusions

This study employed sequential synthesis, process intensification, and multi-objective optimization to develop schemes for purifying levulinic acid. Meticulous set selection streamlined the evaluation process, identifying the synthesis route offering the most promising economic and environmental benefits. Notably, the TCS2 hybrid sequence emerged as particularly promising, exhibiting superior economic viability and environmental sustainability. While process intensification strategies have shown significant improvements, a systematic exploration of process synthesis is imperative to ensure optimal outcomes, balancing economic feasibility and environmental impact reduction. By leveraging synthesis methodologies and optimization techniques, this study advances purification processes for levulinic acid, promoting sustainable bioproduction pathways.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s12155-024-10765-0>.

Data Availability The authors declare that the data supporting the findings of this study are available within the paper and supplementary information files.

Declarations

Conflict of Interest The authors declare no competing interests.

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