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Innovative reactive distillation process for levulinic acid production and purification

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ABSTRACT

Levulinic acid is considered among the top twelve chemicals from biomass in terms of market potential, due to its considerable number of applications. Levulinic acid is obtained by acid hydrolysis of glucose using dilute sulfuric acid as a catalyst. Because of this, the resulting stream has an excess of water, which has an impact on energy consumption in the separation and purification process. So, it is important to analyze sustainable alternatives. Process intensification can help achieve this goal. Particularly, reactive distillation (RD) is an intensified process where is carried out the chemical reaction and distillation in a single equipment, the advantage of this reduction has a direct impact on the capital cost, and energy consumption in the last stages of separation. and environmental impact, improving the sustainability of the process. Additionally, reactive distillation positively impacts performance, and it is used to separate dilute mixtures more efficiently. Therefore, this work's objective is to implement a process intensification using a reactive distillation column to reduce energy consumption, process costs, and the final cost of Levulinic acid production. A conventional scheme is used to compare the energy, cost, environmental, and conversion impacts when using reactive distillation. The results show a total conversion of glucose to Levulinic acid using RD and similar purities are obtained when using the conventional reactor. In addition, it presents savings in the cost of the equipment by 23% and 24% in energy consumption compared to the conventional system.

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Abbreviations: NREL, National Renewable Energy Laboratory; LA, Levulinic acid; PVC, Polyvinyl chloride; CAGR, Compound annual growth; HMF, 5-hydroxymethylfurfural; PI, Process intensification; RD, Reactive distillation; CSTR, Continuous stirred-tank reactor; DETL, Differential evolution algorithm with list taboo; TAC, Total annual cost; NRTL, Non-Random Two-Liquid; HOC, Hayden-O'Connell; TL, Tabu List; DE, Differential evolution; Q, Reboiler duty; N, Number of stages; N_f , Column feed stage; RR, Reflux ratio; D, Distillate flow rate; τ , Residence time; H, Holdup; R_S , Reactive stages; ϕ , Column diameter; y_iP_C , Purities; x_iP_C , Minimum purities; w_iF_C , Recovery flows; uF_C , Minimum recovery flows; HHV, Higher Heating Value; CS, Conventional System; RDS, Reactive Distillation System; %wt, Weight percentage; R1, Reactor in Conventional System; C1, Column 1 in Conventional System; C2, Column 2 in Conventional System; C3, Column 3 in Conventional System; CR1, Column 1 in Reactive Distillation System; CC2, Column 2 in Reactive Distillation System; CC3, Column 3 in Reactive Distillation System; P, Pressure; T, Temperature; W_w , Water weight percentage; W_G , Glucose weight percentage; W_{AS} , Sulfuric acid weight percentage; W_L , Levulinic acid weight percentage; W_F , Formic acid weight percentage

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1. Introduction

Given changing world energy needs, research, and a road map for the biorefinery of the 21st century are vital. This biorefinery vision will contribute to sustainability by its inherent dependence on sustainable bioresources and by recycling waste with the entire process becoming carbon neutral. It leverages our knowledge in plant genetics, biochemistry, biotechnology, biomass chemistry, separation, and process engineering to have a positive impact on the economical, technical, and environmental well-being of society. An integrated biorefinery is an approach that optimizes the use of biomass for the production of biofuels, bioenergy, and biomaterials for both short- and long-term sustainability (Popa, 2018). The economic production of biofuels is often a challenge. A very promising approach to reducing biofuel production costs is to use so-called biofuel-driven biorefineries for the co-production of both value-added products (chemicals) and biofuels from biomass resources in a very efficient integrated approach (de Jong et al., 2012).

National Renewable Energy Laboratory (NREL) identifies twelve building block chemicals (value-added products) that can be produced from sugars via biological or chemical conversions. The twelve sugar-based building blocks are 1,4-diacids (succinic, fumaric, and malic), 2,5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxy butyrolactone, glycerol, sorbitol, and xylitol/arabinitol (Werpy et al., 2004).

Levulinic acid (LA) has enormous potential as an economical raw material to produce a range of chemical substances of industrial importance such as Methyl tetrahydrofuran, an interesting compound used as an additive for fuels with a potential of 10000–1000000 million pounds/year; delta-amino levulinic acid, a biodegradable herbicide with 175–350 million pounds/year; Di phenolic acid, a plasticizer with 35 million pounds/year and 1,4-butanediol a monomer with 200 million pounds/year (Bozell et al., 2000). The global levulinic acid market exhibited moderate growth from 2015 to 2020. Levulinic acid is used to maintain the acidic balance of various pharmaceuticals, agrochemicals, and solvents. It is also used for the manufacturing of personal care products, food additives, resins, coatings, fuel additives, and biofuels. The growing agriculture and biofuel industries are among the key factors driving the growth of the market. Levulinic acid is increasingly being utilized in solvents, pesticides, fertilizers, and herbicides as a green alternative. Furthermore, the increasing product adoption rate as a substitute for phthalate plasticizers in the manufacturing of polyvinyl chloride (PVC) products is another major growth-inducing factor. In comparison to phthalate plasticizers, levulinic acid is relatively less lethal for consumers. Additionally, the growing utilization of levulinic acid in the production of nylons and rubbers is positively impacting the market. Other factors, including the flourishing construction and automotive industries, along with the increasing R&D activities in the field of chemistry and biotechnology, rapid industrialization, and urbanization across the emerging nations, are projected to drive the market further. The global levulinic acid market is expected to grow at a compound annual growth (CAGR) of around 5% during the forecast period (2021–2026) (Research, I, 2021).

LA can only be produced exclusively using chemical processes catalyzed by acid, unlike other high-value biomass derivatives, which can be obtained from a biological route such as fermentation, hydrogenation, or oxidation in the

production process. This attribute makes levulinic acid especially attractive because a variety of inexpensive lignocellulosic feeds can be used for the direct production of this thermodynamically stable molecule (Serrano-Ruiz et al., 2010). To be able to transform lignocellulosic biomass to LA using acid hydrolysis, it is necessary to start from glucose, therefore, it is first necessary to pretreatment the biomass that include thermal hydrolysis to eliminate the hemicellulose and enzymatic hydrolysis to eliminate the lignin. The glucose obtained is subjected to acid hydrolysis and transformed into 5-hydroxymethylfurfural (HMF) and water (Schmidt et al., 2017). In the second stage, HMF reacts with water in the acid medium (sulfuric acid), forming levulinic acid and formic acid. For purification purposes, the amount of water represents the biggest problem in the purification of levulinic acid, so this high energy consumption is the limiting factor for further expansion at an industrial level (Alcocer-García et al., 2019). Under this scenario, the need to generate a profitable process that can improve current technology with economic and environmental advantages is clear. In this sense, for improving the production of levulinic acid two strategies may be approached:

In reaction zone. This is through the synthesis of new routes or processes to produce levulinic acid from biomass that generate a more concentrated stream and thereby reduce the cost of purification.

In the purification zone. The implementation of more efficient separation processes ensures the reduction of purification energy consumption.

The processes for the separation of liquid mixtures include many forms of distillation and depend on the vapor-liquid balance of the components in the mixture and their thermodynamics. In the case of purification of non-ideal mixtures (e.g., separation of azeotropes), the separation processes consume an important amount of energy and lead to high capital costs and environmental pollution (Chaudhari et al., 2018), which justifies searching for alternatives to conventional distillation, which is normally used for the purification of levulinic acid (De Rijke et al., 2019; Dunlop and Chemistry, 1948; Seibert, 2010). Likewise, the problems related to the high consumption of energy required by the distillation processes and the need to reduce energy costs have promoted the search for solutions to achieve efficient use of energy in the distillation process (Alcocer-García et al., 2019; Bonet-Ruiz et al., 2010; Vural-Gursel et al., 2012; Kiss, 2013). Hybrid schemes have been proposed for the purification of levulinic acid to remove excess water through the use of liquid-liquid extraction (Nhien et al., 2016) and schemes to reduce energy consumption such as dividing wall columns (Alcocer-García et al., 2019).

On the other hand, Process intensification (PI) has been defined as a design philosophy that aims to enhance process performance by improving phenomena that limit it at different scales (Lutze et al., 2012). Then, process intensification consists of the development of innovative technology and techniques that, compared to those currently commonly used, are expected to provide dramatic improvements in manufacturing and processing. In this way, PI may substantially reduce: the relationship between the size of the equipment and production capacity, the energy consumption, or the production of waste, and ultimately, translate into cheaper and more sustainable technologies (Stankiewicz and Moulijn, 2000). Therefore, through intensification, greater efficiency, lower expenses, operations that are more

respectful of the environment, reduction in size, or any combination of the above are achieved (Torres-Ortega et al., 2018). Therefore, various authors have reported intensified processes with favorable economic, environmental (Yang et al., 2019; Gutiérrez-Guerra et al., 2009; Jantes-Jaramillo et al., 2008; Westerberg, 1989), and energy savings (Emtir et al., 2003; Emtir et al., 2001; Alcantara-Avila et al., 2008; Torres-Ortega et al., 2015), such as systems thermally coupled (Torres-Ortega et al., 2015; Vazquez, Castillo et al., 2009; Segovia-Hernández et al., 2004; Gómez-Castro et al., 2008), thermally coupled dividing wall columns (Alcocer-García et al., 2019; Gómez-Castro et al., 2008; Gómez-Castro et al., 2013; Méndez, Valencia et al., 2008), hybrid systems such as reactive distillation (RD) (Jiao et al., 2012; Adams and Seider, 2009; Hernández et al., 2009; Kiss et al., 2019), Petlyuk systems (Abad-Zarate et al., 2006; Halvorsen and Skogestad, 1997; Segovia-Hernández et al., 2005), among others. The use of intensified distillation processes for multicomponent systems has been recognized as an alternative to reduce energy consumption and operating costs (Errico et al., 2009; Rong, 2014). These types of schemes can offer operational advantages compared to conventional distillation systems. However, the modeling and simulation of these intensified processes can be difficult since there are no design methods to effectively determine the optimal values of the degrees of freedom that allow the suitable operation of the separation scheme (Salas-Aguilar et al., 2018).

Especially, RD allows chemical reaction and separation to take place simultaneously inside the column (Fig. 1), thus providing a valuable synergistic effect that overcomes the equilibrium limitations of many reactions, e.g., (trans)-esterification, etherification, hydrolysis, (de)alkylation, (de)hydration, (de)-hydrogenation, amination, amidation, aldolization, chlorination, condensation, isomerization, dimerization, and oligomerization (Kiss, 2013; Sundmacher and Kienle, 2006; Kiss, 2014; Kiss et al., 2016). RD can be also used for fast reactions where the high concentration of one of the products or reactants may lead to undesired side reactions, hence the strong need to reduce their concentration in the reacting phase to minimal levels to hinder the undesired side reactions. RD can be also used to separate azeotropes, based on the difference between the reaction rates of the substances forming the azeotrope with another reactant. For instance, one compound from an azeotrope could be reacted to form products that are easier to separate (by distillation) from the other substances in the azeotrope. Furthermore, the products could undergo a reversible reaction to form the original substance using a RD process to achieve the desired separation of the azeotrope mixtures (Li et al., 2016; Li et al., 2018). In our case, the RD would facilitate the removal of excess water and thereby reduce energy consumption in later stages. Furthermore, RD can also be used to separate azeotropes, in our case the azeotrope that forms between water and formic acid.

Although reactive distillation is an intensified process with enormous potential, it is used at an industrial level to produce a wide range of products. With energy-saving potential, process intensification combining two or more conventional unit operations within one unit has been paid more attention in chemical process engineering. Considered the most typical case of process intensification, RD can help reduce operating costs, capital costs, and environmental impacts (Li et al., 2019) and translate into cheaper and more sustainable technologies.

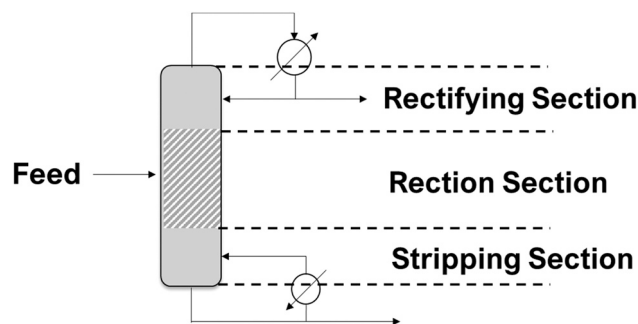


Fig. 1 – Conventional topology of reactive distillation system.

On the other hand, there is currently a strong transition from the oil-dependent industry to a more sustainable one based on biomass (Anyaocha and Zhang, 2022). One of the biggest challenges in this transition towards bioprocesses is to ensure the sustainability of the bioprocess (Liu, 2020; Pogaku et al., 2013), through integrating metrics such as economic profitability, environmental impact, and safety. Process intensification is a tool that allows the development of more sustainable technologies (Stankiewicz and Moulijn, 2000). Examples of the implementation of process intensification in bioprocesses, using reactive distillation for the production or purification of bioproducts, such as bioethanol (Kaymak, 2017), biodiesel (Albuquerque et al., 2020), butyl acrylate (Niesbach et al., 2015), lactic acid (Mayorga et al., 2021), n-butyl levulinate (Chung et al., 2015). Although purification schemes for bioproducts or biofuels have been studied, the use of reactive distillation for the production or purification of building blocks has not been implemented. Therefore, based on the importance of levulinic acid and the potential of RD, its use to produce levulinic acid is proposed.

Furthermore, within the literature review, a process using reactive distillation to obtain levulinic acid from glucose has not been reported. On the other hand, investigations of levulinic acid are mainly focused on its purification, such as reactive liquid-liquid extraction and recovery of levulinic acid (Brouwer et al., 2017) where a double liquid-liquid extraction is carried out using trioctylphosphine oxide and Methyl-isobutyl-ketone as solvents, liquid-liquid extraction using Methyl tetrahydrofuran to replace the hexane used (Silva et al., 2018), the effect of organic solvents such as γ -valerolactone in separation section of levulinic acid (Tuppurainen et al., 2018), hybrid systems use the combination of liquid-liquid extraction, decanter and distillation columns (Nhien et al., 2016), and the use of intensified schemes to reduce energy consumption such as thermally coupled schemes and dividing columns (Alcocer-García et al., 2019); these studies focus on the purification of levulinic acid from the mixture resulting from acid hydrolysis, leaving aside the reactive part.

In search of the development of sustainable process schemes, RD remains one of the best process intensification technologies that meet all the principles of green engineering: a design for separation, maximizing efficiency, use of renewable vs depleting sources, preventing rather than treating, and minimize excess, integrate local material and energy flow, output-pulled vs input-pushed, and design for a commercial afterlife. RD has several advantages, including a low number of processing units, improved overall rates, the ability to overcome unfavorable equilibrium, the ability to

avoid difficult separations, improved selectivity, lower energy consumption, lower CO₂ emissions, and the use of little or no solvent. RD remains an important PI technique capable of bringing green chemistry and sustainable engineering into the chemical process industry, given the outstanding progress in equipment development, modeling and simulation, design and control strategies, real-time optimization, and the rapid pace of exploring new applications (Constable, 2002).

Constraints such as the need for a common operation range for distillation and reaction (similar temperature and pressure), proper boiling point sequence (product should be the lightest or heaviest component, whereas side or by-products boil at intermediate temperatures), and proper residence time characteristics limit the application of RD (Luyben and Yu, 2009; Heimlich and Martin, 1960).

Therefore, in this work, reactive distillation is proposed, both to improve the conversion of glucose to levulinic acid, and to facilitate its separation to obtain a more sustainable process, this by promoting the formation of LA in a better way than the conventional process and at the same time separating the largest amount of water from the process; and thereby reduce the capital cost, the use of services and globally the impact generated by the conventional process. Furthermore, to obtain a fair comparison, the conventional process using a continuous stirred-tank reactor (CSTR) followed by three distillation columns and the intensified process consisting of a reactive distillation column followed by two distillation columns were optimized using the differential evolution algorithm with tabu list (DETL), to minimize energy consumption.

In addition, to integrate sustainability metrics (Chang et al., 2006) once the optimal designs of the proposed design have been obtained, a sustainability analysis was carried out using the total annual cost (TAC) and CO₂ emissions as metrics. These metrics are evaluated in a post-optimization stage since both are related to energy consumption and it would be redundant to place them as an objective function within the optimization. However, its calculation helps to show the advantages of implementing reactive distillation.

2. Feasibility of reactive distillation

The amount of water present in the outlet stream of the reactor, in the conventional process, represents the biggest problem in the production and purification of levulinic acid, which is why this high energy consumption. As described in the last few paragraphs, reactive distillation (RD) is an innovative technology that could improve levulinic acid production and purification through an intensified perspective. Furthermore, the current literature does not provide information on conventional or intensified technologies to produce levulinic acid using reactive distillation.

Although reactive distillation is an excellent alternative, its area of application is restricted. Therefore, it is necessary to analyze the feasibility of using reactive distillation. Weingarten et al. (2012) describe some limitations that must be taken into account at the time of design of a reactive distillation column. The principal limitation is that there must be no mismatch in the temperatures that are favorable for reaction and the temperatures that are favorable for separation. Because reaction and separation both occur in a single vessel at essentially a single pressure, the temperatures throughout the column are fixed by tray compositions. The second major limitation for the application of reactive

distillation is that the relative volatilities of the components must be such that the reactants can be contained in the column and the products can be easily removed from the top and/or from the bottom. Another limitation of reactive distillation is the need for reasonably large specific reaction rates. If the reactions are slow, the required tray holdups and several reactive trays would be too large to be economically provided in a distillation column. Other Restrictions Reactive distillation is limited to liquid-phase reactions because there is little holdup in the vapor phase. The heat of the reaction must be modest to prevent substantial changes in vapor and liquid rates through the reactive zone. A highly exothermic reaction could completely dry up the trays.

Therefore, these limitations were reviewed for our specific case study. Regarding the temperatures for the reaction to occur, it has been reported that the decomposition of glucose at HMF begins at 100 °C (Girisuta et al., 2013) thus giving the first stage of acid hydrolysis. This decomposition can continue at temperatures above between 160 °C and 200 °C (Shah et al., 2012; Chakraborti et al., 2018); and the boiling point of the most volatile component is 100 °C. Therefore, it fulfills the first and second criteria, because exist conditions where the reaction and separation are favored and the most volatile component of the mixture can be separated by the dome. Regarding the hold-up, small values would be expected since the decomposition reaction of glucose to HMF and the conversion of HMF to levulinic acid and formic acid are fast (Ambrose and Ghiassee, 1987). Finally, in this case, the reactions are of the endothermic type. Therefore, with good handling of the reboiler duty, the stages are prevented from drying out.

On the other hand, according to Pazmiño-Mayorga et al. (2021), before any synthesis or design task, it is necessary to determine the feasibility of any reactive distillation scheme. Some of his guidelines coincide with those mentioned by Luyben et. al. However, the following should also be considered: the presence of more than one product, in this case, the products are levulinic acid, formic acid, and water. For none of the components, neither the operating pressure nor the temperature is close to the critical region. In this case, the regions critical for levulinic acid (443.65 °C and 38.88 atm) (Subawalla and Fair, 1999) and formic acid (314.85 °C y 57.34 atm) (Huang et al., 2006) are conditions superior to those carried out acid hydrolysis.

In addition, an important feature of this process is that an azeotrope is present in the formic acid/water system in the reactive distillation column. The normal boiling points of formic acid and water are 100.55 °C and 100.02 °C, respectively. The azeotrope contains a mass fraction of water of 0.2475 at 1 atm and 106.81 °C. Therefore, using reactive distillation is promoting the formation of LA in a better way than the conventional process and at the same time separates the largest amount of water from the process.

3. Case study

Acid hydrolysis reactions to obtain levulinic acid can be carried out using enhanced alternatives, such as reactive distillation columns. The use of RD to produce levulinic acid has not been explored. Therefore, this study pretends to show that it meets all the preliminary requirements to affirm the complete viability of the RD technology to produce and purify levulinic acid.

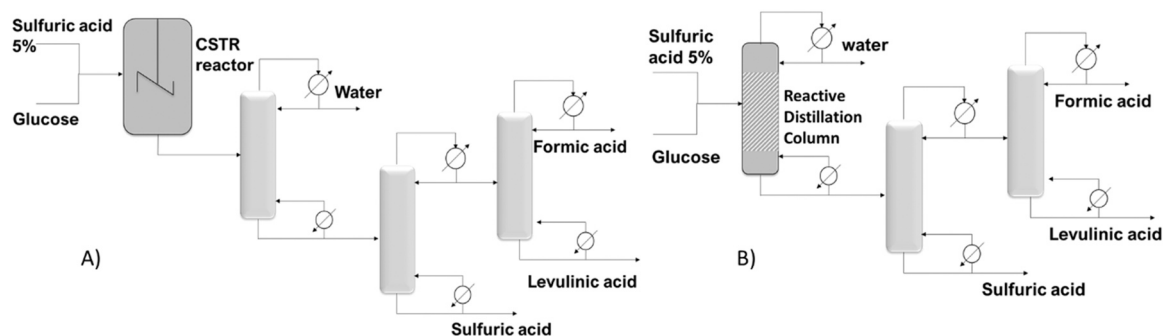


Fig. 2 – Studied processes. A) Conventional System, B) Reactive Distillation system.

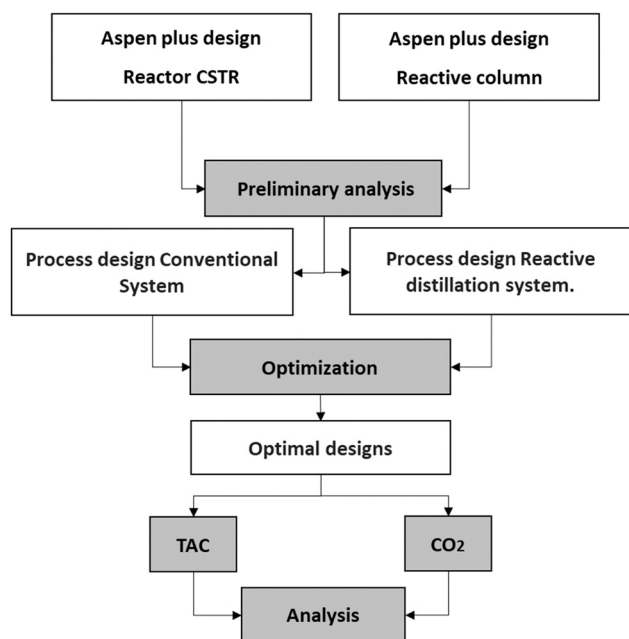
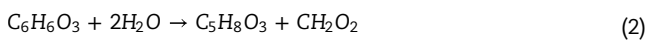


Fig. 3 – Methodology.

For the reaction part, the kinetics were reported by Shah et al. (2012). In the first stage, the glucose that reacts undergoes a decomposition process in the presence of sulfuric acid as a catalyst, to degrade to HMF and water:



In a second stage, HMF reacts with water in the acid medium, forming levulinic acid and formic acid:



Because the products obtained are organic acids and polar compounds, the NRTL-HOC thermodynamic model was used. For its part, the Non-Random Two-Liquid (NRTL) model is recommended for highly non-ideal chemical systems and can be used to calculate the liquid-vapor equilibrium. On the other hand, the Hayden-O'Connell (HOC) equation of state calculates the thermodynamic properties of the vapor phase of organic acids. A 5% diluted sulfuric acid stream and a 70% diluted glucose stream were considered. The estimated production of levulinic acid is 5×10^7 Kg/year, this was set since in the literature it is estimated that production on this scale is favored by the economy of scale (Alcocer-García et al., 2019; Nhien et al., 2016).

The processes were simulated using Aspen Plus. The kinetics of the reactions, for reaction (1), the published value (Shah et al., 2012) of the activation energy was 86.33 kJ/mol

and a pre-exponential factor of 0.0837, while for reaction (2) the values were 56.95 kJ/mol and 0.317, respectively. The operating conditions of the reactor are 170 °C and 1 atm (Shah et al., 2012). Therefore, in this work, two processes were studied in the conventional system and the reactive distillation system (Fig. 2):

- Conventional system. In the conventional process, the glucose is transformed in a CSTR reactor, the resulting mixture is separated by 3 distillation columns, Fig. 2A.
- Reactive distillation system. In the intensified process, the glucose is transformed into a reactive distillation column, one component of the mixture is separated in this column and the rest of the components are separated by two distillation columns, Fig. 2B.

4. Methodology

In this section, the methodology followed in this work is required. In the first stage, an analysis of the residence time and temperature profiles is carried out, in preliminary designs of the reactor and the reactive distillation column. Once the feasibility was determined, an optimization process was carried out to find the optimal designs that minimize the reboiler duty. Finally, a comparative analysis was carried out using the total annual cost (TAC) and CO₂ emissions as criteria. The methodology is summarized in Fig. 3.

4.1. Preliminary analysis

One of the objectives of the preliminary analysis is to establish the residence time in the CSTR reactor. That is why it is necessary to explore how long a high conversion of glucose occurs. It is important to know it since this variable is essential to obtain the desired products and will be part of the variables to be optimized.

On the other hand, for the reactive distillation column, it is necessary to verify that the temperature profiles in the column are within the range of temperatures at which acid hydrolysis occurs (Barbosa and Doherty, 1988). In addition, some heuristic rules for the design of a reactive distillation column previously proposed by Subawalla and Fair were taken into account (Melles et al., 2000). This heuristic was summarized in an algorithm that can be used to estimate parameters such as column pressure, reactive zone location, total theoretical stages, reactant feed location, reflux ratio, and column diameter. Those operative variables were further varied having as target and constrain both the purity of levulinic acid and the minimization of energy consumption, as shown in Fig. 4. The variables that have the most impact on the minimization of

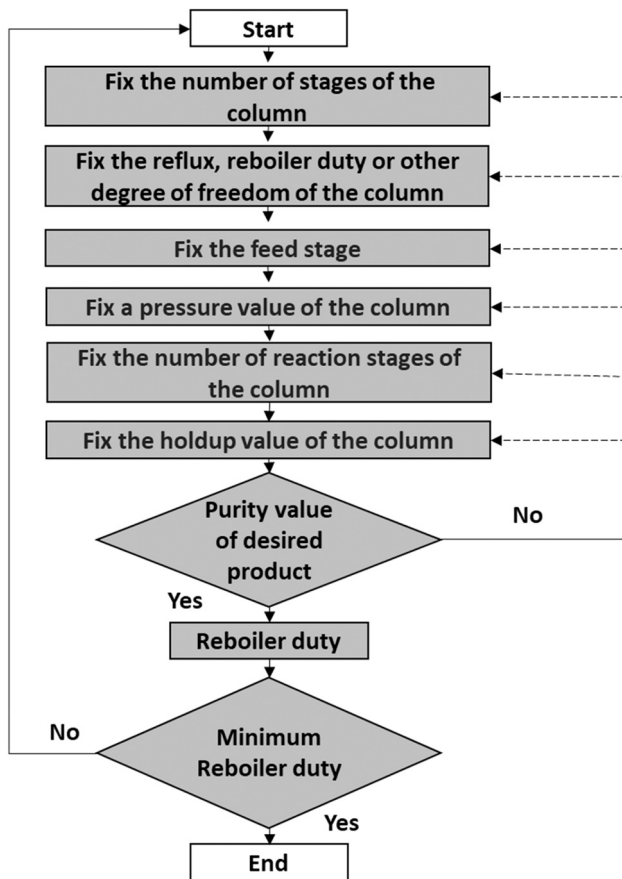


Fig. 4 – Algorithm to make a reactive column.

energy consumption are: the column pressure, the number of stages, the reboiler duty, and the bottoms flow rate. On the other hand, other variables such as the feed stage or holdup showed a minimal impact, practically negligible in the minimization of the energy consumption. The implementation of such an algorithm is relatively simple. However, it cannot guarantee the optimal column design. As highlighted by Huang et al. [Srinivas and Rangaiah \(2007\)](#), there is a lack of heuristic rules for the optimal design of reactive distillation columns. For the holdup, the calculation is not possible to set an arbitrary value. To find the appropriate holdup value it was necessary to follow the methodology reported by Barbosa and Doherty [\(Hayes et al., 2008\)](#). The methodology consists firstly; of specifying both the compositions of the products (top and bottom) and the value of the reflux ratio (previously obtained by the Subawalla and Fair methodology). Then, the aim is to find a suitable value for the holdup. In other words, to find the volume on the trays in which the reaction proceeds, such that when calculating the composition on each tray, the composition profiles of the stripper and rectifier intersect each other [\(Burke, 2013\)](#).

Once the design variables of the reactive distillation column and the CSTR reactor were established, the distillation columns were designed to separate the mixture resulting from both pieces of equipment. Resulting in the conventional system and the reactive distillation system shown in [Fig. 3](#). Although these systems have been designed under rigorous methods, they have degrees of freedom such as several stages, reflux, diameter, bottom flows, feed stage, so the selection of these variables becomes an optimization problem. This analysis is important to establish values as a starting point for the optimization of systems.

4.2. Optimization process

The optimal design of the conventional system and reactive distillation systems to produce and purify Levulinic acid is a non-linear and multivariable problem, and the objective functions used as optimization criteria are generally non-convex 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 [\(Amezquita-Ortiz et al., 2022\)](#) improves the computational efficiency of differential evolution (DE) employing testing challenging phase equilibrium calculations followed by parameter estimation problems in dynamic systems known to have multiple minima. The optimization method is described in [Supplementary Material](#).

The optimization of the sustainable schemes for the production and purification of Levulinic acid will be restricted to purities (y_i) required in the market for each product. The minimum purity targets were set at 98% (%wt) for levulinic acid, 85% for formic acid, and 99.9% for sulfuric acid. The purities for levulinic acid and formic acid were considered according to the current industrial uses [\(Parhi et al., 2019; Taqvi et al., 2016\)](#) and the purity of sulfuric acid to be reused as a catalyst. In this case, sulfuric acid is considered a product so that it can be used again in the process, and it is not necessary to feed a fresh stream. Furthermore, sulfuric acid is a strong acid, so for safety reasons, it is advisable to remove it from the process.

The objective function is to minimize the reboiler duty (Q), subject to:

$$\text{Min } (Q) = f(N, N_f, RR, D, B, \tau, H, R_s, \varphi, T) \quad (3)$$

Subject to

$$y_i P_c \geq x_i P_c$$

$$w_i F_c \geq u F_c$$

Where N is the number of stages for the distillation columns, N_f is the column feed stage, RR is the reflux ratio, D is the distillate flow rate, B is the bottoms flow rate, τ is the residence time in the reactor, H is the holdup, R_s is the reactive stages, a φ is the column diameter and T is the reactor temperature. In addition, the optimization problem is restricted to the purities $y_i P_c$, that must be equal to or greater than $x_i P_c$ and the recovery flows of the $w_i F_c$ products that must be greater than or equal to $u F_c$. Due to the complexity of the problem, Differential Evolution with Tabu List (DETL) was used as the optimization algorithm.

This work aims to show the advantages of using reactive distillation in the production and purification of Levulinic acid in terms of energy savings and allows outlining the role of design variables in the intensified process. A mono objective optimization is performed, where the objective function is the reboiler duty. Minimization of reboiler duty has been used in various works as a sustainability metric [\(Gadalla et al., 2005; Kiss et al., 2012; G.K, 1969\)](#). This function was chosen because the reboilers are a typical process industry utility device and they are responsible for supplying the heating steam. Commonly, this steam is generated by

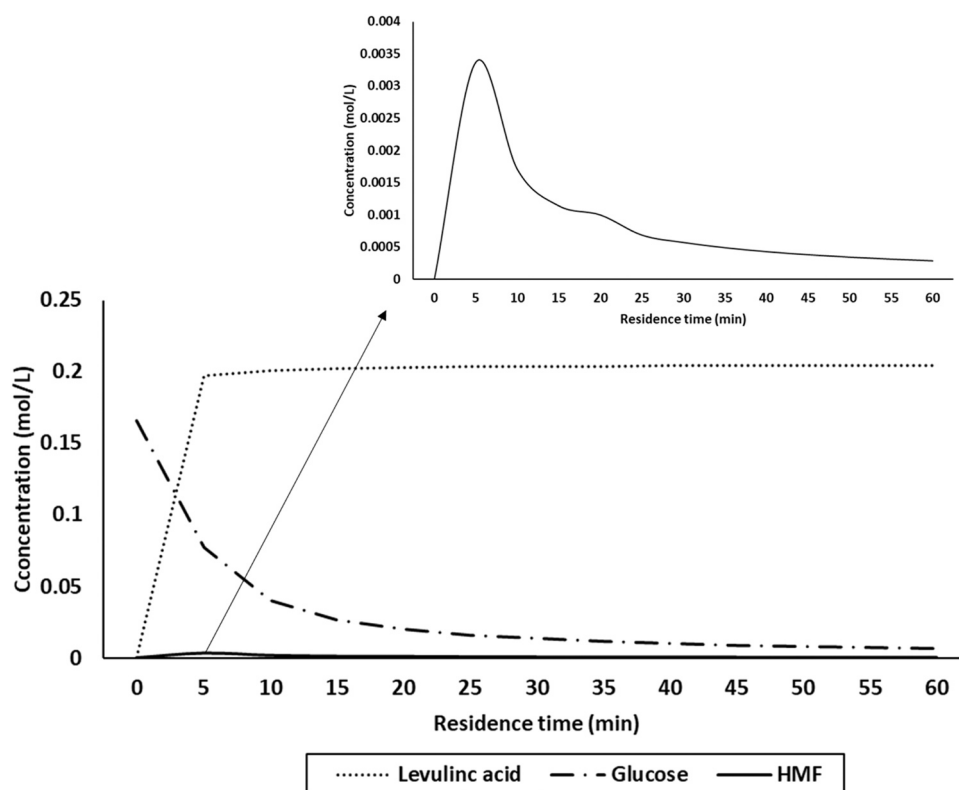


Fig. 5 – Analysis of the effect of residence time on glucose conversion in CSTR reactor.

burning fossil fuels, which directly contributes to CO₂ emissions. Therefore, to reduce CO₂ emissions from distillation systems, efforts should be focused on energy-saving techniques and modifications (Ulrich, 1984). Since, by reducing energy consumption, a less polluting process would be generated where the use of energy is more efficient and adheres to the principles of sustainability.

In addition, distillation remains one of the most important thermal separation methods in the chemical process industry. Nonetheless, despite its many well-known benefits and widespread use, one major drawback is the significant energy requirements since distillation can generate more than 50% of plant operating cost (Turton et al., 2008). Therefore, the service cost has a high impact on the process cost, so by minimizing the consumption of services (reboiler duty), a cheaper process is guaranteed.

Based on the optimal designs, an analysis was carried out using the TAC and the emissions of CO₂ as metrics. To calculate the total annual cost (TAC), which is used as an objective function, we used the method published by Eswara et al. (2013), which was modified by Rangaiah, 2010 where the cost estimate of a plant is made separated from industrial units, and the use of equations published by Contreras-Zarazúa et al. (2018). The CO₂ is produced by the burning of fossil fuels, which are used to produce vapor that works as a heating service. Therefore, the CO₂ emissions are strongly related to the energy consumption of the processes. In this work, it is assumed that the steam required for the reboilers is generated by the burning of natural gas. González-Navarrete et al. (2022), reported the composition of natural gas and the Higher Heating Value (HHV) of each compound. The calculation of each of the metrics is detailed in Supplementary Material.

5. Results

In this section, the results of the preliminary analysis for the feasibility of the designs and the results of the optimization are presented.

5.1. Preliminary analysis results

Within the literature, the operating conditions at which the acid hydrolysis is carried out to obtain levulinic acid are specified. However, they do not specify reaction times, so a sensitivity study was performed in a CSTR reactor. Fig. 5 shows the residence time analysis, where the conversion of glucose to levulinic acid is observed. HMF is an intermediary, it disappears quickly and does not accumulate. Although the glucose is almost completely consumed, the conversion is not 100%, this conversion could be achieved by modifying the operating conditions or increasing the residence time.

On the other hand, the additional heat from exothermic reactions will raise the temperature of the reactive section, so the temperature profile needs to be monitored to avoid catalyst degradation at the lower end of the reactive section (Shah et al., 2012). In this case, the degradation temperatures of the products are much higher than the range of temperatures at which the reactive distillation column operates, except for glucose, which begins to degrade after 100 °C (Shah et al., 2012). However, in this reaction, what is sought is for this decomposition to occur, to obtain its final decomposition products, which are levulinic acid and formic acid. Therefore, a reactive distillation column was designed to verify that it did not exceed 250 °C, which is the upper limit of the temperature at which acid hydrolysis is carried out. In Fig. 6, the temperature profile of the reactive distillation

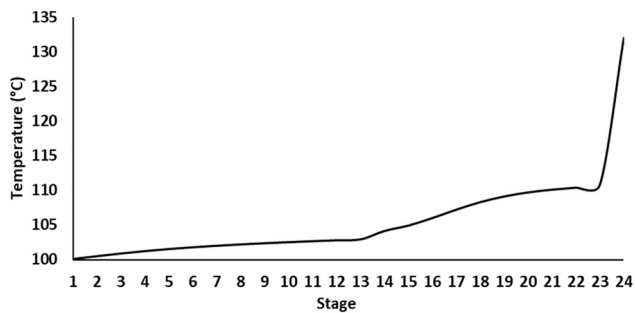


Fig. 6 – Temperature profile in the reactive distillation column.

column is observed, it remains within the range established by the acid hydrolysis literature, which is between 100 and 250 °C.

5.2. Optimization results

Once the feasibility of the process was established, the optimization was performed using the differential evolution algorithm with a tabu list (DETL). Among the variables of the conventional system are reactor temperature, residence time, number of stages, feed stage, diameter, reflux ratio, bottom flows, and dome flow. For the system with reactive distillation, the variables were: Number of stages, feed stage, diameter, reflux ratio, bottom flows, dome flow, and hold-up. For more information on the design variables of the systems studied, see [Supplementary Material](#). The minimization of energy consumption through the monitoring of the reboiler duty is shown in [Fig. 7](#).

[Chen et al. \(2017\)](#) propose that in the DETL algorithm the number of individuals to be evaluated in an initial stage is 10 times the size of the population, in this case, it would be 1200 individuals. However, works where the DETL algorithm is used in complex distillation systems find their optimal values between 50,000–100,000 iterations. [Alcocer-García et al. \(2019\)](#); [Jeswiet and Kara \(2008\)](#); [Nhien et al. \(2016\)](#). Therefore, in this case study, 50,000 iterations were proposed.

It is complex to be able to determine the number of iterations at which the convergence of the algorithm will be found or the objective function value to which it will converge, for these reasons the number of generations is used as a criterion for stopping the algorithm. However, a higher number of iterations increases the reliability of finding the

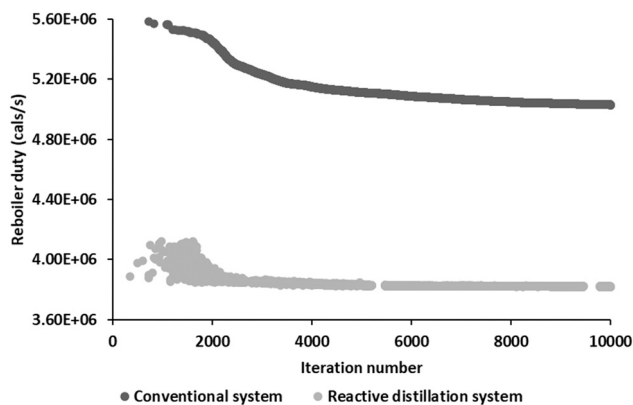


Fig. 7 – Evolution of the algorithm in the minimization of reboiler duty.

global minimum but slows convergence [92]. Therefore, the analysis of the optimization results occurs in a stage after the optimization, sometimes the global minimum is very dispersed, so the limits of the variables must be redefined or increase the number of the interactions, but in others, as in this case study, shows a clear trend of the optimal values, because from iteration 10,000 it begins to have a very small decrease, which means that once the search limits of the algorithm have been established, it quickly converges towards the optimal values.

Regarding the behavior of the algorithm in the case of the reactive distillation system, some discontinuities are observed because the algorithm works randomly, and solutions may be found that do not comply with the restrictions of optimization, so they suffer penalties that impact the value of the reboiler duty and exceed the reboiler duty range shown in [Fig. 7](#) ([Fig. 8](#)).

The designs obtained through optimization are shown in [Table 1](#).

In both processes, the reaction part consumes the largest amount of energy, 68% for CS and 78% for RDS. It is important to note that in the case of the RDS, it consumes less energy than the conventional reactor, this may be because continuously removing the water from the column, allows better contact between the reactants.

The purities reached by both designs were similar, as well as the flows obtained. As for the hold-up of the reactive column, this presented a small value, which means that the conditions to which the reaction is carried out easily shift to products. Comparing the reflux ratio of the CR1 and C1 columns, in both of which the water is separated by the dome, we can see that in the case of CR1 the reflux ratio is much lower, which has a direct impact on the reboiler duty. Similarly, if we compare the other two columns in both designs, there is a difference in the reflux ratio, but not as significant as occurs with the first column.

The operating temperature of the reactive distillation column, as mentioned in the part of the methodology and the preliminary analysis, is considered an important variable for the feasibility of the process. Therefore, the range of temperatures at which the optimal design operates was analyzed, the result is shown in [Fig. 9](#). Obtaining that the reactive distillation column of the optimal design operates within the permitted ranges of acid hydrolysis for this specific reaction. An important aspect of this type of system is the viscosity, in this case, the viscosity of the mixture is low to the conditions of pressure and temperature, thus guaranteeing the transport of mass in the column.

The best designs of each scheme are shown in [Figs. 10 and 11](#).

It can be observed that the flows and compositions are similar in both cases. Among the differences between both designs is that the purities achieved in the conventional system are higher in the case of formic acid and sulfuric acid, in the case of water and levulinic acid, the purities are practically identical. In addition, if we observe the amount of levulinic acid obtained from the conventional system, it is higher by 4 kg than that with reactive distillation. However, when comparing the energy and environmental benefits that come with implementing reactive distillation, these minor differences in the amount of product and compositions become insignificant ([Figs. 10 and 11](#)).

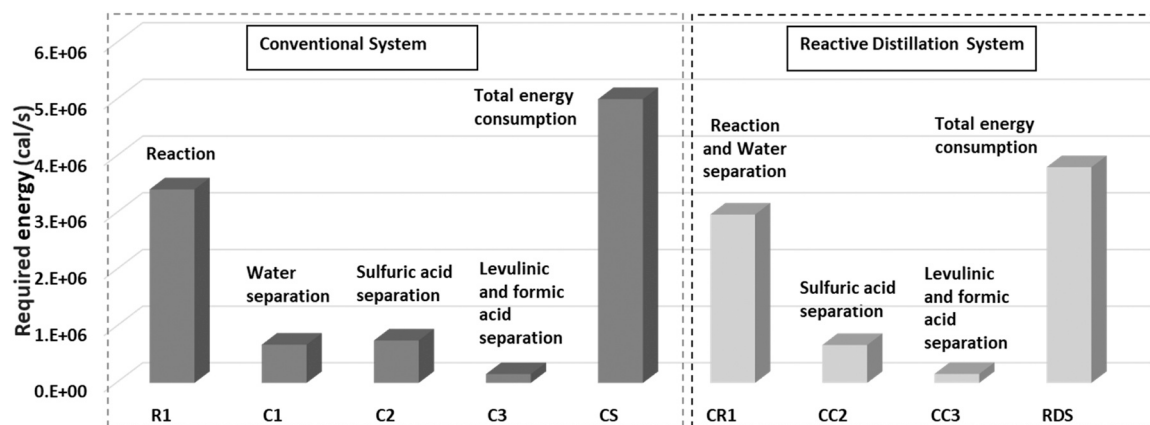


Fig. 8 – Energy comparison between CS and RDS.

Table 1 – Optimal design parameters.

	Conventional System (CS)				Reactive Distillation System (RDS)		
	R1	C1	C2	C3	CR1	CC2	CC3
Reactor	R1	–	–	–	–	–	–
Temperature (°C)	168.82	–	–	–	–	–	–
Residence time (min)	352	–	–	–	–	–	–
Columns	–	C1	C2	C3	CR1	CC2	CC3
Stages	–	38	60	38	42	70	24
Feed stage	–	9	37	7	15	51	17
Reflux ratio	–	0.39	0.96	0.42	0.003	0.75	0.38
Distillate Flow (kg/h)	–	20015.04	7270.70	945.07	20005.34	7288.28	967.39
Bottoms Flow (kg/h)	–	7977.73	707.035	6325.63	7994.66	706.37	6320.89
Diameter (m)	–	1.17	1.87	1.68	1.14	1.73	1.38
Reactive stages	–	–	–	–	15–42	–	–
Holdup (l)	–	–	–	–	0.56	–	–
Pressure (atm)	1	1	1	1	1	1	1
Reboiler Duty (cal/s)	3419093	680164	753169	158439	2975095	673960	161223
Levulinic Acid (%wt)	–	–	–	0.99	–	–	0.99
Formic Acid (%wt)	–	–	0.88	–	–	0.86	–
Sulfuric Acid (%wt)	–	0.99	–	–	0.99	–	–
TAC (\$/y)	1.07×10^7	–	–	–	8.27×10^6	–	–
Total Reboiler Duty (cal/s)	5.01×10^6	–	–	–	3.81×10^6	–	–
Emissions with different fuels (Tons CO ₂ /year)							
Coal	54.87	–	–	–	41.72	–	–
Heavy oil	32.33	–	–	–	24.59	–	–
Natural Gas	24.00	–	–	–	18.25	–	–
Natural Gas ^a	24.66	–	–	–	18.75	–	–
Biomass	48.99	–	–	–	37.25	–	–

^a This study Performing a general analysis in terms of energy consumption, the RDS presents a saving over the CS of 24%. This is because the energy consumption of the reactive column (RC1) of the RDS is 27% lower than the consumption of R1 and C1 of the CS. In addition, by implementing RC1, it is possible to reduce the reboiler duty of columns CC2 and CC3 by 8% compared to the energy consumption of columns C2 and C3 of CS. The reduction in energy consumption is because in the RC1 column the reaction and the separation of the process water are carried out simultaneously, see Fig. 8.

5.3. Economic and Environmental results

For the CS an emission of 24.66 tons of CO₂/year is obtained and for the RDS 18.75 tons of CO₂/year, which means that with the implementation of the reactive distillation column, 24% of CO₂ emissions would be mitigated. Therefore, the reduction in CO₂ emissions is directly proportional to energy consumption. An analysis of the emissions that would be generated using different energy mix (coal, heavy oil, natural gas, and biomass) was carried out. Based on the work of Jeswiet et al. [93] where the generation of CO₂ from these fuels is estimated, the emissions were calculated. Calculations of these emissions are described in Supplementary Material and results and the results are shown in Table 1. The results indicate that using the RDS instead of the CS the following values would not be emitted for the different fuels: coal 13.15 tons of CO₂/year, heavy oil 7.75

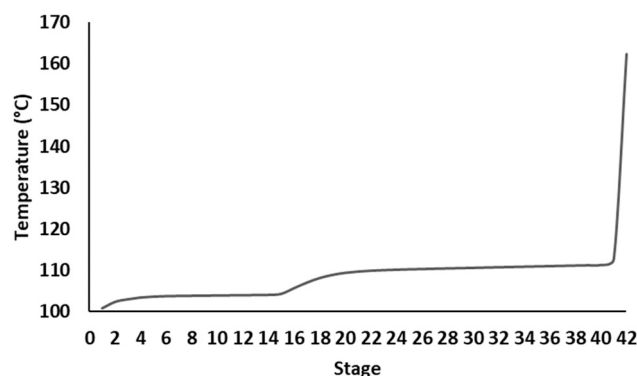


Fig. 9 – Temperature profile in reactive distillation column in the optimum design.

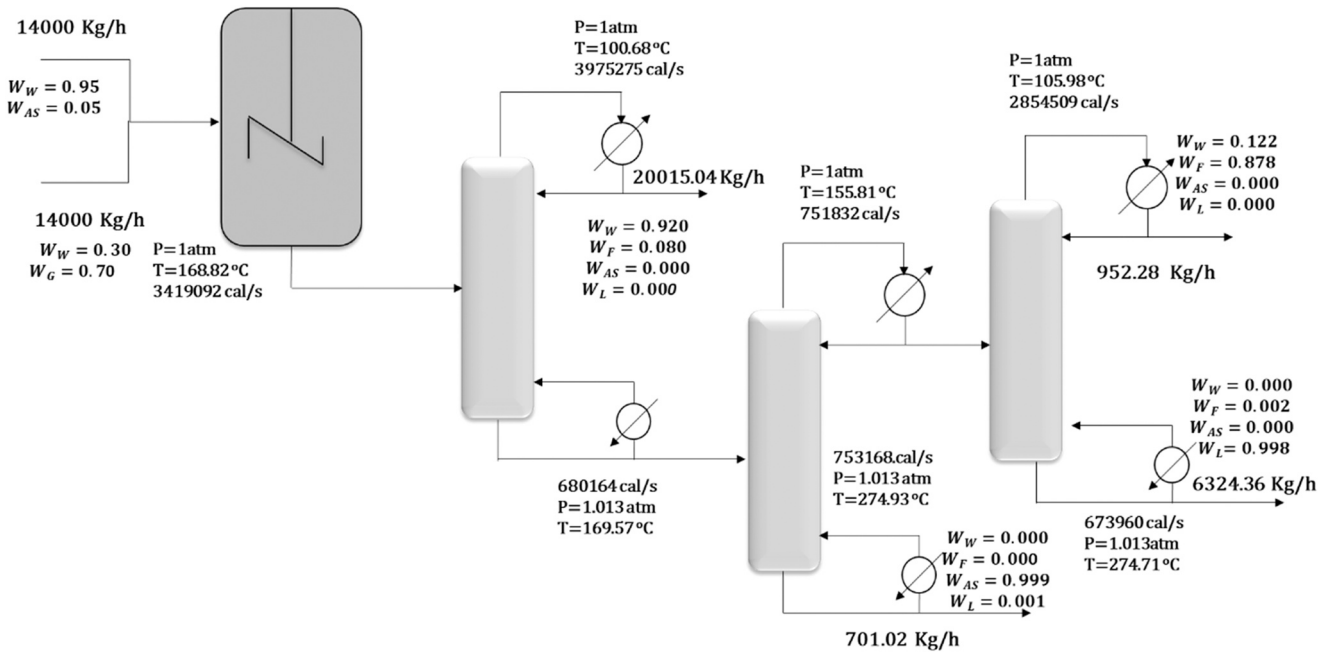


Fig. 10 – Optimal configuration of CS.

tons of CO₂/year, natural gas 5.75 tons of CO₂/year, natural gas (this study) 5.91 tons of CO₂/year and biomass 11.74 tons of CO₂/year. Due to geographical, economic, political, and social issues, the cost associated with each fuel may vary. However, in weighted and exclusively technical terms such as kg of CO₂ and reboiler duty, reactive distillation presents energy savings and reduction in emissions.

One of the advantages of implementing reactive distillation is the decrease in energy required in stages after the reactive column. In this study, the energy required to purify

levulinic acid from the bottom stream of the reactive distillation column is 8.35×10^5 cal/s, which represents an emission of 0.65 kg CO₂ per kg of purified levulinic acid. [Alcocer-García et al. \(2019\)](#) y [Nhien et al. \[94\]](#), present alternatives for the purification of levulinic acid, report an energy consumption of 1.14×10^6 cal/s and 1.13×10^6 cal/s, respectively. Assumed that the steam required for the reboilers is generated by the burning of natural gas, in both cases, they generate an approximate emission of 0.90 kg CO₂ per kg of purified levulinic acid. Therefore, regarding the emissions

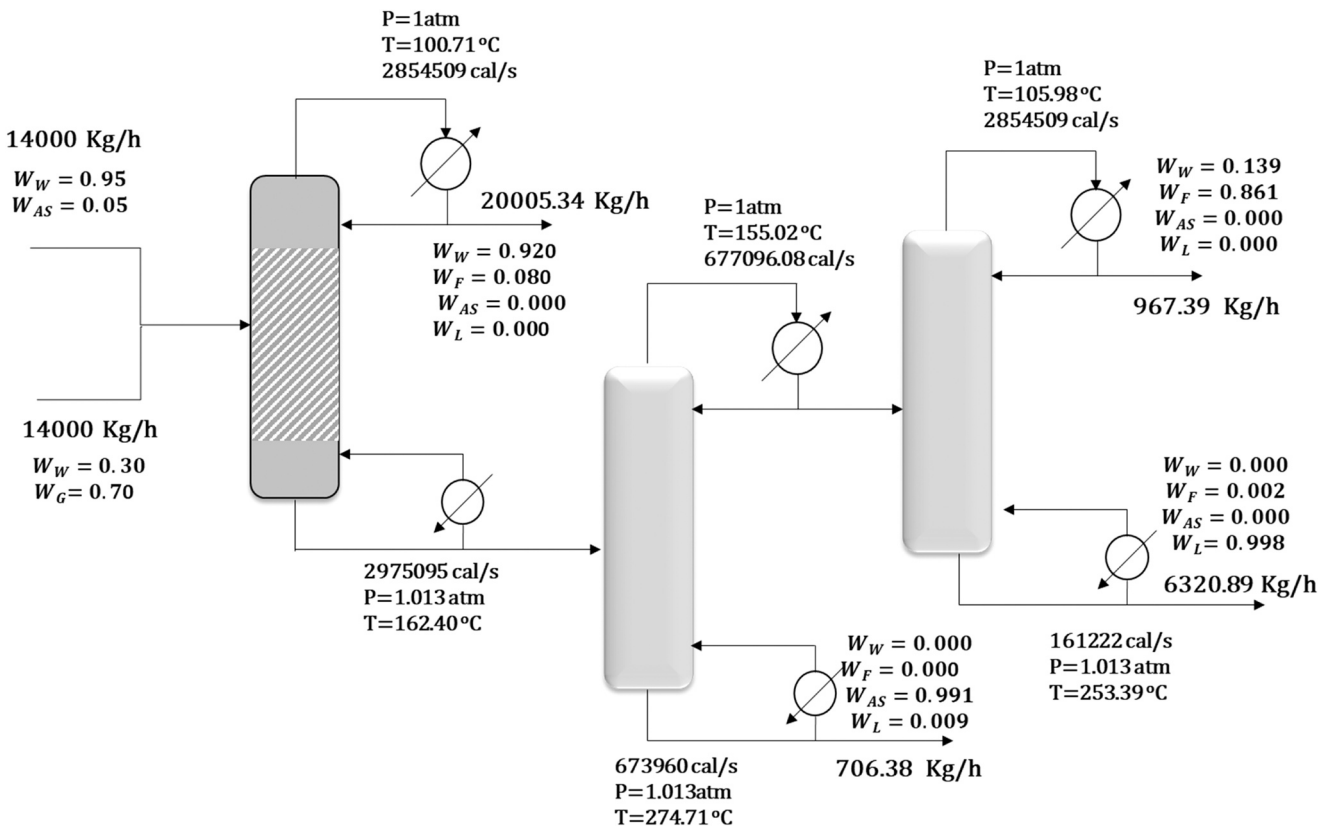


Fig. 11 – Optimal configuration of RDS.

generated in the levulinic acid purification part, the proposed system saves 27.7% compared to the works mentioned.

Moreover, the total annual cost results show that the CS presents a value of 1.07×10^7 \$/year and the RDS a value of 8.27×10^6 \$/year, which represents a saving of 23% compared to the CS. This saving is due to equipment reduction, impacting the cost of construction material. In addition, as mentioned above, there is a saving in energy consumption, which in turn is associated with the cost of services, so this decrease in energy consumption has an impact on the TAC.

The annual production of levulinic acid was used as the normalization value. Obtaining for the normalized annual total cost the values of 1.99×10^{-1} \$/Kg LA and 1.54×10^{-1} \$/Kg LA, for CS and RDS, respectively. For energy required per kilogram of LA produced the value for the CS is 2.85×10^6 cal/Kg LA and for the RDS is 2.17×10^6 cal/Kg LA. Finally, the values of the CO₂ emissions per kilogram of LA produced are 4.59×10^{-4} Kg CO₂/Kg LA and 3.49×10^{-4} Kg CO₂/Kg LA, for CS and RDS, respectively. In all indicators it is noticeable that the CS presents higher values, therefore, the RDS system presents a more sustainable alternative, compared to the CS system, since it is cheaper, consumes less energy, and emits less CO₂.

6. Conclusions

Process intensification for the production and purification of levulinic acid was performed by using a reactive distillation column. In terms of conversion of glucose to levulinic acid, the reactive distillation obtained results similar to those obtained by the conventional process. A preliminary analysis was carried out to evaluate the feasibility of implementing the reactive distillation column, obtaining that the column operates within the established ranges to favor acid hydrolysis. In addition, the optimization process was carried out to obtain the optimal designs of the conventional design and the intensified design. Thanks to the intensification, the advantages of the implementation of the reactive distillation column were demonstrated since it favors energy savings by 24% compared to the conventional design. This reduction is due to the energy supplied for the reaction to separate the most abundant component of the mixture, thereby favoring its separation and the separation of the other components in later stages. It is important to mention that in both processes, the part with the highest energy consumption is the reactive part, so it is a guideline for future implementations of schemes with reactive distillation integration since this high energy consumption can be used to separate a component of the mixture. On the other hand, the reduction in equipment due to the integration of the reactor in the column, impacts the total annual cost, generating savings of 23% compared to the conventional scheme. Therefore, in this work, the advantages of implementing reactive distillation were shown and presents an alternative that improves the sustainability of the production of levulinic acid. This configuration meets the characteristics of a circular economy, and the results may indicate the possibility of using these technologies intensified at an industrial level for the production and purification of Levulinic acid.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.cherd.2022.04.041](https://doi.org/10.1016/j.cherd.2022.04.041).

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