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Innovative Reactive Distillation Process for the Sustainable Purification of Lactic Acid

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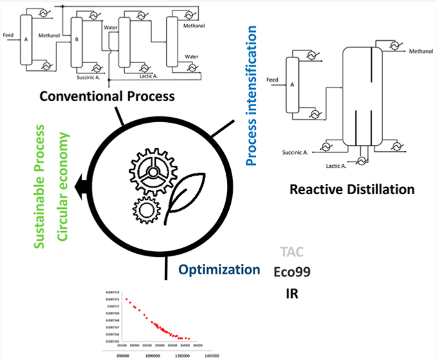
ABSTRACT: Lactic acid is commonly used in a wide range of fields, such as cosmetics, pharmaceutical products, chemistry, and food. During recent years, its use for new applications, such as the production of biodegradable and biocompatible polymers, green solvents, and oxygenated chemicals, have received considerable attention. However, the relatively high production cost of lactic acid hinders many large-scale applications. It is necessary to develop more efficient methods of separation and purification to cheapen lactic acid production processes. The main objective of this study is to investigate the use of process intensification, particularly the reactive distillation process, for a sustainable purification of lactic acid. To do so, there have been proposed, on the one hand, four intensified alternatives in which synthesis and design are based on thermal couplings and, on the other hand, three alternatives looking for water mass integration. Design and optimization of those modified configurations are carried out employing a stochastic optimization method, using as objective functions some metrics associated with the concept of sustainability (economics, environmental, and inherent safety indexes). A study on the dynamic performance of the configurations through the use of singular value decomposition is carried out in a complementary way. The results in the first redesign stage show improvements in all performance indexes. However, a great difference between the implementation of a thermal coupling that substitutes a condenser instead of a reboiler has been identified. The best scheme, based on a sustainability framework, resulted in a modified process, including a dividing wall column-based scheme.



1. INTRODUCTION

Biomass carbohydrates are the most abundant renewable resources available, and they are currently viewed as a feedstock for green chemistry.[1] Two types of sugars are present in biomass: hexoses, of which glucose is the most representative, and pentoses, of which xylose is most common. Fermentation of sugars represents an important route to produce new bioproducts. Five important bioproducts can be obtained from the fermentation of glucose: lactic acid, succinic acid, itaconic acid, glutamic acid, and 3-hydroxypropionic acid.[2]

Lactic acid (2-hydroxypropionic acid) can be produced by chemical synthesis or by fermentation of different carbohydrates, such as glucose (from starch), maltose (produced by specific enzymatic starch conversion), sucrose (from syrups, juices, and molasses), lactose (from whey), among others.[1] However, lactic acid is commercially produced today mainly through the fermentation of glucose. Lactic acid is a compound with high global demand. The estimated global demand for lactic acid is 200,000 to 350,000 t per year with annual growth rates between 12% and 15% (see Figure 1).[3]

Demand for lactic acid is high in the food, pharmaceutical, textile, and chemical feedstock industries where it is used to produce lactate esters, propylene glycol, 2,3-pentanedione, acrylic acid, acetaldehyde, pyruvic acid, 1,2 propanediol, and propanoic acid. It is also used in the cosmetic industry as a humectant in the preparation of creams and soaps. Moreover, lactic acid consumption has increased considerably because of its use as a basic input in the production of polylactates and polylactic acid for the manufacture of biodegradable plastics.[4,5]

Lactic acid exists in two optically active isomeric forms, L(+) and D(−). Compared to the biological route, chemical synthesis is at a disadvantage because the lactic acid produced is a mixture of optically inactive D(−) and L(+) lactic acid. Because of this, about 90% of all lactic acid in the world is produced by the biotechnological route.[2] An important step in the lactic acid bioproduction is the recovery from fermentation broth. The conventional process for the recovery of lactic acid is still far from ideal since it involves the precipitation of calcium lactate after the separation of microorganisms and the conversion of the

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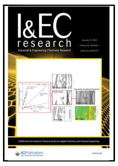

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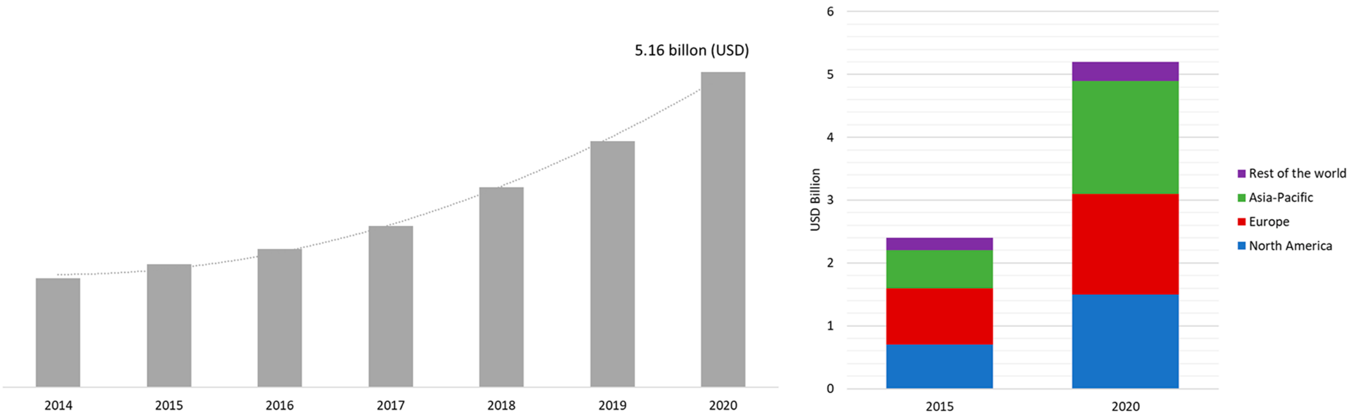

Figure 1. Global and regional demand of lactic acid (USD billion).

salt into lactic acid by the addition of sulfuric acid. The dilute lactic acid produced is then subjected to purification. The separation and purification stages account for up to 50% of the production cost. One point to highlight is that the biological production of lactic acid has significant advantages over the chemical production. Advantages include the high specificity of the product, i.e., production of the optically pure isomeric form by selecting the appropriate microorganisms used in the fermentation.

However, the concentration of lactic acid produced in the fermentation broth is very dilute and impurities that are generally present (unconverted acids, alcohol, side esters, sulfates, heavy metals, proteins, residual sugars, and nutrients) need to be separated. In addition, lactic acid has a strong affinity for water, is a high-boiling component, and tends to oligomerize at high temperatures. Therefore, these factors make lactic acid purification energy an intensive task. Various methods of purification have been investigated. Numerous separation and purification techniques have been proposed for lactic acid production, such as precipitation,[6] solvent extraction,[7] adsorption,[7] short-path evaporator,[8] and membrane separation processes, such as reverse osmosis, electrodialysis, and ultrafiltration.[9] However, these processes result in low lactic acid recovery and have the following limitations: in solvent extraction, a relatively large amount of solvent is required; high-purity lactic acid is difficult to obtain; ultrafiltration and osmosis are not suitable for a large amount of raw material; efficiency declines in parallel with a drop in membrane performance; and adsorption presents several problems, including particle selectivity, capacity, and regeneration.

Process intensification (PI) is an effective strategy to achieve increased energy efficiency. PI aims at reducing the mass and heat transfer resistances while overcoming thermodynamic limitations through integrated design and operation. In recent years, PI has attracted considerable academic interest as a potential means for process improvement to meet the increasing demands for sustainable production.[10]

One of the most common examples of the process intensification field is the reactive distillation, where the integration of reaction and separation is performed in a single unit, allowing the simultaneous production and removal of products, thus improving the productivity and selectivity, reducing the energy use, eliminating the need for solvents, and leading to intensified, high-efficiency systems with green attributes. Reactive distillation has attracted considerable attention, especially for chemical equilibrium-limited, liquid-phase reactions, which conventionally require a large excess of one of the reactants.[11] The technological benefits of reactive distillation can be summarized as follows: (a) increased conversion; (b) increased selectivity; (c) reduced energy consumption; (d) overcoming of azeotropes; (e) simplified separation of close-boiling components, and (f) capital savings. Recently, intensified process with reactive membranes[12] or reactive distillation has been proposed to alleviate these limitations.[13] The recovery of nonvolatile lactic acid from the fermentation broth is difficult due to the similarity of the boiling points. The purification of lactic acid using reactive distillation can be described as follows: the lactic acid is reacted with methanol, and methyl lactate is produced. Methyl lactate can be more easily purified by distillation. Then, methyl lactate is sent to a hydrolysis column and recovered by the hydrolysis reaction. The advantages of this purification method are the ability to handle large capacities of raw materials and to achieve high lactic acid recovery. This is the most promising solution to the lactic acid purification problem. This method was first described in a U.S. patent by Cockrem and Johnson.[14] The application of intensified distillation systems, such as conventional reactive distillation or thermally coupled reactive distillation systems (thermally coupled arrangements are realized by setting up two-way vapor/liquid flows between different columns of the simple column configurations[15,16]), shows great benefits to achieving an economic process. A highlight is that sustainable design considers economic, environmental, and societal outcomes with equal measures and ensures that the consumption of resources does not exceed nature's capacity to provide the needed ecosystem goods and services. PI is a design concept that offers innovative solutions for making a substantial improvement in terms of cost, energy efficiency, emission, environmental footprint, processing volume, and safety of a chemical process. Incorporation of PI principles at the conceptual design stage can pave the way for more sustainable solutions.[17] Also, according to Schöggl et al.,[18] sustainability contributes to the circular economy environment through the measurement of both economic and green chemistry indicators. In summary, PI is a strategy that can generate sustainable designs and is therefore framed within the concept of circular economy. In this sense, the use of intensified systems in the lactic acid purification process is generating sustainable alternatives to this industrial problem, in a circular economy environment.

In this study, we extended the lactic acid recovery process based on conventional reactive distillation to a modified process using thermally coupled reactive configurations. In addition, three alternatives for integrating a water stream will be explored to reduce the overall water consumption in the whole process. As far as the authors are aware, these types of intensified processes have not been optimized, from the point of view of sustainability indicators (framed within the concept of circular economy), for lactic acid purification. The main contribution of this work is to explore the possibility of using these complex, intensified configurations at an industry level, in a framework of sustainability. These systems provide choices of special interest for the separation of multicomponent mixtures because of their potential energy savings and reduction in total annual costs.[19] Also, in this study, the advantages of those intensified configurations are analyzed using economics, environmental, and inherent safety indexes as indicators of sustainability using a stochastic optimization strategy and complementing the study by analyzing the dynamic properties of the configurations to establish the ease of its operation at an industrial level.

2. OPTIMAL SUSTAINABLE PROCESS

Over the last five decades, with the development of process systems engineering, chemical engineers have developed many methods and tools for reducing the environmental impact of chemical processes. Today, the goal of such approaches is to not just reduce emissions from an individual manufacturing process but also ensure reduction in energy consumption, operating costs, maximize process safety, and generate operable processes. This goal of sustainable process systems engineering presents formidable challenges due to the complex nature of the interacting factors, and sustainable process design solves large multiobjective optimization problems due to the nonlinear nature and the presence of degrees of freedom in the mathematical models that represent the processes to be designed.[20] Furthermore, modification in the topology for the same process can also modify sustainability indexes.[21] Despite the many definitions of the term sustainable, it is possible to identify some basic requirements that need to be satisfied before making claims about sustainability. In particular, Jiménez-González et al.[22] propose clear mathematical strategies to evaluate those sustainability metrics. In this sense, sustainability can be viewed as a framework with targets to achieve economic, environmental, inherent safety indexes, and dynamic behavior, among others.[21−27] This work tries to analyze different topologies based on a modification of the conventional intensified design, for the reactive distillation process for lactic acid purification, and select the most promising ones according to sustainability metrics as proposed in the paper of Jiménez-González et al.[22]

For this case study, the economic metric was measured through the total annual cost (TAC) as suggested by Turton et al.[23] In the case of environmental metrics, Eco-Indicator 99 (Eco-99) was used, which is based on the life cycle assessment and the approach was proposed by Goedkoop and Spriensma.[25] The security metric was calculated through the concept of individual risk (IR) index. The IR can be defined as the risk of injury or decease to a person in the vicinity of a hazard.[28] The main objective of this index is the estimation of likelihood affectation caused by the specific incident that occurs with a certain frequency. Finally, controllability characteristics are evaluated using the condition number as an index. Singular value decomposition of the relative gain matrix of the assessed design at a nominal point was used to get the condition number. In terms of controllability, a high condition number suggests that satisfying the complete set of control objectives (regardless of the control method employed) will be inconvenient.[29] The calculation of each of the metrics is detailed in the Supporting Information.

The optimal design of sustainable reactive distillation systems to purify lactic acid is a nonlinear and multivariable problem, and the objective functions used as optimization criteria are generally nonconvex with several local optimums. However, the task is complicated and is likely to fail to achieve convergence. To solve this case study, a metaheuristic optimization method based on the theory of natural selection was applied. This evolutionary method employs the classical differential evolution steps. However, its actions are improved through the Tabu List (TL) concept. Initially, this hybrid optimization algorithm was proposed because it[30] improves the computational efficiency of DE employing testing challenging phase equilibrium calculations followed by parameter estimation problems in dynamic systems known to have multiple minima. Operationally, the hybrid algorithm is coded in Visual Basic. Through dynamic data exchange (DDE), the numerical method generates input vectors that are evaluated in the process model (Aspen Plus). Then, the model evaluates the input vector and generates output vectors. After that, the hybrid method analyzes the input and output data and, according to the evolutionary nature of the algorithm, the process begins to iterate. The operational parameters for the stochastic method were 120 individuals, 900 generations, 50% of the number of individuals as tabu list, 0.6 for the crossover, and a Taboo radius of 1×10^{-6}. These parameters were obtained from a tuning process in previous calculations.

The optimization of the sustainable schemes for the purification of lactic acid will be restricted to purities (y_i) required in the market for each product. The indexes described above are used as the objective function, subject to

$$\begin{aligned}&\min(\text{TAC, IR, Eco99})\\&\quad\text{subject to: } y_i \geq x_i\end{aligned} \tag{1}$$

In general, it might be difficult to determine which sequence is optimal, in the overall notion of sustainability and green chemistry, when using a multiobjective optimization strategy. As a result, the goal of this research is to give a more comprehensive picture of the selection of the optimal design using a normalizing technique. The normalization of the goal functions (TAC, IR, and CN) allows the optimal sequence for the ideas of sustainability to be identified. In accordance with Koski,[31] the goal functions should be normalized as follows:

$$\begin{aligned}&f_i(x) = \frac{F_i(x) - \min F_i(x)}{\max F_i(x) - \min F_i(x)}\\&\quad i = \text{objective functions, } X \in NP\end{aligned} \tag{2}$$

Details of the optimization technique and determination of the optimal solution can be found in the Supporting Information.

3. CASE STUDY

Esterification and hydrolysis with methanol and oligomerization reaction of the lactic acid can be performed using intensified alternatives, such as reactive distillation columns.

The capabilities of using such technology were preliminarily elucidated by Kim et al.[13] Moreover, this case study fulfills all the preliminary requirements to claim the complete feasibility of the RD technology to purify lactic acid. For example, according to

Shah et al.,[32] before any synthesis or design task, it is necessary to determine the feasibility of any reactive distillation scheme. Following their guidelines, the fulfillment of those requirements in this case study must be highlighted: (1) the presence of more than one product, (2) there is a match between temperatures required for reaction and separation (from a quite simple point of view, this case study proposes the reaction near 50 °C and the boiling point for both reactants, CH_3OH and $C_3H_6O_3$, is 64 and 122 °C respectively), and (3) for none of the components, neither the operating pressure nor the temperature are close to the critical region.

The fulfillment of these three requirements in the industrial feasibility of reactive distillation for the purification of lactic acid is demonstrated in the U.S. patent by Michael and Madison.[14]

The reaction performed in both columns can be represented by the following reaction sequence:

$$\underset{\text{lactic acid}}{CH_3CH(OH)COOH} + \underset{\text{methanol}}{CH_3OH} \overset{k_{f,1}}{\underset{k_{r,1}}{\longleftrightarrow}} \underset{\text{metillactate}}{CH_3CH(OH)COOCH_3} + \underset{\text{water}}{H_2O} \tag{3}$$

$$\underset{\text{lactic acid}}{CH_3CH(OH)COOH} + \underset{\text{lactic acid}}{CH_3CH(OH)COOH} \overset{k_{f,2}}{\underset{k_{r,2}}{\longleftrightarrow}} \underset{\text{dilactate}}{C_6H_{10}O_5} + \underset{\text{water}}{H_2O} \tag{4}$$

$$\underset{\text{dilactate}}{C_6H_{10}O_5} + \underset{\text{lactic acid}}{CH_3CH(OH)COOH} \overset{k_{f,3}}{\underset{k_{r,3}}{\longleftrightarrow}} \underset{\text{trilactate}}{C_9H_{14}O_7} + \underset{\text{water}}{H_2O} \tag{5}$$

Kinetic equations are represented in pseudohomogeneous form and kinetic parameters are shown in Table S2.

From an operational point of view, a determining factor is the dome temperature. If lactic acid is subjected to temperatures above 80 °C,[13] there is a high probability that it will oligomerize. In that sense, the operating pressure plays a fundamental role to avoid such a reaction and to carry out a successful separation. In this work, it is assumed that the solid catalyst occupies 50% of the tray holdup volume and that the density of the catalyst is 770 kg/m^3, which was used to calculate the holdup volume. For chemical systems with nonidealities and strong interactions between acids in the vapor phase, the UNIQUAC-HOC and NRTL-HOC property models are sufficient. The UNIQUAC-HOC model was used to avoid introducing additional factors that might affect the comparison with previously published benchmark studies.[13,33] For a representative broth obtained from a bioprocess producing lactic acid, the feeding conditions to the reactive distillation are displayed in Table 1. It is important to mention that this is a simplified case study to test the feasibility of these structures. In complex columns, it is possible to assemble new topologies and to know if it is possible to perform the esterification process in these columns. Note that, from the bioprocess, the mixture includes succinic acid and water. The retrofitted reactive distillation configurations studied are described in the following paragraph. Additionally, Table S3 shows the binary interaction parameters for all chemical compounds.

Table 1. Characterization Feed from Fermenter[13]

			% mol		
flow rate (kmol/h)	pressure (atm)	temperature (°C)	lactic acid	water	succinic acid
50	2	35	8.4	90.5	1.1

Using a separation scheme based solely on conventional distillation columns is considered a base case. It is important to note that the feed flow and the compositions were taken from Kim et al.[13] to have a comparison with previously reported results. Observe that the fermentation broth fed into the first column (Table 1) is preconcentrated in column A (see Figure 2). Once the largest amount of water has been removed, before the azeotropic point, it is fed to a second column where an esterification reaction assisted by methanol is carried out (eq 3). Additionally, through the lower part of the column, high-purity succinic acid is obtained. The distillate flow feeds the third column, where a hydrolysis process is carried out to form lactic acid again (eqs 4 and 5). Finally, in the last distillation column, the alcohol used in the esterification is purified to be recirculated to the second column; the same happens with water.

3.1. Synthesis of Intensified Alternatives.

The methodology shown by Errico et al. is follows.[34] The methodology consists of four steps and assists in the determination of stripping and rectification zones, thermal couplings, intensified sequences, and the location of side-streams.

- Step 1. Identification of the reference configuration: The first step is to define a reference configuration (as shown in the middlebox of Figure 2).
- Step 2. Generation of modified thermally coupled configurations: The crucial part of the present stage is to generate the modification of the reference configuration by replacing the auxiliary equipment (reboiler/condenser) with interconnection streams (liquid−vapor). As shown in the first stage (Figure 2), such equipment is replaced by interconnection streams, leaving room for multiple options.
- Step 3. Identification of thermodynamically equivalent configurations: It is important to consider ideal mixtures as this will help generate thermodynamically equivalent configurations with the movement of column sections. However, since it is an azeotropic mixture, it is not so simple. Figure 2 (third stage) shows such recombination of sections regarding the second stage. Several possible configurations can be obtained by moving the individual sections simultaneously or independently.
- Step 4. Construction of side-stream configurations: Now, from the thermodynamically equivalent configurations, it is possible to generate the new subspace of systems with less than $N - 1$ columns. The methodology is straightforward and consists of the elimination of side columns, leaving only one column section. By eliminating the single rectifying section employing a side-stream (third stage), there are then produced the systems with less than $N - 1$ columns. The connection between the subspace with less than $N - 1$ columns and the corresponding single column sequences is demonstrated. For a given thermodynamically equivalent structure, the location of the side-stream will depend on the section removed and the final position of each zone.

In this specific case, the initial stage of the synthesis of this intensified process was carried out by sequentially applying thermal couplings. Observe in Figure 2 that, from conventional distillation columns, different intensified alternatives are obtained. In the first modification stage, a single thermal

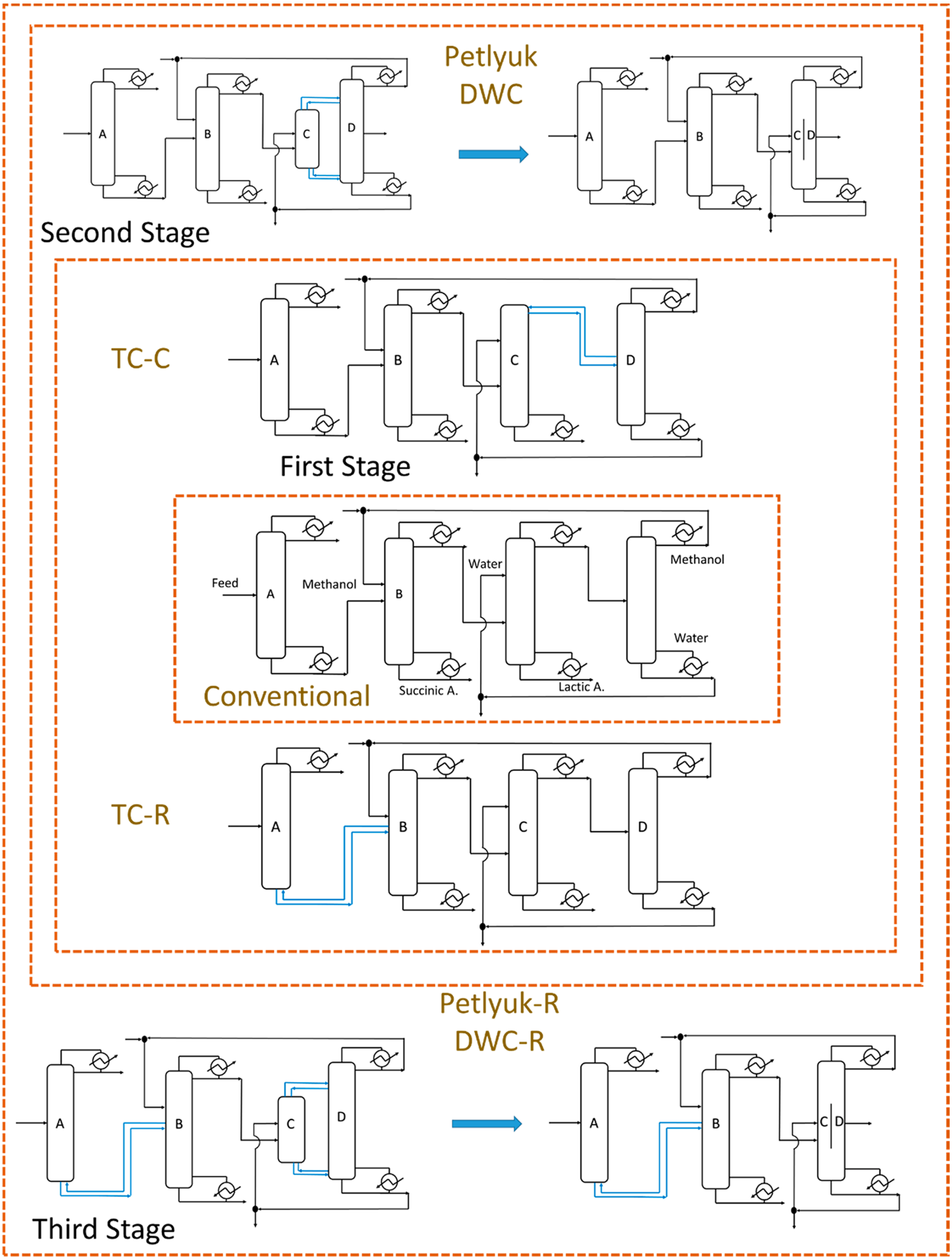

Figure 2. Intensification methodology applied to the base case.

coupling could be applied in the nonproduct stream (TC-C, TC-R). Whereas in the second modification stage, the scheme TC-C is fully thermally coupled using a second thermal coupling (DWC). Finally, based on the DWC scheme, a thermal coupling is introduced again between the first and second columns (DWC-R). An important point to clarify is that although the base columns that are integrated to generate the DWC may have different pressures, according to Ling and Luyben[35] and Van Duc Lon and Lee,[15] pressure is chosen to be greater (between the columns to be integrated) to guarantee that the system is

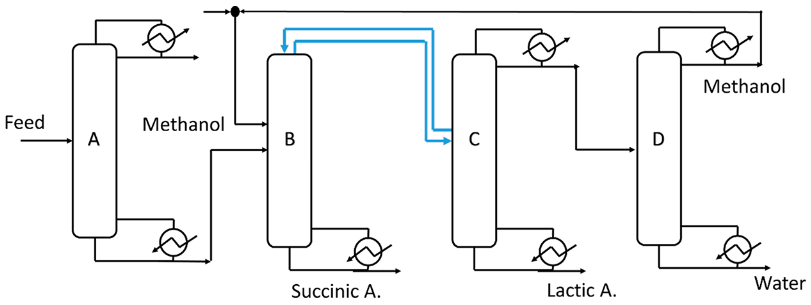

Figure 3. Intensified alternative with mass water integration (TC-IM).

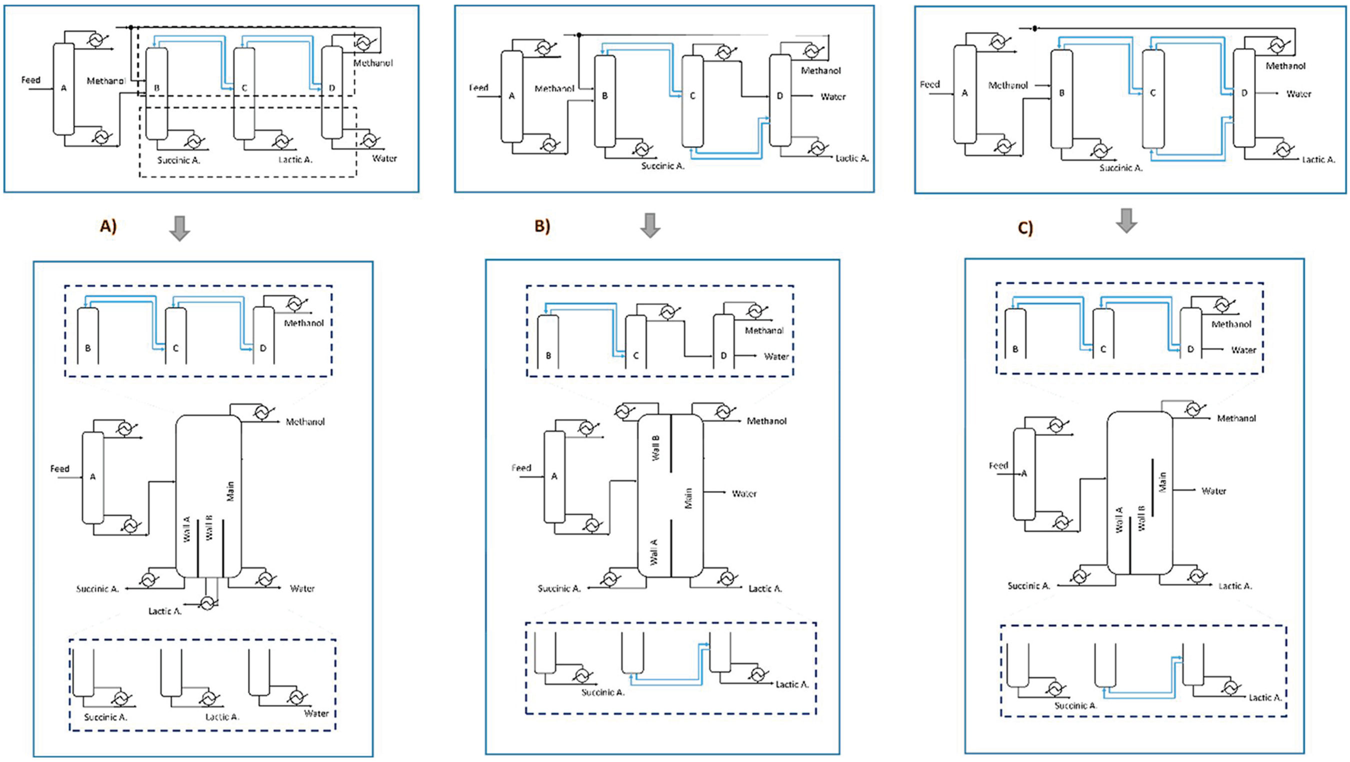

Figure 4. Generation of intensified alternatives with mass water integration DWC-A (A), DWC-B (B), and DWC-(C). All figures are presented in both expanded and DWC form.

designed at the pressure that the most volatile component is distilled, and in this way, it is possible to maintain the energy savings in the DWC.

Several thermal couplings can be applied sequentially to generate a highly intensified separation scheme. On the other hand, enough water is probably produced in the esterification reaction to avoid an additional stream, feeding water into the third column. For example, note that in eqs 3−5, as a product of the reactions themselves, a certain amount of water is generated. In other words, water is generated by the esterification reaction. This water can be sent immediately to the next hydrolysis reaction, and thus, it is possible to avoid consuming fresh water through an external water stream. In this sense, it is possible to generate additional alternatives that avoid the entry of an extra stream of water into the process. Note that the amount of water to be added in the conventional scheme is a degree of freedom to be considered in the optimization process to obtain the best results. On the other hand, the water generated from the esterification reaction and fed into the hydrolysis reaction is generated from the internal chemical reaction and equipment operating variables, so there may be a variation between the two water flows. As will be seen in the results section, these configurations required different operating conditions, but, thanks to processing synthesis work, it is possible to generate the alternatives presented in Figures 3−4. It is important to highlight that in the cases where the columns operate at different pressures, the thermal coupling (recycles between the columns) can be carried out using pumps and/or compressors appropriately. According to Van Duc Long and Lee,[15] carrying out this type of retrofit in the configurations, by using equipment to adapt the pressure differences in the columns, does not substantially impact energy consumption and, therefore, the energy savings that characterize these configurations are not substantially affected.

Note in Figure 3 the possibility of generating intensified alternatives and eliminating a freshwater stream for the third column for lactic acid generation. Furthermore, it is possible to generate more intensified alternatives by integrating the rectification or depletion sections in the main body of the distillation column, as shown in the lower part of Figure 4. This type of synthesis work has proven to be effective in separating alternatives with relatively good energy savings, according to the

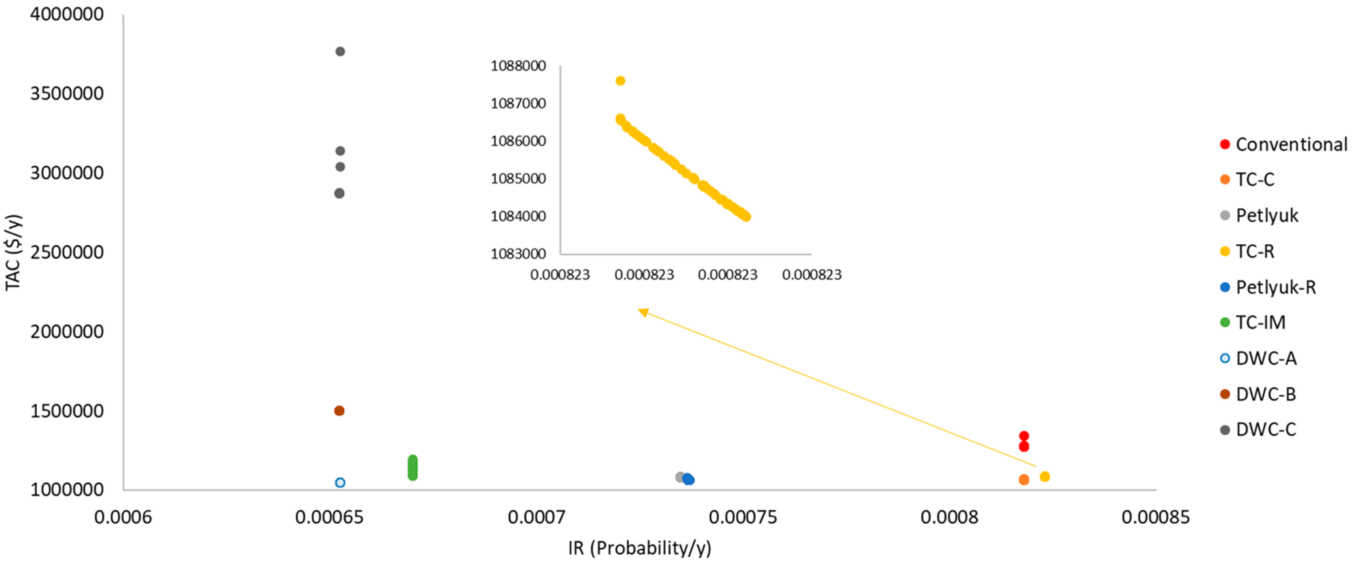

Figure 5. Pareto front valuating the TAC and the inherent safety.

work presented by Rong[36] and many others.[37,38] Environmental pollution is a major concern nowadays because of the adverse impacts it has raised in several aspects, such as human health, weather, regional identity, food, security, biodiversity, and economics. Research efforts using process integration strategies have addressed this concern. For instance, the rational use of water in the process industry has been the subject of several papers, in which the minimization of fresh water and wastewater in single process industries has been considered.[39−41] For this reason, the idea of minimizing the use of fresh water in the lactic acid purification process by reusing water through mass integration is a challenge that is addressed through these intensified novel designs.

4. RESULTS

This section presents the main results obtained, as well as various trends that were observed in the optimization process. The purity constraints were set as 90 wt % for lactic acid, 99.9 wt % for succinic acid, and 99.9 wt % for both methanol and water for recycling. The relative low purity for lactic acid was set that way since it is commercially required in different qualities, for the food industry (80%) and the pharmaceutical and plastic industry (90%).[42−44] With regard to methanol, a minimum purity of 99.7% was established to be considered as a recycle stream to the esterification column.

Figures 5−7 show the results obtained after the optimization process. At this stage, no substantial improvement was observed, so we assume that the optimal zone for the objective functions evaluated was found. All results were obtained after 108,000 evaluations (120 individuals, 200 generations). Although three objective functions were considered simultaneously, the results are presented in two-dimensional graphs for a better understanding.

With regard to the first five alternatives, it is easy to see that the DWC-R possesses the lowest TAC and the lowest environmental load and is the second one in the inherent risk. On the other hand, a trend in the objective functions, according to the retrofit stages, can also be observed. It is evident that, in general, with thermal coupling as the first modification stage, it generates a substantial improvement in almost all the indicators, except IR. However, the improvement is not generated in the same way when a thermal coupling eliminates a condenser, as when the reboiler is eliminated. Particularly in TAC calculation, the thermal coupling between the first two columns generates a reduction of 11% compared to the conventional scheme. On the other hand, replacing the condenser between the last two columns generates a reduction of 17% (see Tables 2, 3, 4, and 5). The reduction in TAC is largely due to the percentage of energy saved. Although the reboiler duty of the first column was eliminated in the TC-R scheme, there was a 76% increase in the reboiler duty of the second column compared to the conventional scheme. This increase took place since a single reboiler heated both columns. On the other hand, in the TC-C scheme, there was no substantial increase in the energy requirements of the third column. In contrast, there was a 14% reduction in the reboiler duty of the last column. These results speak of the high energy demand that is involved in concentration (removal of water) in the first column.

The behavior when the environmental impact is calculated is relatively similar. With regard to inherent safety, the reboiler duty in the first two columns appears to harm the probability of an accident, whereas in the TC-C scheme, it does not. With accordance to the model for individual risk calculation, the high dependence on the amount of matter associated with each piece of equipment is clear. In this sense, the presence of thermal coupling in the first columns generates a large and continuous exchange of matter between columns. Consequently, there is a slight increase in the inherent risk of the TC-R scheme with respect to the conventional scheme of around 1%.

In the next stage of intensification, interesting things were observed. Like in the first modification stage, the thermal coupling that replaces a reboiler to generate the DWC scheme did not generate great economic savings. On the contrary, there was a slight increase in energy consumption and in the TAC values. Although due to the elimination of the reboiler a savings in capital cost was generated, it was not enough to generate savings in the TAC. In the same sense, the environmental load had a slight increase (3%) compared to the TC-C scheme. The fact that there is an inlet and outlet stream of vapor/liquid in the prefractionator reduces the net balance of matter present in the prefractionator. Consequently, the individual risk decreases by about 10%.

Table 2. Design Parameters of the Conventional TC-C and TC-R Schemes

	conventional				TC-C				TC-R			
columns	C1	C2	C3	C4	C1	C2	C3	C4	C1	C2	C3	C4
stages	43	8	60	32	42	8	59	31	46	8	60	31
feed stage	23	4, 4	42, 42	14	24	5, 4	41, 46	17	15	4, 4	40, 34	23
side stage								16	46			
reflux ratio	0.1	0.05	0.12	1.82	0.04	0.026	–	1.77		0.29	0.05	0.9
distillate flow (kmol/h)	40.4153	25.734	34.673	16.64	40.41	25.73		16.73	40.4	25.7	34.7	16.6
bottoms flow (kmol/h)	9.58	0.53	5.05	18.03	9.58	0.53	5.05	18.03	–	0.53	5.05	9.58
interconnection flow (kmol/h)							5.899		14.5858			
diameter (m)	1.03	1	0.86	1.02	1.03	1	0.86	1.02	1.03	1	0.86	1.02
reactive stages		3 to 7	28 to 47			3 to 7	27 to 56			2 to 7	27 to 48	
holdup (*l*)		29.14	97.062			28.9034124	91.6844112			30.5	96.6	
pressure (atm)	0.1902	0.4599			0.211	0.37			0.12	0.37		
reboiler duty (cal/s)	448115				338868				417337			
succinic acid (% wt)		0.999				0.999				0.99		
lactic acid (% wt)			0.94				0.914				0.95	
methanol (% wt)				0.999				0.995				0.99
TAC ($/y)	1274559				1062454				1134718			
EI99 (Eco-points/y)	405025				302771				376834			
IR (probability/y)	0.000818084				0.000818023				0.000823006			

Table 3. Design Parameters of the DWC and DWC-R Schemes

	DWC				DWC-R			
columns	C1	C2	C3	C4	C1	C2	C3	C4
stages	43	9	60	32	44	9	60	32
feed stage	20	5, 7	28, 52	7, 25	15	4, 4	40, 34	23
vapor interconnection flow (kg)			36.75		14.5858			
input stage (vapor)			76		46			
side stream (vapor)				25		5, 25		21
side stream (liquid)				6		6		6
side stream (water)				21		21		17
reflux ratio	0.1	0.05		1.8518	0.1	0.29	0.05	0.9
distillate flow (kmol/h)	40.4	25.7		16.65	40.4	25.7	34.7	16.6
bottoms flow (kmol/h)	9.58	0.53	–	5.04	–	0.53	–	5.08
diametro (m)	1.03	1	0.86	1.02	1.03	1	0.86	1.02
reactive stages		4 to 7	26 to 56			2 to 7	27 to 44	
holdup (l)		42.37	90.07			30.5	96.6	
pressure (atm)	0.194	0.569	1	1	0.12	0.37	1	1
reboiler duty (cal/s)	349927	338292						
succinic acid (% wt)		0.999				0.99		
lactic acid (% wt)			0.958				0.95	
methanol (% wt)				0.999				0.99
TAC ($/y)	1086548				1062449			
EI99 (Eco-points/y)	313189				303062			
IR (probability/y)	0.000734825				0.000736675			

Table 4. Design Parameters of the Thermally Coupled Sequence with Water Integration

	TC-IM			
columns	C1	C2	C3	C4
stages	43	9	76	26
feed stage	20	4, 4	–	7, 25
vapor interconnection flow (kg)			36.75	
input stage (vapor)			53	
interconnection flow (vapor kmol/h)		28.53		25
interconnection flow (liquid kmol/h)			2.8	6
side stream (water)				21
reflux ratio	0.1	–		2.095
distillate flow (kmol/h)	40.41	–		16.682
bottoms flow (kmol/h)	9.58	0.53	–	4.873
diameter (m)	1.03	1	0.86	1.02
reactive stages		4 to 7	26 to 66	
holdup (l)		42.37	90.07	
pressure (atm)	0.19004	0.5331	1	1
reboiler duty (cal/s)	387370			
succinic acid (% wt)		0.999		
lactic acid (% wt)			0.958	
methanol (% wt)				0.999
TAC ($/y)	1111585			
EI99 (Eco-points/y)	365591			
IR (probability/y)	0.000818369			

Finally, in the third modification stage, starting from the DWC scheme, the reboiler of the first two columns is eliminated through a thermal coupling to generate the DWC-R scheme. With observance of the performance indexes, there was no economic savings or decrease in the environmental impact compared to the DWC scheme. On the contrary, there was an increased risk inherent in the separation scheme. It is clear that, for the particular case of lactic acid purification, the thermal couplings that replace reboilers do not generate a considerable improvement compared to the thermal couplings that replace a condenser. Additionally, replacing a reboiler with a thermal coupling increases the risk associated with the separation process. It is also clear that any thermal coupling generates improvements compared to the conventional process, but not between one stage and another in the modification process.

On the other hand, when looking at the values resulting from the optimization of the alternatives with water integration, only one alternative proved to be promising. The DWC-A alternative presented better values in all the objective functions than the alternatives designed only with thermal couplings.

Then, the alternatives were based on a dividing wall. The DWC topology allows the integration of several walls in a single unit that reduces the capital cost and more competitive alternatives can be generated, from the economic point of view. However, it should be considered that, in this work, the TAC is being evaluated as an economic indicator, which is composed of the capital cost and the cost of services. It can be seen why the other alternatives presented in the form of a dividing wall are not economically viable. That is, the costs associated with utilities increase considerably, making these alternatives unfeasible.

The increase in energy consumption of the alternatives could have been caused by some issues, for example, the topological complexity of the alternatives based on DWCs that simultaneously perform a chemical reaction. Additionally, the elimination of the water stream made the reaction-separation conditions more energetically strenuous for most of the alternatives.

As a result of the higher demand for energy requirements, the total annual cost and eco-indicator 99 markedly increased for most of the dividing wall schemes.

However, the inherent safety results showed a substantial improvement. In accordance with the model presented in this work for the calculation of inherent safety and the cited

Table 5. Design Parameters of the DWC Sequence with Water Integration

	DWC-A				DWC-B				DWC-C			
columns	C1	wall A	wall B	main	C1	wall A	wall B	main	C1	wall A	wall B	main
stages	43	9	60	32	42	9	59	31	42	9	60	31
feed stage	23	4, 4	1, 52	20	24	4, 4	1, 52	16, 18	15	4, 4	1, 52, 60	20, 31
side stage								15				14
reflux ratio	0.085	–	–	1.88	0.0805	–	1.596	1.872		–	–	10.06
distillate flow (kmol/h)	40.4106	–	–	16.66	40.4143	–		16.496	40.41	–	–	16.506
bottoms flow (kmol/h)	9.5893	0.531	6.09	2.985	9.587	0.5319	–	4.239	–	0.528	–	4.22
interconnection flow (kmol/h)		28.637	2.899/59.654	40.008		28.535	2.89/23.61		14.5858	28.462	2.71/59.86/27.67	42.19/19.59
diameter (m)	1.017	1.16	1.008	1.02	1.017	1.07	1.0183	1.03	1.017	1.1088	1.014	1.08
reactive stages		3 to 7	28 to 47			3 to 7	27 to 47			2 to 7	27 to 48	
holdup (*l*)		29.14	97.062			28.903	91.684			30.5	96.6	
pressure (atm)	0.189	0.4599	1	1	0.181	0.37	1	1	0.18	0.37	1	1
reboiler duty (cal/s)	391938				536473				1447227			
succinic acid (% wt)		0.999				0.999				0.99		
lactic acid (% wt)			0.939					0.914				0.95
methanol (% wt)				0.999				0.995				0.99
TAC ($/y)	1044799				1498392				2871129			
EI99 (Eco-points/y)	356249				500695				963497			
IR (probability/y)	0.000652447				0.000652398				0.000652398			

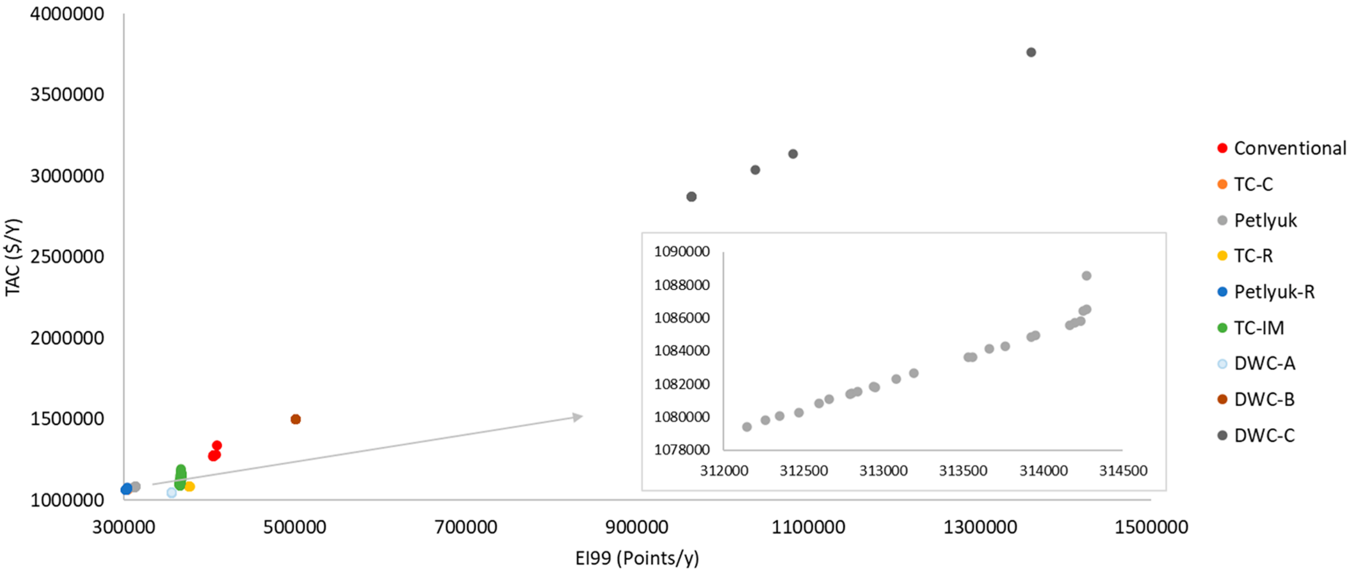

Figure 6. Pareto front valuating the TAC and the eco indicator 99.

references, the number of equipment evaluated is a relevant aspect, so that by reducing the number of equipment, there is a substantial improvement in this aspect. In general, the designs based on dividing wall columns showed an improvement in this indicator.

An overall comparison indicates that the DWC-A alternative showed an improvement in two indicators. It showed an improvement of approximately 4% in the economic indicator and an improvement of approximately 13% in the safety index, compared to the best first-stage synthesis design. A considerable penalty is observed in eco-indicator 99 due to the increase in energy requirements, however, this increase did not affect the economic indicator with the same magnitude due to the savings in capital cost.

In addition, all the alternatives based on the dividing wall present a water savings of 252 kg/h, which represents an annual consumption of 2,143,819 kg of water. In accordance with the World Health Organization (WHO), an average person needs approximately 36,000 kg of water per year to meet basic consumption and hygiene needs.[45] Thus, making a direct generalization with the mass integration of water in this process, water savings can be generated so that 60 people can have their basic water consumption.

From a circular economy point of view, it is evident that a single thermal coupling increases sustainability. Considering, for example, TC-R and TC-C schemes, in comparison with the conventional scheme, the economic, environmental, and safety issues are improved. Although the flow of steam and liquid in the thermal couplings would seem to affect the esterification or hydrolysis reactions, the optimization process allows one to know the appropriate placement and flows to avoid a decrease in the performance and productivity of the reactive columns. However, due to the nature of the mixture, there is a notable difference in the coupling. As mentioned before, the substitution of a condenser by a thermal coupling decreases the energy requirements and, as a consequence, the economic and environmental impact. Otherwise, the substitution of a reboiler by a thermal coupling does not contribute to those circular economy indexes. Contrarily, due to the intensive energy requirements, inherent safety is compromised. Regarding TAC and EI99, the reduction in capital cost tries to compensate for the low reduction in energy requirements. Tables 2−5 show the main design parameter for all purification alternatives. There is a slight variation in the stages of each column by design. The explanation is due to the intimate relationship that the design variables have. When generating thermal couplings, there is a notable change in the energy requirements. Consequently, the lower energy consumption allows moving design variables, reflux ratio, or stages, for example, to minimize target functions. In addition, the mass integration of a water flow generates more sustainable production alternatives for water consumption, a highly precious commodity with vital functions.

The principle of selecting the operating pressure of any distillation column is one of the most important design decisions. In the particular case of the conventional sequence, the pressure has a great impact, since, as mentioned above, a determining factor is the temperature in the column dome, because if the lactic acid is subjected to temperatures above 80 °C, there is a high probability that it will oligomerize.[13] The above-mentioned case is avoided by achieving vacuum pressures, which can be seen in Table 2 (lactic acid, water, and succinic acid have boiling points of 82 °C, 50 °C, and close to 110 °C, respectively). As mentioned by Luyben,[46] many separations benefit from allowing low temperatures; the pressures in most columns are set by the desire to use cheap cooling water as a heat sink in the condenser. For components with low vapor pressures, this criterion results in pressures below atmospheric. However, there seems to be some hesitation in using vacuum distillation columns, especially in azeotropic separations. Luyben[46] illustrates that there are operational and economic advantages to using vacuum distillation in some systems. With regard to the behavior of the objective functions, note in Figure 5 the antagonistic relationship between TAC and inherent safety. In other words, the lower the risk of accidents, the higher the TAC increase. This trend is largely due to operating variables and the nature of the mixture to be separated. For example, a decrease in the risk of the process has been observed with an increase in the reflux ratio. As a consequence, there is a direct increase in energy requirements and, obviously, in the TAC.

In the same way, an antagonistic behavior is observed in Figure 6 in the TAC and EI99. Remember that the EI99

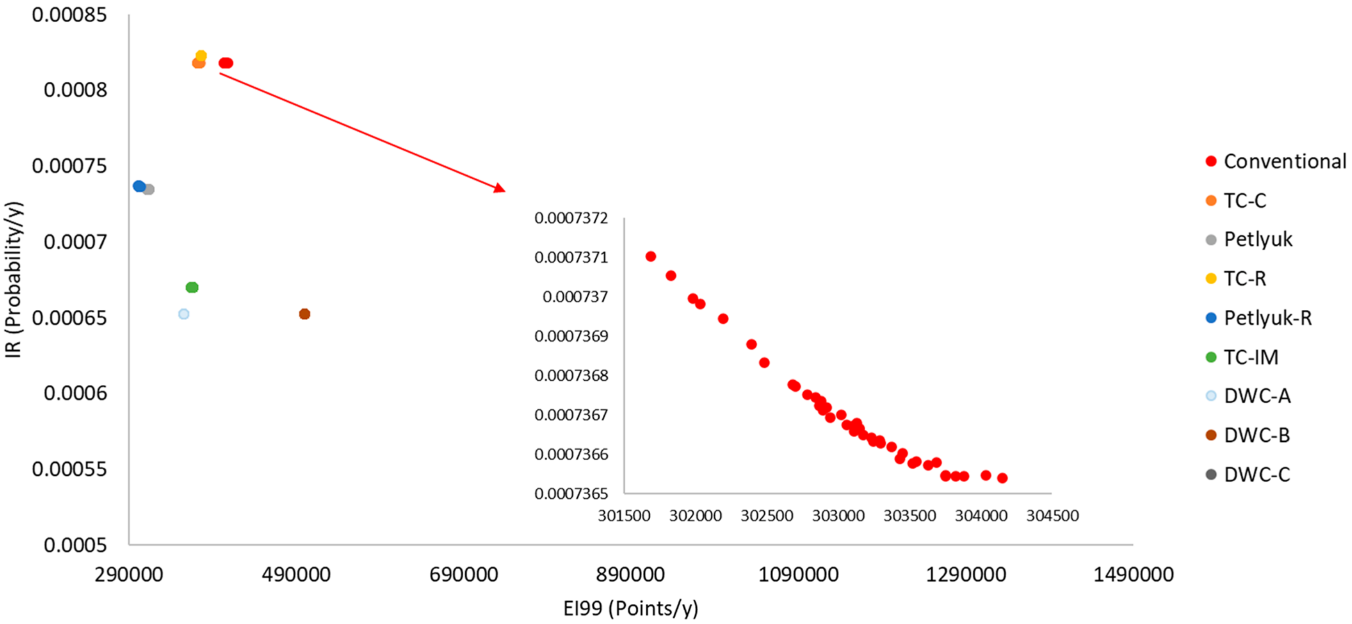

Figure 7. Pareto front evaluating the inherent safety and the eco indicator 99.

evaluation considered the impact of the heating steam, the steel to build the column, and the electricity for pumping, with the main weight of the heating steam. In this sense, the Pareto front indicates that the optimum zone can be found where the contribution of the three categories can remain relatively stable. However, if you leave that area, either due to energy, steel, or electricity consumption, the TAC increases considerably.

Finally, Figure 7 shows the relationship between the environmental impact (EI99) and the individual risk of the process (IR). In a similar situation to Figure 6, one way to reduce the environmental impact is by reducing the energy requirement. This change is largely associated with designing equipment with low reflux ratios. In the particular case of organic compounds diluted in water, designing with low reflux ratios results in higher internal concentrations of the organic compounds. On the other hand, high reflux ratios are an indication of a greater amount of water that can return to the interior of the column, generating lower concentrations of the organic compounds. This type of relationship between design variables and objective functions generates antagonistic behavior. One point to highlight in the optimized designs is that the water separated in the first column can be used in the hydrolysis column, and the recovered methanol can be recycled to the esterification column. This is a very important point since water has to be removed and its removal is energy intensive. Additionally, the reuse of methanol and water, recovered during the process, allows generating an environment of sustainability and economic profitability, which makes intensified designs very attractive to be applied at an industrial level. This is due to the reduction in the use of fresh water and raw material (methanol) for the process. This class of mass integrations between recovered flow streams generates important economic and energy savings in the intensified processes.[47] Finally, considering the DWC and DWC-A schemes as a good alternative, Figures 8, 9, 10, and 11 show the composition and temperature profiles, as well as the complete balance for the reference case and the DWC-A scheme, and additionally, Table S4 shows data about composition, temperature, and pressure in DWC-A.

Finally, the control study resulted in very interesting trends. The minimized condition number is connected to stability aspects. Therefore, it is possible to qualitatively interpret the values of the condition number, beyond its numerical value. In such a way that lower values is connected to stability aspects and in that sense to a good dynamic behavior.[48] Preliminarily, the dynamic properties of the conventional alternatives are relatively poor, compared to the schemes with a higher degree of intensification. That is, the alternatives with higher topological simplicity would have more problems to be controlled under closed-loop analysis.

Within the alternatives where the freshwater stream is not omitted, there is a very clear trend in the presence of thermal couplings. It is clear that the higher the number of couplings, the better the control properties. However, it should be noted that not all thermal couplings improve this indicator in general. Observing the topological differences between the different alternatives without mass integration, it should be noted that the thermal coupling between the first two columns has the greatest impact on the dynamic properties of the alternatives.

On the other hand, a comparison between the alternatives with and without integration of the water current indicates that, for the great majority of alternatives, this movement has a penalty on the dynamic properties. However, as in the case of the alternatives without mass integration, the DWC-C scheme with the highest degree of energy integration resulted in the best control properties. Even better than the alternatives with the presence of the freshwater current.

In this sense, although the DWC-A alternative turned out to be the most economically and environmentally viable of all the alternatives presented in that work, its typological structure would hinder the controllability of this alternative. On the other hand, the least viable alternative, in terms of economic and environmental impact, turned out to be the one that would be the least difficult to control in a closed-loop test. Table 6 shows a summary of the objective functions of the separation alternatives analyzed.

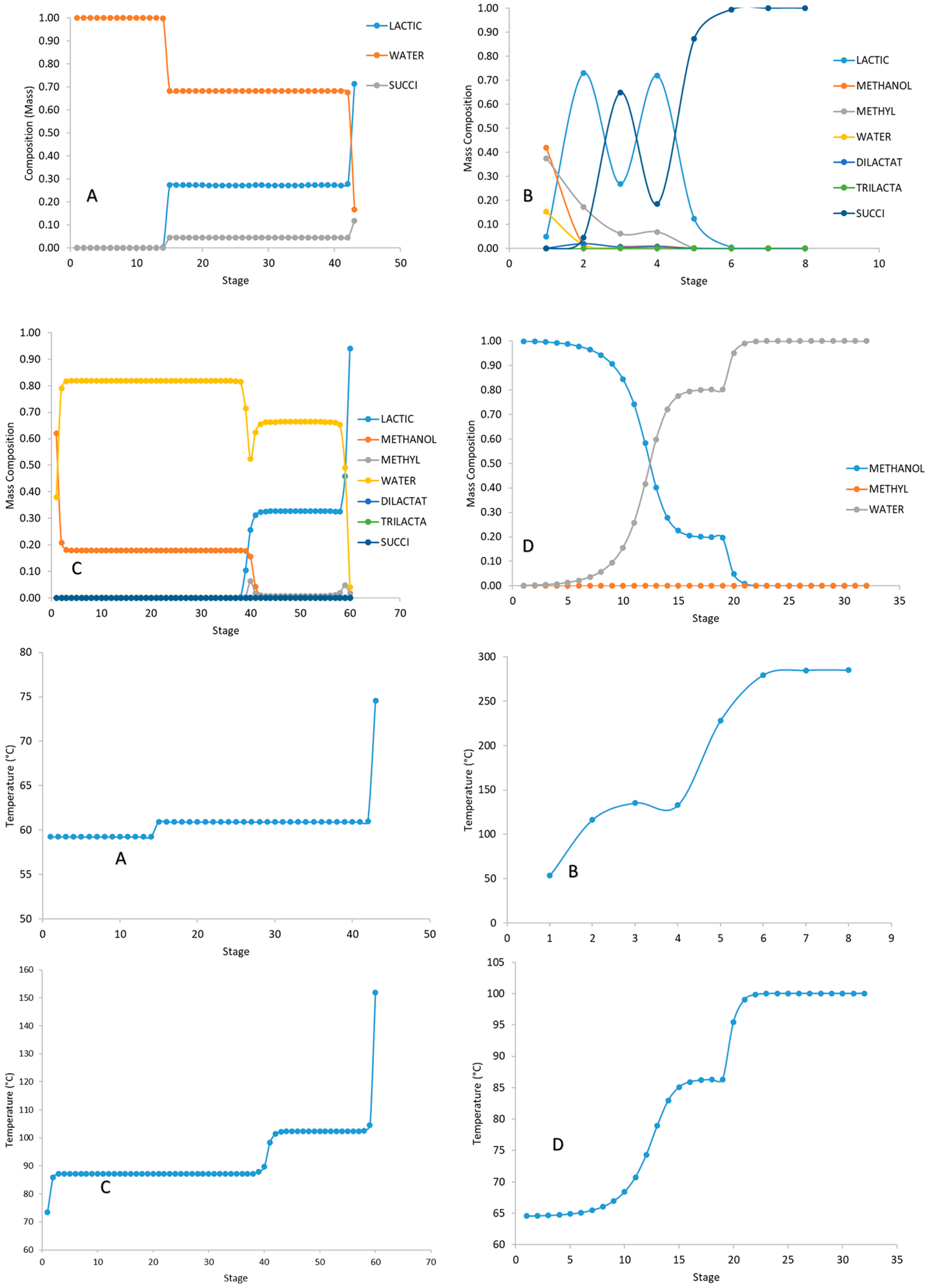

Figure 8. Composition and temperature profiles for the conventional scheme, columns A−D.

5. CONCLUSIONS

An analysis of various lactic acid separation and purification schemes was performed in this work. It was observed that the substitution of reboilers for thermal couplings does not reduce the environmental or economic impact significantly; on the contrary, a slight increase in the risk of the schemes with this topology was observed. On the other hand, the coupling that replaced a condenser did cause a general improvement in the performance indicators. The same indexes are slightly compromised when a reboiler is substituted by a thermal

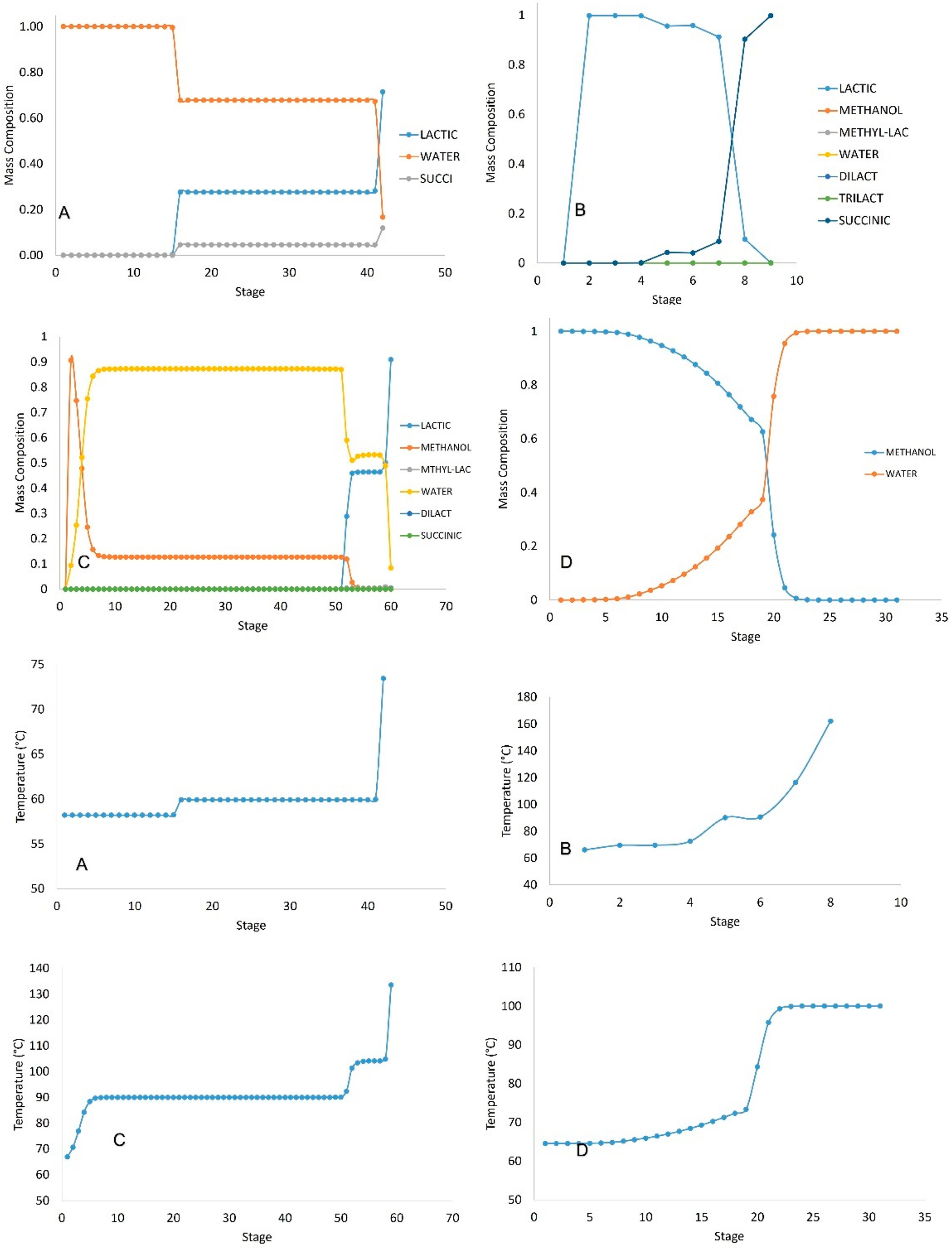

Figure 9. Composition and temperature profiles for the DWC-A scheme, columns A−D.

coupling. Once all the separation schemes had been evaluated, the scheme that showed the best performance was the DWC-A. This scheme represented an approximate saving of 4% and 12% in the TAC and IR, respectively. An interesting trend was observed regarding equipment sizing; bigger equipment impacts directly in capital cost and the impact of steel index in EI99. However, note that the IR values depend greatly on the amount of matter inside the equipment, which is related to column size; as long as the inner matter increases, the IR increases.

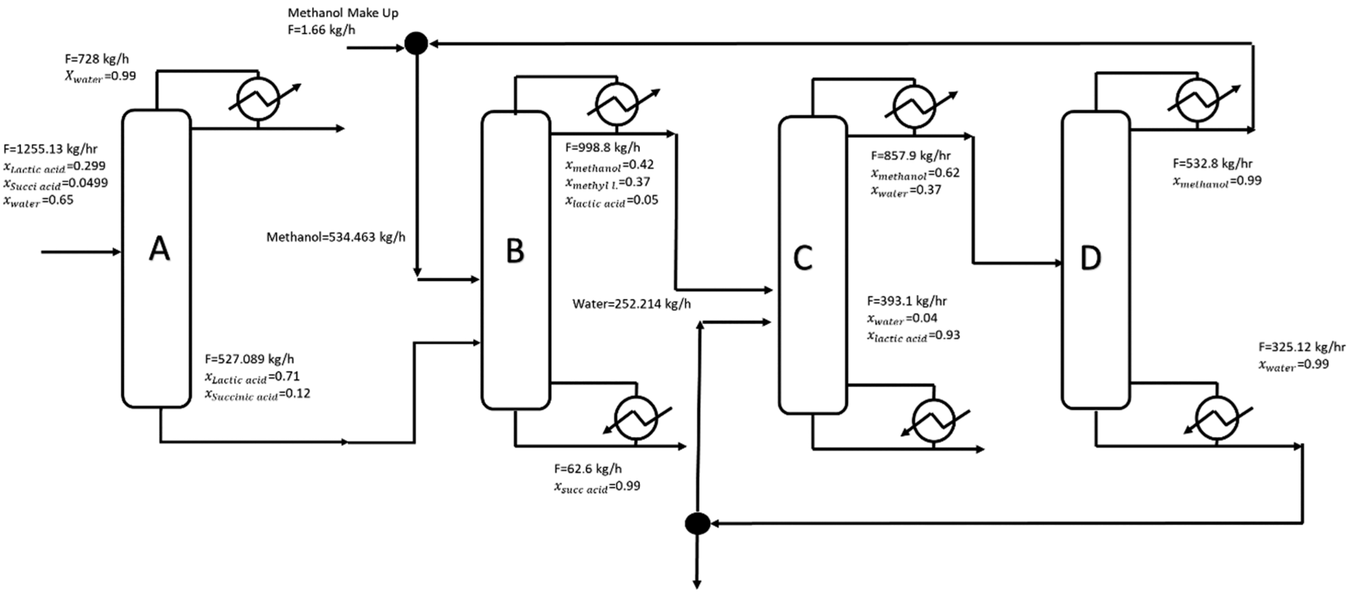

Figure 10. Mass balance for the conventional scheme, columns A−D.

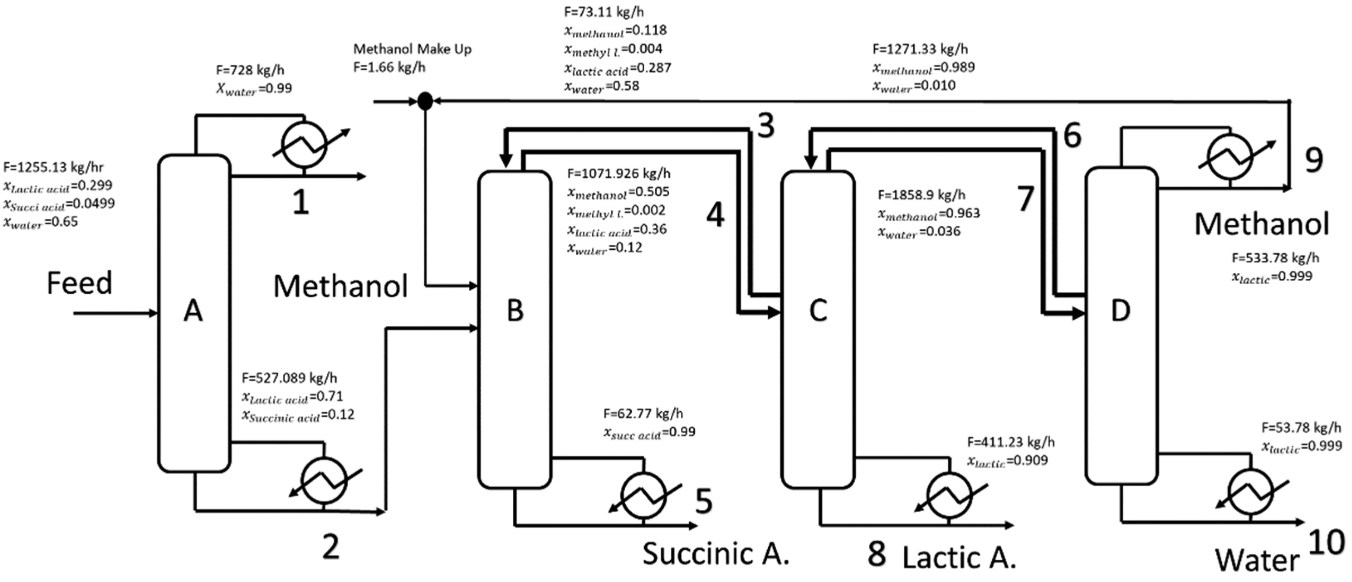

Figure 11. Mass balance for the DWC-A, columns A−D.

Table 6. Objective Functions of All the Alternatives Evaluated

	reboiler duty (cal/s)	TAC ($/y)	EI99 (Eco-points/y)	IR (probability/y)	condition number
conventional	448115	1274559	405025	0.000818084	8.24×10^{24}
TC-C	338868	1062454	302771	0.000818023	
TC-R	417337	1134718	376834	0.000823006	9039.28
DWC	349927	1086548	313189	0.000734825	13654.40
DWC-R	338292	1062449	303062	0.000736675	7887.27
TC-IM	387370	1111585	365591	0.000818369	8.21E24
DWC-A	391938	1044799	356249	0.000652447	3.2×10^{18}
DWC-B	536473	1498392	500695	0.000652398	2800423.9
DWC-C	1447227	2871129	963497	0.000652398	54.186

The comparison between alternatives with and without mass integration was favorable, from an economic and environmental point of view, for the alternatives with integration. The DWC-A scheme had less impact in these areas. However, a basic controllability study indicated some important points: the alternatives with greater topological simplicity do not have the best control properties, and it is possible to generate better controllability in schemes with mass integration, but this controllability is associated with a higher cost and environmental impact.

As a product of the esterification reaction, water is inevitably produced in the esterification reaction. On the other hand, this water can be used directly in the next column section where the hydrolysis reaction is developed. In that sense, the proposals generated in this work demonstrate that it is possible to couple the direct production of water in this pair of columns. Evidently, there is a stream where water is produced in a considerable amount in the last column section. It is likely that the stream arising at the bottom of the fourth column can be redirected to direct use for the hydrolysis reaction. However, there is no evidence at this time on the impact that this recirculation of water could have. The operation seems feasible; however, there are quite a few unknowns that arise from this possible implementation, such as how would it affect the controllability of the process, would there be a significant improvement in product orientation, and so on. With regard to the scope of this proposal, the possibility of saving water has been demonstrated, which clearly decreases the environmental impact in the production of lactic acid through this proposal.

From the author's perspective, the best scheme, based on a circular economy framework, resulted in a DWC-based scheme. This configuration complies with circular economy characteristics and results may indicate the possibility of using those intensified technologies at an industrial level for lactic acid purification with good circular economy indicators and relatively good water savings.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c04050.

> Sustainability, economic, environmental, and inherent safety metrics; controllability index calculations; optimization strategy and objective function; normalization procedure; kinetic data; binary interaction parameters; and composition, temperature, and pressure (PDF)

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Notes

The authors declare no competing financial interest.

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