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Multi-objective optimization of intensified processes for the purification of levulinic acid involving economic and environmental objectives

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ABSTRACT

Levulinic acid obtained from acid hydrolysis of lignocellulosic biomass is considered within the twelve main chemicals from biomass in terms of economic potential due to its large number of applications. As product of hydrolysis is obtained a quite diluted stream which contains a lot of water. Consequently, the processing cost is high and it has limitations for further scaling up at industrial level using conventional separation schemes. In the downstream process proposed in this work, initially the water content is removed using a liquid-liquid extractive column, then it is purified by means of a distillation columns-based process. Recently, a set of separation designs has been implemented, including the use of decanters and intensified columns, which has reduced the cost of the process. However, these studies have only focused on optimizing the total annual cost, losing sight of the environmental impact of the process. In addition, some improvements may be applied from the process intensification point of view either by thermally couplings or considering a single or multiple walls in a column. Therefore, in this work four LA purification designs are studied, a conventional distillation sequence, a dividing wall column arrangement and a decanter, a dividing wall column configuration with a decanter and thermal coupling, and two dividing wall column and decanter. Those schemes were designed and optimized under a rigorous optimization process by means of a multi-objective hybrid algorithm, differential evolution with tabu list considering two objectives: 1) the total annual cost as the economic criterion and 2) the eco-indicator 99 as the environmental index. The results indicated that the intensified design (using a single dividing wall column) presents better results, with economic savings about 8.42% and a decrease in 10.94% the Eco-indicator 99 in comparison with the optimal conventional sequence.

1. Introduction

Levulinic acid (LA) is a specialized chemical in a relatively small market of high added value (i.e. approximately 1 million pounds/year at 8.81–13.22 dollar/kg) [1]. Additionally, levulinic acid has enormous potential as an economical raw material to produce a range of chemical substances of industrial importance such as: chiral reagents [2], biologically active materials [3], polyhydroxyalkanoates [4], polymers [5,6], polymerization initiators [7], anti-flocculating compounds [8], personal products [9], lubricants [10], absorbers [11], inks [12], coatings [13], electronics [14],photograph [15], batteries [16], drug synthesis [17] and corrosion inhibitors [18], among others.

On the other hand, the greatest potential of levulinic acid in a market projection for 2020 as reported by Bozell et al. [1] is its use in the manufacturing of: Methyltetrahydrofuran, an interesting compound used as an additive for fuels with a potential of 10000–1000000 million pounds/year; delta-amino acid levulinic, a biodegradable herbicide with 175–350 million pounds/year; Diphenolic acid, a plasticizer with 35 million pounds / year and 1,4-butanediol a monomer with 200 million pounds/year.

LA can only be produced so far exclusively using chemical processes catalyzed by acid, unlike other high-value biomass derivatives which can be obtained from a biological route such as fermentation. This characteristic makes levulinic acid especially attractive since currently there is a wide variety of relatively inexpensive lignocellulosic material for its production [19]. The transformation of LA from lignocellulosic material starts with a pretreatment which includes both a thermal hydrolisis and enzymatic hydrolisis to separate hemicellulose and lignin

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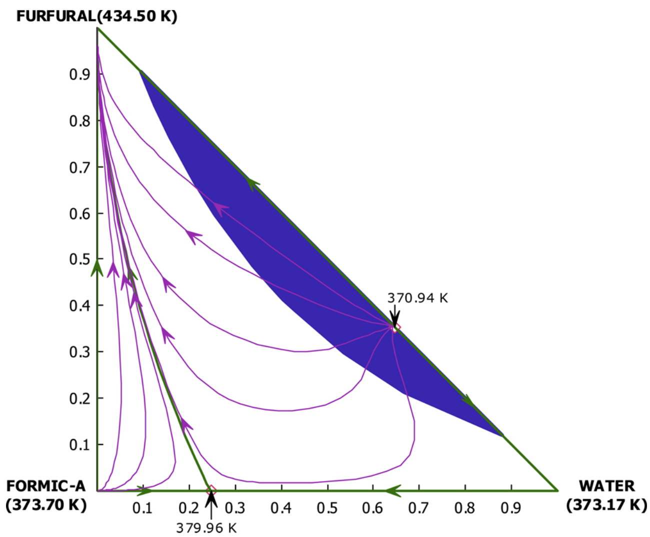

Fig. 1. Azeotropes of the mixture Furfural-water and formic acid.

from glucose respectively. The glucose obtained is subjected to an acid hydrolysis and transform it into 5-hydroxymethylfurfural (HMF), which is an intermediate to reach the LA [20].

The mass composition of the mixture obtained from acid hydrolysis is usually: 1–5% formic acid, 1–5% furfural, 3–8% levulinic acid and the rest is water [21]. For purification purposes, the amount of water represents the biggest problem in the purification of levulinic acid. Note, the presence of water generates the formation of two azeotropes, consequently, the purification of LA is indeed a high energy-demandant process. Fig. 1 shows a ternary diagram furfural-water-formic acid at 101.325 K Pa using the thermodynamic model NRTL − HOC to predict the interaction among those components. This model was used since is able to predicts the equilibrium for polar mixtures and the HOC state equation reliably predicts the solvation of polar compounds and dimerization in the vapor phase that occurs with mixtures containing carboxylic acids [22]. The mixture water-furfural has a minimum-boiling (unstable node) heterogeneous azeotrope with a mass composition of 64.54% and 35.46% mol for water and furfural at 370.94 K respectively, and a maximum-boiling (saddle) homogeneous azeotrope between formic acid and water with an azeotropic temperature of 379.96 K, a mass composition of 24.75% and 75.28% for water and formic acid respectively. In that ternary map, there are two distillation regions divided by the distillation boundary (green line). The LL-region in color blue shows the two liquid phases and the potential of using a decanter to remove the water in this mixture. Several technologies have been developed for the purification of this complex mixture; to increase the concentration of the diluted stream and a promising technology is the combination of either a decanter (splitting the liquid phase division) or liquid-liquid extraction (LLX) with advanced distillation technologies [23,24]. Dunlop [25] proposed the first scheme to separate that mixture, in brief the process consists of a liquid-liquid extractive (using isobutyl-methyl-ketone as extractant agent) column followed by a conventional sequence of distillation columns, however, the main drawback is use of an external solvent. Seibert et al. [26] have proposed a patent to purify LA and formic acid using furfural as extractant, the process consists of a liquid-liquid extraction column and a series of distillation columns; the advantage of this process is the use of furfural, one of the products as solvent, thus the economic and environmental potential increase. Recently, Nhien et al. [27] have presented the first intensification scheme for LA separation, which consists of a liquid-liquid extraction column, followed by a conventional column and a dividing wall column with a decanter.

Bearing in mind the potential of levulinic acid in a bio-based economy, it is important to research and propose separation alternatives from the process intensification view that could reduce the economic impact. In addition, considering that since decades ago, awareness of the environmental impact of chemical processes has taken hold, there is a growing consensus among organizations committed to the environmental performance of the current industry [28–30]. In this manner, it is clear the need of downstream processes that may accomplish both economic and environmental performance, however, this task is not trivial. Note, the separation schemes for such task are modeled including mass and energy balances, equations to represent liquid-liquid-vapor equilibrium, turning the model highly non-linear, potentially non-convex, with degrees of freedom, and subject to be optimized. [31]. Those complex optimization problems may be well solved through stochastic optimization algorithms, since it is not necessary to have the explicit equations of the model [32], in other words, the equations may be solved in a simulator which handle and solve this rigorous model, Aspen plus for example. This kind of optimization process has proved its capabilities for handling quite complex models without losing the rigorousness, the non-linearity and the potential non-convexity [33–35].

Therefore, the objective of this work is the multiobjective optimization taking the total annual cost (TAC) and the eco-indicator 99 (EI99) as performance indexes using a stochastic optimization algorithm, differential evolution with the tabu list (DETL). The optimization process approaches 4 different schemes for the purification of levulinic acid: a conventional distillation sequence (CS), a dividing wall column arrangement and a decanter (DWCS-D), a dividing wall column configuration with decanter and a thermally coupled scheme (DWCS-DA), and two dividing wall columns with a decanter (TDWS-D). Although, previously similar schemes have been studied, this work adds modifications to their architecture, like modifying the external cooling system before the decanter by a total condenser, adding thermal coupling between columns and using multiple divided wall column. As results, this multi-objective optimization will allow obtaining designs where both objective functions are balanced and reach its minimum values.

2. Problem statement

As has been previously mentioned, the main drawback in the LA purification is the amount of water in the mixture to be purified. In this sense, for improving the production of levulinic acid two strategies may be approached: (1) a chemical approach (synthetic routes that generate a greater production of levulinic acid from biomass), and (2) the optimization of more efficient separation processes than ensure the reduction of the purification energy consumption.

In this work, the efforts are focused only on solving the problem regarding energy consumption in LA purification. This proposal is based on finding processes that ensures a reduction in energy consumption. These processes are designed/optimized considering a process intensification point of view, in other words, the schemes were designed/optimized using thermally couplings and dividing wall columns. The proposed configuration of this work were based on theoretical studies that have showed a lot of advantages regarding reduction of energy consumption compared to conventional sequences [36–40]. For example, the use of dividing wall columns (DWC), have shown the capability of economic and energy savings about 30% [41,42]. The saving in capital cost is due to the reduction of equipment, a single equipment perform the same task than two conventional columns [43].

Based on the previously mentioned and taking into account that the current processes aim to ensure both the lowest environmental impact and the lowest possible cost, the proposed schemes in this work were designed/optimized through the hybrid stochastic algorithm Differential evolution with tabu list, taking as objective functions: the total annual cost (TAC) and the eco-indicator 99 (EI99) as economic and environmental indicators, respectively. The objective of the optimization is to find economically attractive designs with low environmental impact and to understand the role of the design variables and its connection with the objective functions.

3. Case of study

The LA production rate considered in this study was 5×10^7 kg/year for all proposed hybrid diagrams. A feed stream of 90,000 Kg/h was considered. The mass composition for the feed stream was 86% water, 7% levulinic acid, 4% furfural and 3% formic acid; 298.15 K and 202.65 K Pa. The composition was defined according to Nhien et al. [27]. The flow of furfural used as extractant was considered as a variable to optimize.

All the proposed configurations have been simulated using Aspen Plus V8.8. The NRTL – HOC was selected as the thermodynamic model for calculating the physical properties for the components. The minimum purity targets were set at the 98% (%wt) for levulinic acid, 85% for formic acid and 99.9% for furfural. The purities for levulinic acid and formic acid were considered according to the current industrial uses [44,45].

This study proposed several hybrid designs combining a liquid-liquid extraction column (using furfural as mass separating agent) and distillation columns, all schemes evaluated under a multi-objective optimization strategy using economic and environmental indexes. In brief, we take advantage of simultaneous thermal coupling and heat integration as a process intensification strategy to synthesize this separation schemes. The configurations consist of a conventional scheme (a) and three intensified schemes (b, c, d):

a) Conventional Scheme (CS). For comparison purposes, this design will be further considered as a reference scheme. This design was proposed using the patent published by Seibert et al. [26], to take advantage of furfural as an extractant agent and not to add an external recovery process. This scheme has a liquid-liquid extraction column and three conventional distillation columns, see Fig. 2.

b) Dividing wall column arrangement and a decanter (DWCS-D). This scheme is proposed based on the work of Nhien et al. [27], however, a little modification was implemented by an external cooling system before the decanter. Although this scheme has already been studied, it has not been designed under a rigorous method including its environmental contribution. So, the proposal is to revisit the process including this environmental objective. The dividing wall column was obtained from conventional schemes, through thermal couplings introduction, and movement sections following the procedure of Rong et al. [46,47]. Fig. 3 shows how the dividing wall column with the wall at the top is obtained and its way to simulate it in Aspen plus. Also, observing the triangular diagram in Fig. 1 where the presence of a heterogeneous azeotrope is shown, it is possible to follow the methodology proposed by Doherty et al. [48]. Consequently a decanter is added to take advantage of the presence of the liquid-liquid phase. All synthesis process of DWCS-D is shown in Fig. 4.

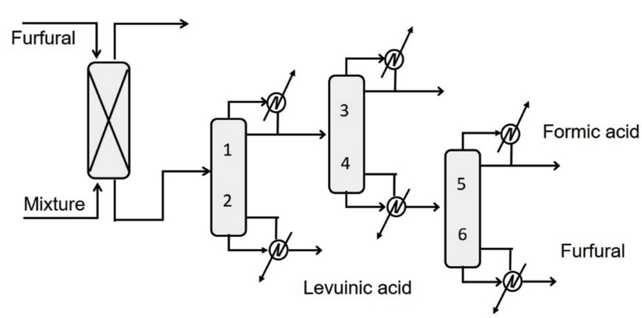

Fig. 2. Conventional sequence (CS).

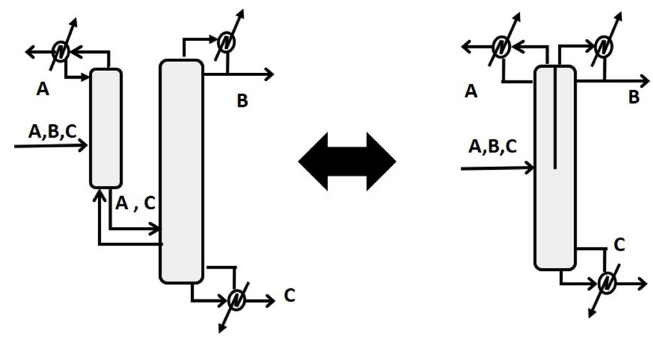

Fig. 3. Dividing wall column and its thermodynamically equivalent scheme.

c) Dividing wall column configuration with a decanter and thermal couplings (DWCS-DA). This scheme includes a liquid-liquid extraction column, using furfural as extractant agent, plus a dividing wall column with decanter. Finally it includes a distillation column with thermal couplings between these two last columns, see Fig. 5. The synthesis of this design was carried out in 4 stages (the dotted arrows indicate the sequence of the process):

I. The starting point is the DWCS-DA scheme.

II. A change between the dividing wall column (II-b) and the conventional distillation column (II-a) is done (II-b and II-a are placed in dotted rectangles, see Fig. 5) with the objective of separating the lighter components (water and formic acid) in the first column.

III. A thermal coupling is set between the last columns. The coupling is done by recirculating a vapour steam flow (blue dotted arrow) which will supply the heat duty to the dividing wall column (see Fig. 5). Several studies [33,34,49–51] have reported energy savings by means of thermal couplings.

IV. A thermal coupling is obtained between the dividing wall column and the conventional column, when the amount of vapor steam flow is able to completely supply the heat duty of the dividing wall column.

d) Double dividing wall column scheme and a decanter (TDWS-D). This design includes a liquid-liquid extraction column, using furfural as an extractant agent and a column with a double dividing wall with a side stream; this design was proposed based on the work of Dejanovic et al. [42] and Ramapriya et al. [52], They employ schemes with double dividing wall to purify quaternary mixtures. The simulation of double dividing wall column in Aspen plus is shown in Fig. 6.

This scheme is intended to increase the potential for both economic and energy savings, as well as improvements in their control properties by increasing the number of recycles. Therefore, starting from the design C, the implementation of a thermal coupling between the dividing wall column and the previously coupled sequence is carried out, thereby a thermodynamic equivalent scheme is generated, see Fig. 7.

4. Optimization procedure

This section describes the optimization objectives and the multi-objective optimization problem. The objective functions considered for this analysis are the total annualized cost (TAC) and the Eco-indicator-

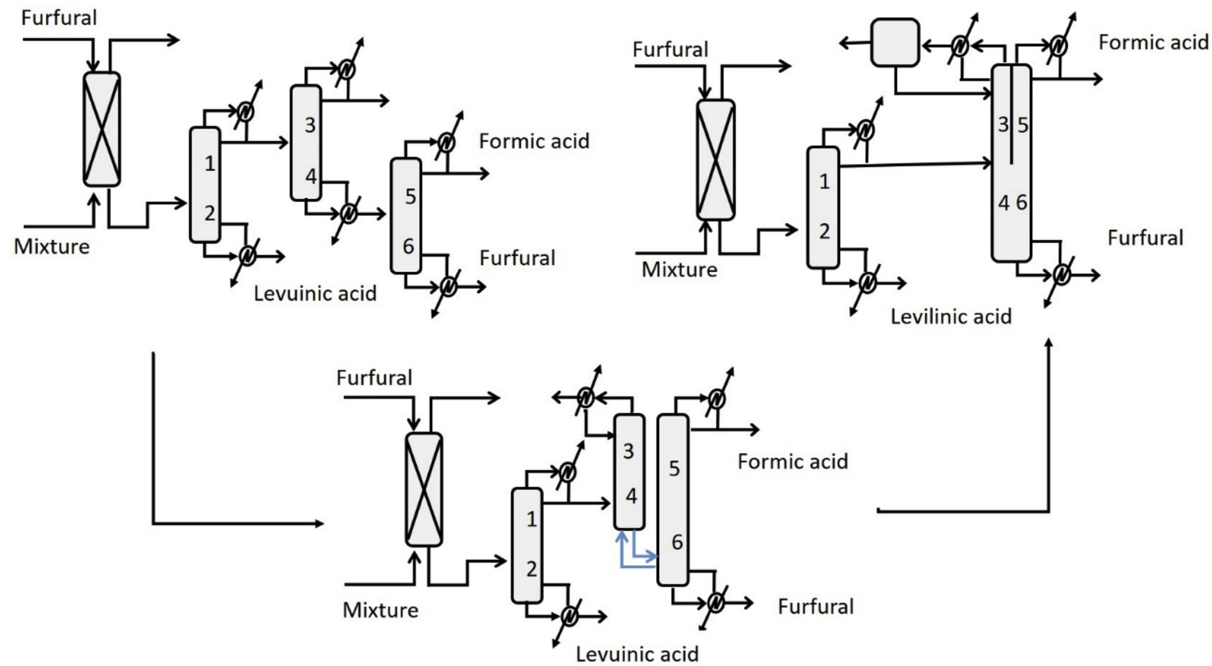

Fig. 4. Synthesis of dividing wall column arrangement and decanter from the reference case (DWCS-D).

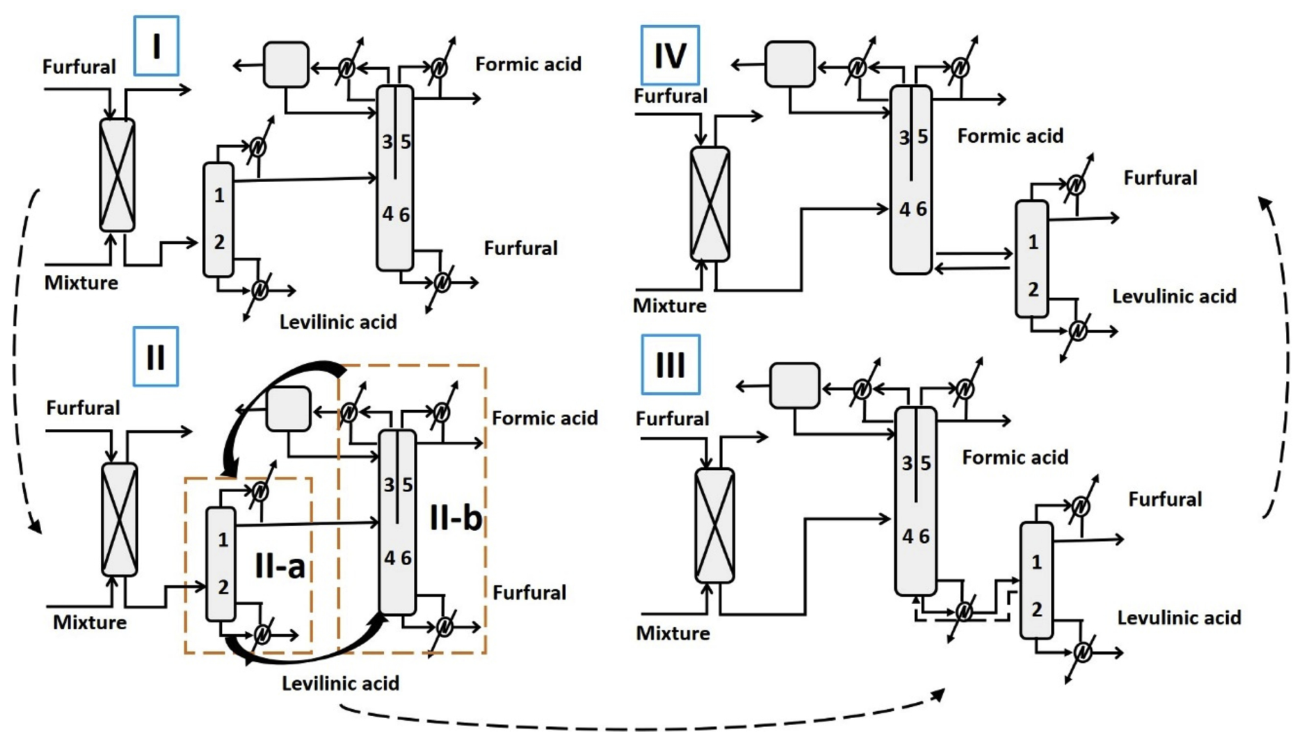

Fig. 5. Synthesis of the dividing wall column configuration with a decanter and thermal coupling (DWCS-DA).

99 (EI99), economic and environmental indexes respectivey. The TAC is proportional to the heat, duty, services, and column size; the EI99 is used to quantify the environmental load of the flow diagrams throughout the life cycle, this includes three main categories of damage: human health, ecosystem quality and depletion of resources.

The design of the different alternatives proposed was performed minimizing the multi-objective function reported in Eq. (1):

$$Min(TAC,\ EI99) = f(N_e,\ N,\ N_f,\ RR,\ D,\ F_L,\ F_V,\ \phi,\ S) \quad (1)$$

Subject to: $y_i P_c \geq x_i P_c$ $w_i F_c \geq u_i F_c$ where N_e is the number of stages

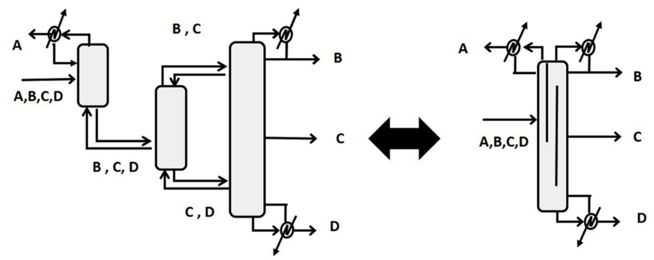

Fig. 6. Double dividing wall columna and its thermodynamically equivalent scheme.

for the extractor, N is 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, 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. In addition, the optimization problem is restricted to the purities y_iP_c, that must be equal to or greater than x_iP_c and the recovery flows of the w_iF_c products that must be greater than or equal to u_iF_c, Due to the complexity of the problem, Differential Evolution with Tabu List (DETL) was used as the optimization algorithm. Differential evolution algorithm is based on 4 main steps: initialization, mutation, crossover and selection [53]. In order to implement the optimization algorithm, Aspen Plus was linked to Microsoft Excel using the dynamic data exchange by COM technology.

4.1. Economic indicator

In order to calculate the total annual cost (TAC), we used the method published by Guthrie [54], which was modified by Ulrich [55] where the cost estimate of a plant is made by separated industrial units, and those equations published by Turton et al. [56], the TAC is calculated with Eq. (2):

Table 1
Unit eco-indicator used to measure the eco-indicator 99 in both case studies.

Impact category	Steel (points/kg)	Steam (points/kg)	Electricity (points/kWh)
Carcinogenic	6.320 E-03	1.180 E-04	4.360 E-04
Climate change	1.310 E-02	1.600 E-03	3.610 E-06
Ionizing radiation	4.510 E-04	1.130 E-03	8.240 E-04
Ozone depletion	4.550 E-06	2.100 E-06	1.210 E-04
Respiratory effects	8.010 E-02	7.870 E-07	1.350 E-06
Acidification	2.710 E-03	1.210 E-02	2.810 E-04
Ecotoxicity	7.450 E-02	2.800 E-03	1.670 E-04
Land Occupation	3.730 E-03	8.580 E-05	4.680 E-04
Fossil fuels	5.930 E-02	1.250 E-02	1.200 E-03
Mineral extraction	7.420 E-02	8.820 E-06	5.700 E-06

$$TAC = \frac{\sum_{i=1}^{n} C_{TM,i}}{n} + \sum_{j=1}^{n} C_{ut,j} \quad (2)$$

Where C_{TM} is the capital cost of the plant, n is the payback period and *Cut* is the cost of the services, respectively. The payback period was considered as 10 years. The equations and parameter for calculating C_{TM} were added in the Appendix A. The values of the economic parameters were taken from Turton et al. [56].

4.2. Environmental indicator

The eco-indicator 99 is one of the best eco-indicators to quantify the environmental impact since its evaluation is based on the life cycle assesment. Its first uses were focused on the construction area [57,58]. Recently, Eco-indicator 99 has been incorporated into the design stage in complex distillation schemes, obtaining intensified designs with lower environmental impact, compared with conventional designs [34,35,59,60].

In the EI99 methodology, the 11 impact categories are aggregated into three major damages categories: human health, ecosystem quality,

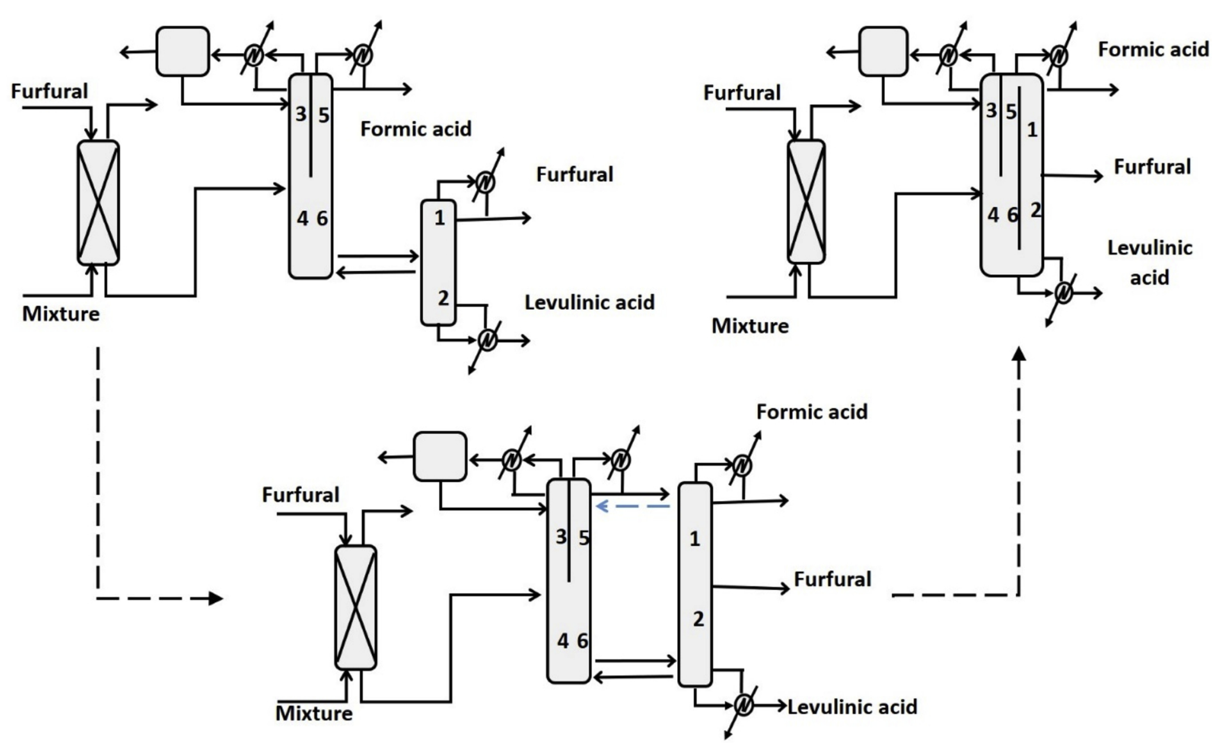

Fig. 7. Synthesis of the multiple dividing wall column and decanter scheme (TDWS-D).

Table 2
Decision variables used in the global optimization process.

Variable	Range of variable	Type of Variable	CS	DWCS-D	DWCS-DA	TDWS-D
Number of stages C1, C2, C3, and C4	10-100	Discrete	X	X	X	X
Feed stage C2	9-99	Discrete	X	X	X	X
Feed stage C3	9-99	Discrete	X	X		X
Feed stage C4	9.99	Discrete	X		X	
Reflux ratio C2	0.01-2/0.01-2	Continuous	X	X		
Reflux ratio C3	0.01-2	Continuous	X			
Reflux ratio C4	5-60/ 5-10 /0.1-5/ 300-350	Continuous	X	X	X	X
Destillate flow C2 (Kg/h)	107000-108000/ 107000-108000/ 5550-6000 / 5550-6000	Continuous	X	X	X	X
Destillate flow C3 (Kg/h)	5550-6000/ 5550-6000/ 280-350	Continuous	X	X	X	
Destillate flow C4 (Kg/h)	280-350/280-350/90000-120000/280-350	Continuous	X	X	X	X
Interconnection steam flow C3 (Kg/h)	1-30000/1-100000	Continuous			X	X
Interconnection steam flow C4 (Kg/h)	1-40000/1-40000/1-200000	Continuous		X	X	X
Interconnection liquid flow C4 (Kg/h)	1-100000	Continuous				X
Furfural flow C4 (Kg/h)	90000-120000	Continuous				X
Diameter C1, C2, C3 and C4 (m)	0.5-5	Continuous	X	X	X	X
Extractant Flow (Kg/h)	100000-120000	Continuous	X	X	X	X

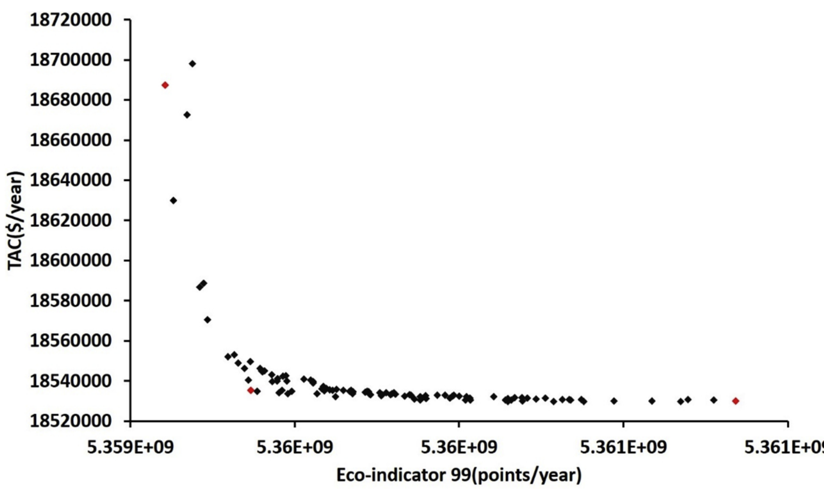

Fig. 8. Pareto front between TAC and Eco-indicator 99 for CS.

and resources depletion. It was quantified following the procedure proposed by Goedkoop and Spriensma [30] as reported Eq. (3):

$$EI99 = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (3)$$

Where β_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\propto_{b,k}$ 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 Pt 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 as the most important in the LA 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 Sprinsma [30], also they are shown in Table 1.

4.3. Optimization methodology

According to Marler and Arora [61], multiobjective optimization (MOO) is the process of systematically and simultaneously optimizing a collection of objective functions. Finding the optimum, then, can be interpreted as finding a good compromise between all the objective functions of the problem.

In terms of mathematical optimization methods, deterministic and stochastic methods can be used to solve high-dimensional, non-linear problems with a very complex search space. Deterministic methods, such as quadratic sequential programming (QSP), have the characteristic of requiring the calculation of first and/or second order derivatives of the function and/or objective limitations, which make these methods not directly applicable to a problem not differentiable or discontinuous. Another disadvantage of such methods is the great dependence of the initial solution chosen in the search for the optimal solution [62,63]. On the other hand, stochastic methods, or global search methods, such as genetic algorithms, have the advantage that they do not require manipulation of the mathematical structure of the function and/or objective limitation and also do not require an initial feasible point [64,65]. Genetic algorithms are robust and more powerful in difficult environments where the search space is usually large, discontinuous, complex and little known. Like any method of stochastic optimization, they are not guaranteed to find the optimal global solution to a problem, but in general, they are good at finding good acceptable solutions [66,67]. Such features have increased the application of genetic algorithms in optimization problems [63,67–69] The optimization technique with the hybrid algorithm of Differential Evolution with tabu List (DETL), has proved to be able to solve complex non-linear and

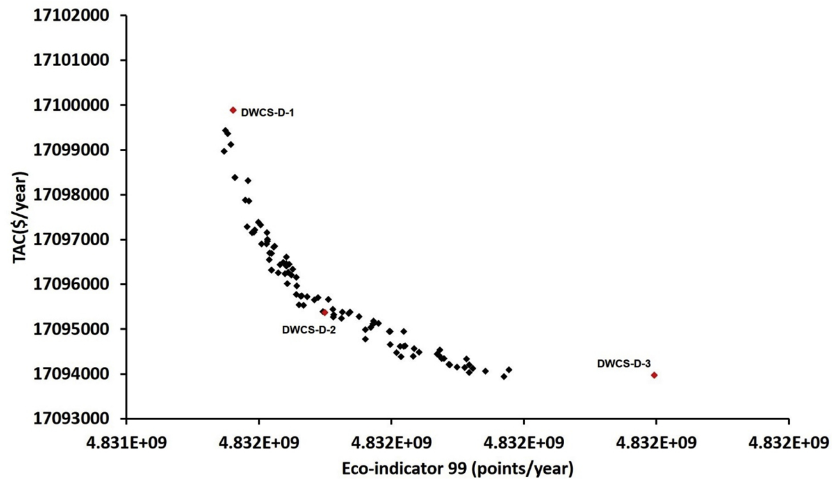

Fig. 9. Pareto front between TAC and Eco-indicator 99 for DWCS-D.

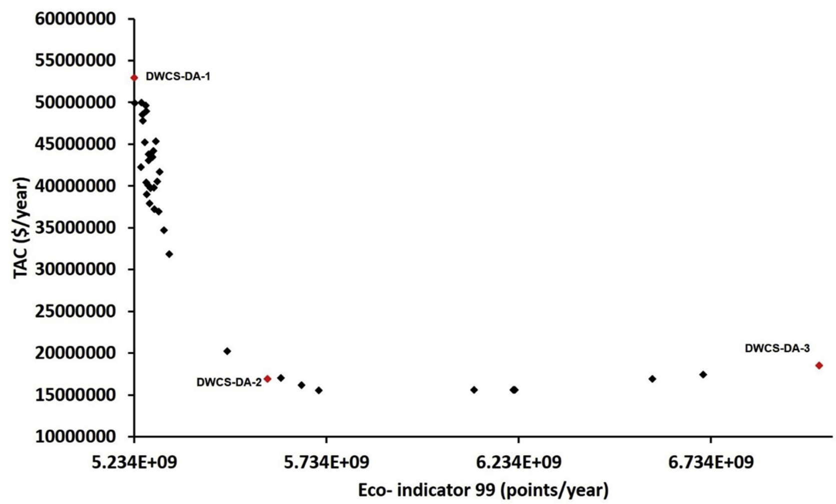

Fig. 10. Pareto front between TAC and Eco-indicator 99 for DWCS-DA.

potentially non-convex problems. In addition, through a reasonable computational time, it is totally feasible to find solutions quite close to the optimal solution [53].

Therefore, in this work the proposed schemes were optimized using the differential evolution method with tabu list (DETL) method, this method showed that the use of some concepts of the metaheuristic tabu can improve the performance of the DE algorithm. In particular, the TL can be used to avoid the revisit of search space by keeping a record of the recently visited points, which can avoid unnecessary function evaluations. The implementation of this optimization method is done

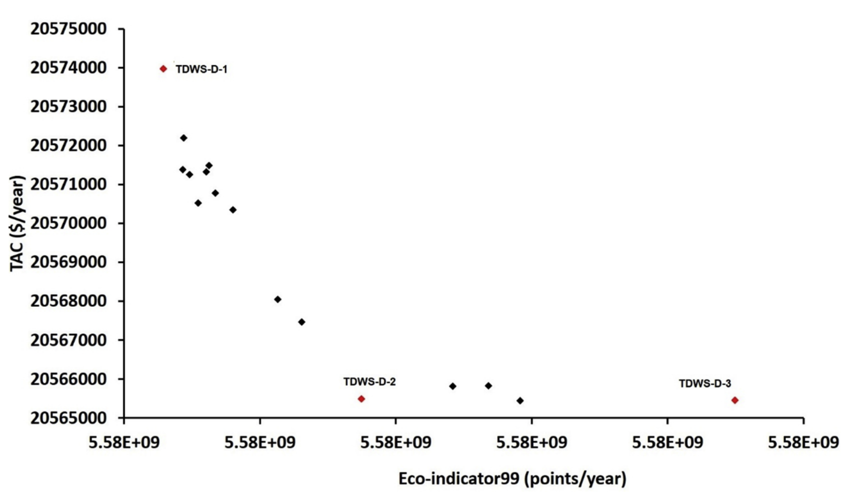

Fig. 11. Pareto front between TAC and Eco-indicator 99 for TDWS-D.

Table 3
Design parameters and performance indexes for CS schemes.

	Parameter	CS-1	CS-2	CS-3
Column 1	Number of stages	22	22	22
	Extractant (kg/h)	106715.2	106722.8	106734.8
	Diameter (m)	1.721	1.434	1.055
Column 2	Number of stages	28	28	28
	Feed stage	13	13	13
	Reflux (kg/kg)	0.076	0.076	0.076
	Reboiler duty (KW)	23024	23026	23030
	Diameter (m)	4.000	3.642	3.800
Column 3	Number of stages	46	46	46
	Feed stage	34	34	34
	Reflux (kg/kg)	0.206	0.206	0.206
	Reboiler duty (KW)	4464	4465	4466
	Diameter (m)	1.650	2.413	2.000
Column 4	Number of stages	60	60	60
	Feed stage	27	28	27
	Reflux (kg/kg)	54.199	54.362	54.683
	Reboiler duty (KW)	3487	3486	3490.
	Diameter (m)	2.8	2	2
Purity	Levulinic acid (%w/w)	0.980	0.980	0.981
	Formic acid (%w/w)	0.850	0.851	0.851
	Furfural (%w/w)	0.999	0.999	0.999
	TAC ($/year)	18687330	18535217	18529906
	EI99 (points/year)	5358974057	5359365770	5360841267

Table 5
Design parameters and performance indexes for DWCS-DA schemes.

	Parameter	DWCS-DA-1	DWCS-DA-2	DWCS-DA-3
Column 1	Number of stages	23	25	23
	Extractant (kg/h)	106975.7	106610.9	106761.8
	Diámeter (m)	1.257	1.054	1.043
Column 2	Number of stages	31	25	28
	Feed stage	13	6	10
	Diameter (m)	1.682	1.437	0.970
Column 3	Number of stages	43	46	40
	Feed stage	31	25	28
	Steam outlet stage	32	26	29
	Steam flow (Kg/h)	47969.3	45756.8	49202.8
	Diameter (m)	3.073	3.040	2.002
Column 4	Number of stages	40	29	18
	Feed stage	6	14	13
	Reflux (kg/kg)	4.620	0.253	0.407
	Reboiler duty (KW)	82855	26478	28991
	Steam flow (Kg/h)	64908.1	61448.1	62624.9
	Steam outlet stage	7	15	14
	Diameter (m)	2.044	1.766	1.527
Purity	Levulinic acid (%w/w)	1	1	0.99971938
	Formic acid (%w/w)	0.877	0.912	0.895
	Furfural (%w/w)	0.999	0.999	1.000
	TAC ($ / year)	52888127	16938630	18509252
	EI99(points/ year)	5234661437	5580697135	7015470224

through a hybrid platform using Microsoft Excel and Aspen Plus. The vector of decision variables (that is, the design variables) is sent from Microsoft Excel to Aspen Plus using DDE (Dynamic Data Exchange) through COM technology. In Microsoft Excel, this vector is attributed to the process variables that Aspen Plus will evaluate. After the simulation is done, Aspen Plus returns the resulting vector to Microsoft Excel. Finally, Microsoft Excel analyzes the values of the objective functions and proposes new values of decision variables according to the stochastic optimization method used [70,71]. The code to link both aspen plus and Microsoft excel is shown in Appendix B. For the optimization of the process routes analyzed in this paper, the following parameters are used for the DETL method: 120 individuals as initial generation, 417 generations, a taboo list of 50% of the total individuals, a Taboo radius of 0.00001, as well as 0.8 and 0.6 for the crossing factor and mutation fractions, respectively. These parameters were proposed based on similar work where complex distillation schemes were approached [33–35]. The tuning process consists of performing several tests with different numbers of individuals and generations, in order to detect the best parameters that allow obtaining the best performance of the convergence of DETL. All the variables to be optimized are found in Table 2. The range of such values was not open. In other words, limits were established on variables such as: reflux ratio, diameter and number of stages, according to the recommendation of Gorak et al. [72] and Douglas [73]. The natural limits for the concentrations were considered between 0 and 1, the mass interconnector flows limits was fixed according the mass balance.

Table 4
Design parameters and performance indexes for DWCS-D schemes.

	Parameter	DWCS-D-1	DWCS-D–2	DWCS-D—3
Column 1	Number of stages	21	21	21
	Extractant (kg/h)	107985.9	107975.2	107930.1
	Diameter (m)	0.689	0.529	0.583
Column 2	Number of stages	28	28	28
	Feed stage	11	11	11
	Reflux (kg/kg)	0.069	0.069	0.069
	Reboiler duty (KW)	23188	23188	23192
	Diameter (m)	3.497	3.577	3.454
Column 3	Number of stages	22	20	20
	Feed stage	4	4	4
	Reboiler duty (KW)	0.000	0.000	0.000
	Diameter (m)	1.673	1.664	1.504
Column 4	Number of stages	67	62	55
	Feed stage	22	20	20
	Reflux (kg/kg)	8.22,342,399	8.205	8.183
	Reboiler duty (KW)	4739.929	4740.040	4739.759
	Steam flow (Kg/h)	30023.45	30024.80	30024.14
	Steam outlet stage	23	21	21
	Diameter (m)	1.908	1.984	1.952
Purity	Levulinic acid (%w/w)	0.980	0.980	0.980
	Formic acid (%w/w)	0.953	0.953	0.953
	Furfural (%w/w)	0.999	0.999	0.999
	TAC ($ / year)	17099885	17095373	17093973
	EI99(points/ year)	4831561205	4831698963	4832196959

Table 6
Design parameters and performance indexes for TWCS-D schemes.

	Parameter	TWCS-D-1	TWCS-D-2	TWCS-D-3
Column 1	Number of stages	24	24	24
	Extractant (kg/h)	106769.1	107752.1	106691.2
	Diameter (m)	0.586	0.634	0.626
Column 2	Number of stages	16	16	17
	Feed stage	12	15	15
	Diameter (m)	0.613	0.573	0.615
Column 3	Number of stages	23	20	20
	Feed stage	16	16	17
	Steam outlet stage	17	17	18
	Steam flow (Kg/h)	62115.8	69032.7	71415.3
	Diameter (m)	1.112	1.301	1.412
Column 4	Number of stages	28	25	25
	Feed stage	3	3	4
	Feed stage 2	26	23	24
	Reflux (kg/kg)	315.192	345.046	304.871
	Reboiler duty (KW)	7703515	7703515	7703515
	Liquid flow (Kg/h)	32266.1	27215.9	33957.1
	Steam flow (Kg/h)	40200.3	102447.3	169897.5
	Liquid outle stage	2	2	3
	Steam outlet stage	17	8	19
	Liquid outlet stage	23	20	23
	Diameter (m)	1.611	2.259	3.563
Purity	Levulinic acid (%w/w)	0.986	0.986	0.986
	Formic acid (%w/w)	0.859	0.859	0.859
	Furfural (%w/w)	0.999	0.999	0.999
	TAC ($ / year)	20573979	20565485	20565457
	ECO (points/ year)	5579720214	5579720287	5579720425

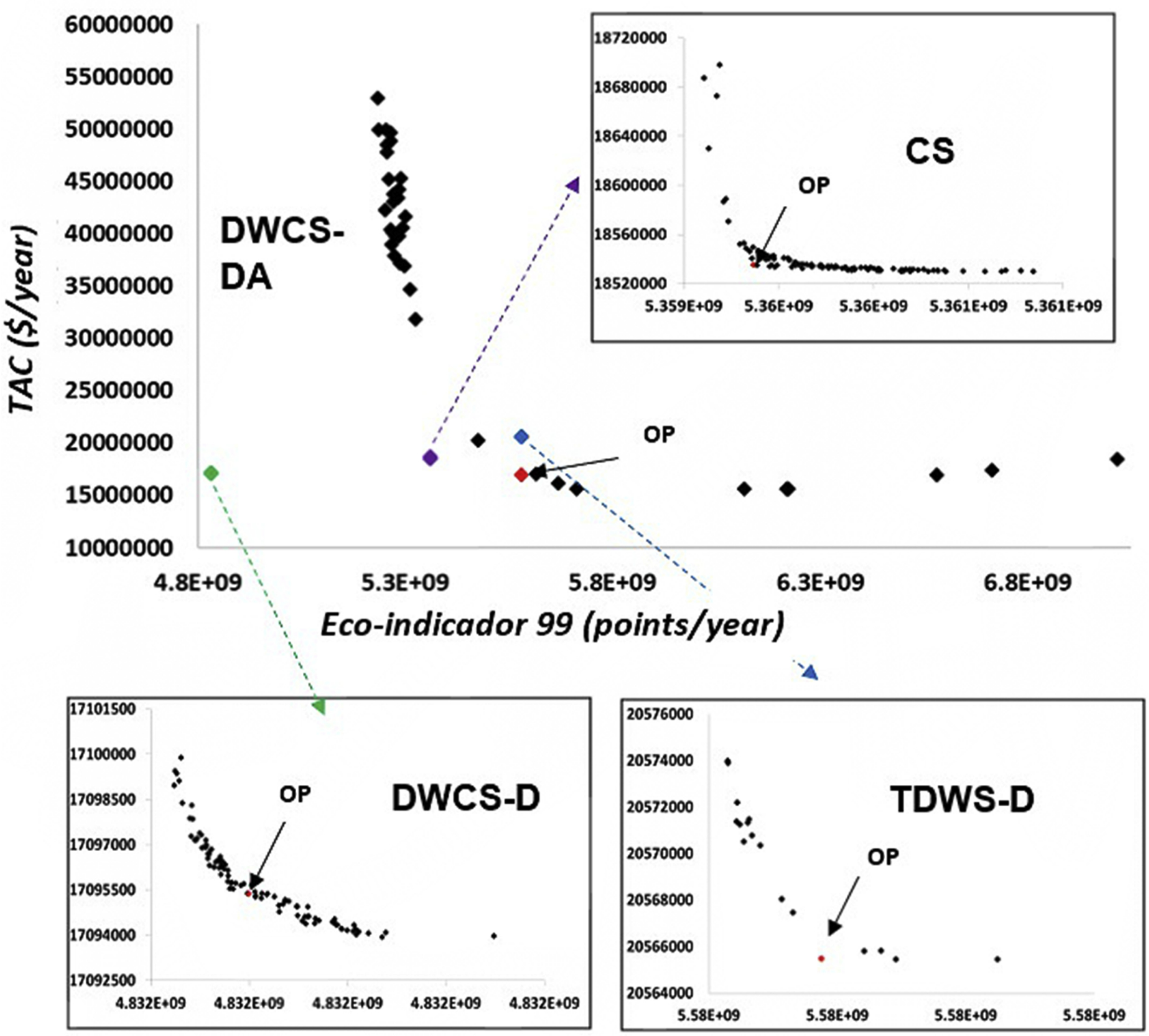

Fig. 12. Superposed Pareto chart of the optimized designs of distillation configurations.

Table 7
Objective function values for the selected configurations in Fig. 12.

Objective Function	CS-2	DWCS-D-2	DWCS-DA-2	TDWS-D-2
TAC [M$ yr^{-1}]	18.53	17.09	16.93	20.56
EI99 [Gpoints yr^{-1}]	5.36	4.83	5.58	5.58
Purity of LA [wt%]	98.02	98.01	99.92	98.58
TAC saving[%]		8.42	9.43	−9.87
EI99 saving[%]		10.92	−3.7	−3.95

5. Results

This section presents the main results of the simultaneous evaluation of the multi-objective function. All the optimization results acomplish all constraints related to purity and recovery. Before the optimization was made, all base case designs were modeled and simulated in Aspen Plus using the rigorous RADFRAC unit. Hence all process schemes were robustly designed considering the complete set of MESH equations (mass balances, equilibrium relationships, summation constraints, and energy balance).

Figs. 8–11 show the convergence behavior of the objective functions after the optimization. All Pareto fronts were obtained after 50,000 evaluations, as afterward, the vector of decision variables did not produce any meaningful improvement. It was assumed that the DETL algorithm achieved the convergence at the tested numerical terms and thus the results reported here correspond to the best solution obtained. On each Pareto front, 3 points are shown, the most expensive design (1), the design considered optimal (2) (considered where both objective functions are balanced and find its minimum values) and the most polluting design (3). The parameters of designs selected are showed in Table 3. In this case (Table 3), those three designs have similar values in some design variables such as reflux ratio and number of stage, however, the increase in the TAC is related to the diameter of the columns. Note, increasing the diameters consequently increase the value of TAC, on the other hand, the EI99 is mainly affected by the increase in reboiler duty, since steam used for heating is one of the largest

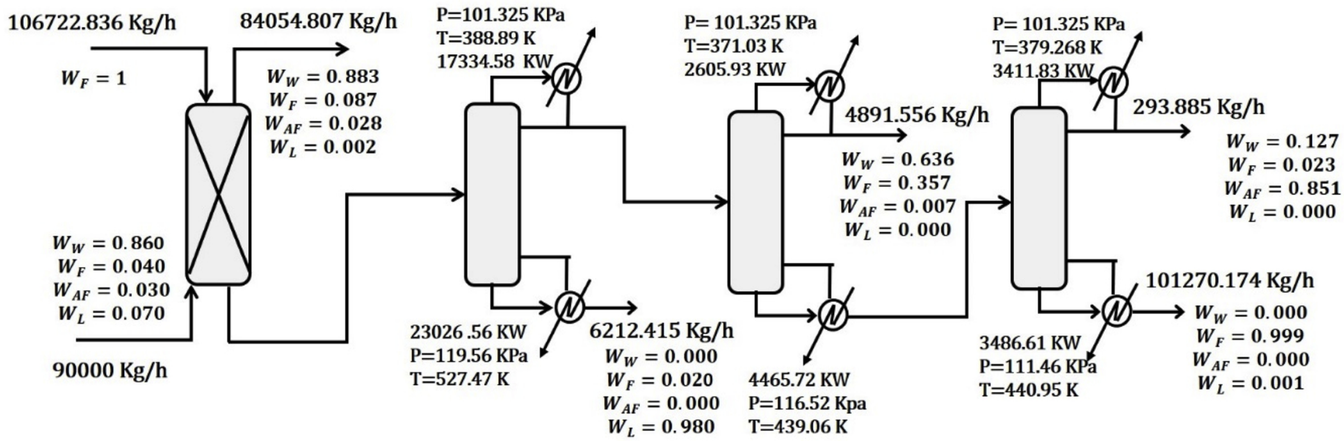

Fig. 13. Optimal configuration of CS.

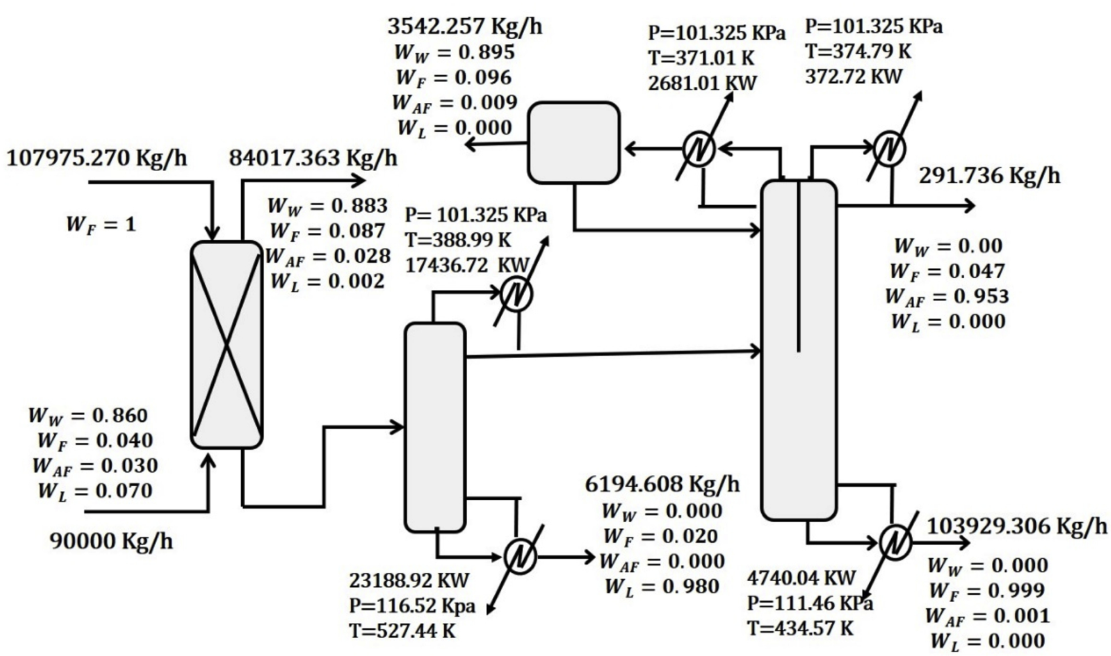

Fig. 14. Optimal configuration of DWCS-D.

contributors to the EI99 [74].

The parameters of the 3 designs studied for the DWCS-S schemes are presented in Table 4. Note that increments on EI99 are due to the steam used in the reboilers, similar that CS schemes. In this scheme, the column 4 represents the shell of the dividing wall column, therefore, the increase or decrease of stages, generates a greater impact on the TAC in comparison with other columns due to the steel cost of the column dividing wall. In other words, the stages of column 4 and the shell of column 3 represent the dividing wall column. Therefore, the greater number of stages will produce an increase on TAC values.

The design parameters of the three selected designs of DWCS-DA are presented in Table 5, all parameters show that none of the design variables of the optimization converged to a unique value, both DWCS-D and CS converge in a large range of values. This diversity of values may be due to the increment in intensification and the movement of the dividing wall column jointly the variation of the extractant mass flow. One of the advantages of these variations is that the designs achieve purities higher than the minimum required, however, there is a great increment in the reboiler heat duty, consequently large values of both TAC and EI99 are obtained. For example, the scheme DWCS-DA-2 presents TAC savings about 67.97% in comparison with the most expensive design but an increase in the EI99 about 5%. On the other hand, the scheme DWCS-DA-3 presents savings in TAC only of 65% compared to DWCS-DA-1; probably, this scheme was expected to be the cheapest one since it is indeed the most polluting design. However, the increase in its reboiler heat duty, become DWCS-DA-3 more expensive than the DWCS-DA-2. In this manner DWCS-DA-2 represents a good alternative with relatively good performances indexes.

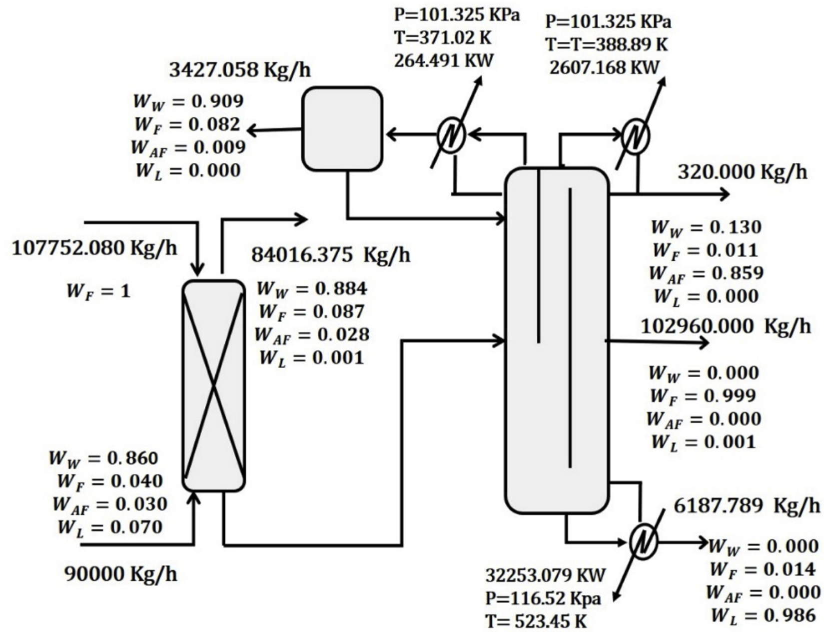

Fig. 16. Optimal configuration of TDWS-D.

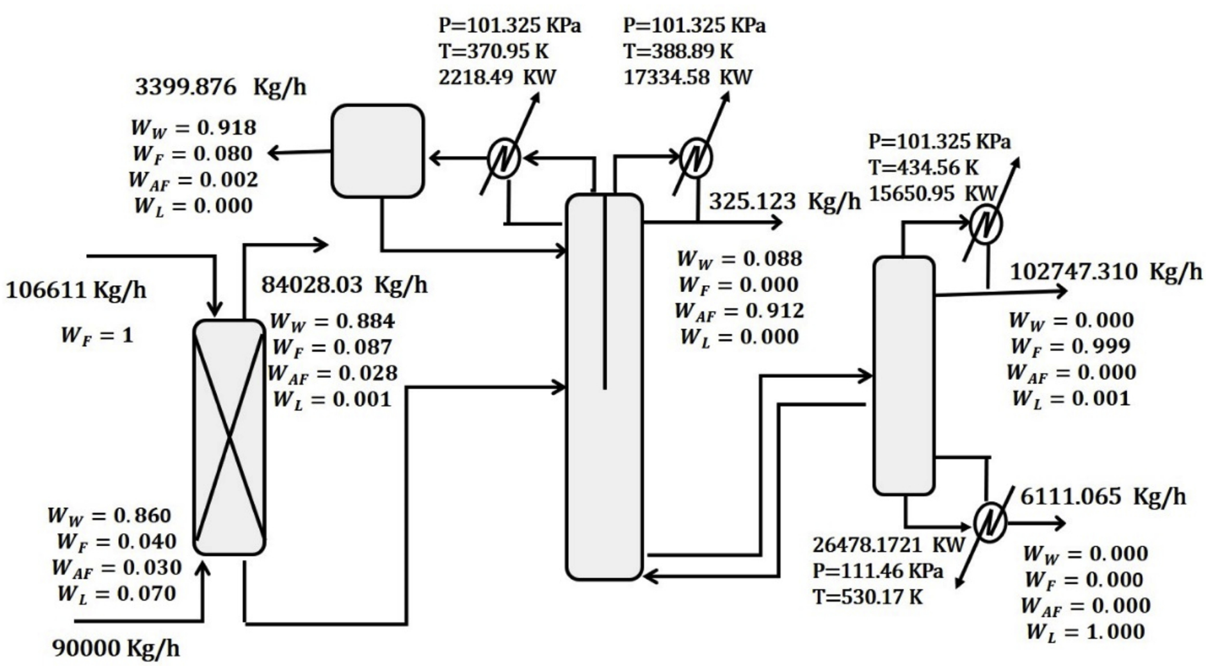

Fig. 15. Optimal configuration of DWCS-DA.

Additionally, the design parameters of the three selected designs for TDWS-D are shown in Table 6. Note, TDWS-D-1 presents the highest TAC value due to the amount of stages; moreover, the reflux ratio in the double wall column is also superior to the other designs, generating an increase in services cost. This reflux ratio value is due to the amount formic acid in the original mix, note it is very small compared to the other components, so it is necessary to increase the reflux ratio for formic acid purification. The internal flows of the three schemes (TDWS-D-1 to TDWS-D-3) are very different, however, both but when TAC and EI99 values did not show a great differences among themselves. This trend is observed because of the flows distribution is compensated by the modifications in the diameter, number of stages and reflux ratio, in other words, there is a great combination of design variables that lead us to similar values of the objective functions.

Fig. 12 shows the results of the multi-objective optimization of the four proposed schemes, the results were placed in different windows due to the scale between Pareto fronts. In each Pareto front the optimal zone for each alternatives is shown. It is considered that in this zone, both objective functions reach its minimum values. Moreover, note a highlighted point considered as the best solution (OP), which is the design number 2 of each Pareto front.

In Table 7, a comparison between the best designs of each scheme (Figs. 13–16) is shown. The differences (percentages) in both TAC and EI99 are presented in comparison with the best design of the conventional scheme (CS-2). Comparing the results, we can observe from the economic point of view that the sequence DWCS-DA-2 has the lowest value of TAC presenting savings about 9.43%. However, DWCS-DA-2 presents an increase about 3.7% in the EI99 values; the main reason of this difference is because of the purity of levulinic acid reached by this scheme is 99.9%, superior to all achieved. The DWCS-D-2 sequence has the lowest EI99 value, presenting an improvement in the environmental indicator about 9.87% and TAC saving about 8.42%, only 1.1% fewer in savings than the DWCS-DA-2 scheme.

The TDWS-D-2 scheme presents the worst results in both objective functions, its values in TAC and EI99 are greater than the conventional scheme about 10.92% and 3.95% respectively. This is mainly for two reasons, because of the formic acid is separated as a top product of the column, and for being a small flow compared to the other compounds in the original mixture. This represents a considerable increase of the reflux ratio and consequently an increment in the reboiler heat duty, internal flows and the energy requirement.

Comparing the DWCS-D-2 and DWCS-DA-2 schemes, the DWCS-D-2 is only 1.1% more expensive and has better values in EI99, so bearing in mind that the objective of this optimization is to find a design that manages to balance both objective functions, the DWCS-D-2 scheme becomes the best option of all schemes evaluated.

6. Conclusions

The multi-objective optimization using the DETL technique was implemented for 4 hybrid schemes to purify LA. Within the schemes studied, thanks to the intensification and optimization, schemes with better economic and environmental potential were obtained in comparison with the conventional scheme. The DWCS-DA-2 design presented the highest economic savings, but the increase in its internal flows generated a negative impact on the Eco-indicator 99. On the other hand, the hybrid sequence DWCS-D-2 composed by a liquid-liquid extraction column, a conventional column and a dividing wall column with a decanter, presented economic saving about 8.42% and a decrease in the Eco-indicator 99 about 10.94%. This observed behavior was due to the equipment sizing and the energy reduction generated by the implementation of the dividing wall column. The scheme TDWS-D-2, which had greater level of intensification, showed an increment in both its internal flows and energy requirements, impacting negatively about 9.87% in TAC and 3.95% in Eco-indicator 99, in comparison with the conventional scheme.

In general terms, if the conventional schemes are redesigned from an intensification point of view may produces several benefits. During this study, the benefits of the process intensification are reflected in both economic and environmental savings, however, it is interesting to realize that process intensification does not always produce large savings. In other words, due to the intensification of the process is not always possible to design separation schemes that can increase the economic and environmental performance. For example, the intensification of the process can occur by increasing the internal flows of the columns, producing increments in energy requirements and, consequently, also increments in both economic and environmental indexes. However, through the implementation of multi-objective optimization, we are ensuring that the designs obtained represent the best options, which guarantee the lowest environmental impact and the lowest economic impact.

Appendix A

In order to calculate the total annual cost (TAC), which is used as an objective function, we used the method published by Guthrie [54], which was modified by Ulrich [55] where the cost estimate of a plant is made separated industrial units, and the use of equations published by Turton et al. [56], that a cost approximation of the process is carried out using Eq. [A1], that is:

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

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 of 10 years. The values of the economic parameters were taken from Turton et al. [56].

The total module cost is calculated with Eq. [A2],

$$C_{TM} = \frac{A_1}{A_2}\sum_{i=1}^{n} C_{BM,i}^{0} \tag{A(2)}$$

Where A_1 represents a current adjustment index, A_2 reference adjustment index and C_{BM}^{0} represents the cost of the nude module which reflects the direct and indirect costs for each unit, which in turn is calculated by the Eq. [A3]:

$$C_{BM}^{0} = C_p F_{BM}^{0} \text{ In most cases } F_{BM}^{0} = (B_1 + B_2 F_M F_P) \tag{A(3)}$$

Where F_{BM}^{0} is the cost factor of the bare module that contains all the adjustment factors, F_M the material factor, F_p the pressure factor, B1 and B2 are factors that are dependent on equipment type and C_p represents the purchase cost of the equipment under base conditions: carbon steel as construction material and ambient operating conditions. In addition, the following service costs were taken into account. High pressure steam ($ 17.7GJ-1), medium pressure steam ($ 14.19 GJ-1), low pressure steam ($ 14.5GJ-1) and cooling water ($ 0.35 GJ-1) [56].

Appendix B

The code for the interaction between aspen and excel was adapted from: Segovia- Hernández et. al. [75]

```
Sub DETL()
Set Aspen = GetObject("C:\Users\PC\Documents \File1-bkp")
Aspen.Visible = False
'SEPD
'Stages SEPD
Range("Temperature!G7").Select
Aspen.Tree.Data.Blocks.SEPD.Input.NSTAGE.Value = ActiveCell.
Value
'Reflux ratio CI
Range("Temperature!H7").Select
Aspen.Tree.FindNode("\Data\Blocks\SEPD\Input\BASIS_L1").Value =
ActiveCell.Value
'Aspen.Tree.Data.Blocks.CI.Input.BASIS_RR.Value = ActiveCell.
Value
'************************************************************
***********************
'SEPE
'Number of stages SEPE
Range("Temperature!I7").Select
Aspen.Tree.Data.Blocks.SEPE.Input.NSTAGE.Value = ActiveCell.
Value
NCI = Range("Temperature!I7").Value
'Reflux ratio
Range("Temperature!J7").Select
Asp en.Tree.FindNode("\Data\Blocks\SEPE\Input\BASIS_L1").Value =
ActiveCell.Value
'As pen.Tree.Data.Blocks.CI.Input.BASIS_RR.Value = ActiveCell.
Value
'Run aspen
Application.DisplayAlerts = False
Aspen.Engine.Run
'____________________________________________________________
'Output data
'Molar Flow B in stream WATERB
Range("Temperature!K7").Select
ActiveCell.Value = Aspen.Tree.Data.Streams.WATERB.Output.
MOLEFLOW.MIXED.BUTANOL.Value
'Mass Flow B in stream BUTOL
Range("Temperature!L7").Select
ActiveCell.Value = Aspen.Tree.Data.Streams.BUTOL.Output.
MASSFRAC.MIXED.BUTANOL.Value
'Molar Flow B in stream BUTOL
Range("Temperature!X7").Select
ActiveCell.Value = Aspen.Tree.Data.Streams.BUTOL.Output.
MASSFLOW.MIXED.BUTANOL.Value
'************************************************************
***************************
'Run status
'Error
Range("Temperature! O7").Select
ActiveCell.Value = Aspen.Tree.FindNode("\Data\Results Summary\
Run-Status\Output\PER_ERROR").Value
ER = Range("Temperature!O7").Value
If ER = 0 Then
'Reboiler SEPD
Range("Temperature!S7").Select
ActiveCell.Value = Aspen.Tree.Data.Blocks.SEPD.Output.REB_
DUTY.Value
'Reboiler SEPE
Range("Temperature!T7").Select
ActiveCell.Value = Aspen.Tree.Data.Blocks.SEPE.Output.REB_
DUTY.Value
End If
'************************************************************
***************************
'Objective function
fn = Range("Temperature!AH7").Value
If IsRunning = True Then
IsRunning = False
End If
Aspen.Close
If ActiveSheet.Range("C1").Value >= 0 Then
Range("A7:AV7").Copy
Sheets("Results").Select
Variable = Range("A1").Value
Range("B" & Variable).PasteSpecial
Application.CutCopyMode = False
Range("A1").End(xlDown).Offset(1, 0).Select
ActiveCell.FormulaR1C1 = "=R[-1]C+1"
Range("A1").Select
ActiveCell.FormulaR1C1 = "=R[3]C+2"
Range("A1") = Range("A1").End(xlDown).Offset(0, 0).Row
Sheets("Temperature").Select
End If
If ER = 0 Then
TempFileName = Range("Resultados!A1").Value
Aspen.SaveAs Filename:=TempFileName & ".bkp"
End If
ActiveWorkbook.Save
End Sub
```

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