



Intensified alternative for sustainable gamma-valerolactone production from levulinic acid

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ABSTRACT

γ -Valerolactone (GVL) is a promising bio-based chemical with applications in renewable fuels and chemicals. While several catalytic strategies for its production exist, a common challenge is the lack of an integrated process that combines both production and purification. Currently, these steps are performed separately, with distillation being energy-intensive, especially at low yields. This study presents a novel approach by integrating both production and purification of GVL in a single, energy-efficient operation using reactive distillation. The novelty of this work lies in the design and optimization of a reactive distillation column, where key operating conditions and design parameters are carefully selected to ensure that both chemical reactions and component purification occur efficiently within the same unit. Experimental data from the literature were used to model the process kinetics, ensuring the simulation accurately reflects experimental conditions. This integrated approach not only reduces energy consumption but also improves the overall efficiency of GVL production, offering a more sustainable and cost-effective alternative for industrial applications. By employing a multiobjective optimization framework, the design balances economic, environmental, and operational objectives, achieving a reduction in total annual cost (TAC) to 43 % and environmental impact (Eco Indicator 99, EI99) to 45 % of the values associated with conventional processes. Moreover, energy consumption is decreased by 63 %, and GVL production is increased by 25 %, demonstrating the significant potential of reactive distillation for improving both efficiency and sustainability.

1. Introduction

The advent of Industry 4.0, characterized by the integration of digital technologies, automation, and smart systems, is transforming manufacturing processes. This paradigm focuses on using cyber-physical systems, the Internet of Things (IoT), and big data analytics to create efficient, interconnected, and flexible production environments. As sustainability and circular economy principles become increasingly important, there is a need for processes that minimize environmental impact and optimize resource use. By combining Industry 4.0 technologies with sustainability goals, this study proposes an intensified solution that reduces energy consumption and environmental impact, contributing to a more resilient industrial future (Lasi et al., 2014).

Traditional industrial processes, such as the production of biofuels

like bioethanol and biobutanol, face significant challenges in terms of economic feasibility. The inefficiencies in these processes, including low yields in fermentation and high energy consumption in purification, have made them less competitive compared to fossil fuel-based alternatives (Pereira et al., 2024). This has prompted a shift in focus towards the development of alternative bio-based chemicals and materials that can offer higher value and align with the principles of sustainability and industry 4.0 (Kabugo et al., 2020). The pursuit of high value-added products derived from biomass, such as bioplastics, specialty chemicals, and bio-based solvents, is gaining traction as these materials can be produced more efficiently and sustainably using advanced manufacturing technologies (Lasi et al., 2014).

One such promising bio-based chemical is γ -valerolactone (GVL), a versatile compound that can be synthesized from plant biomass

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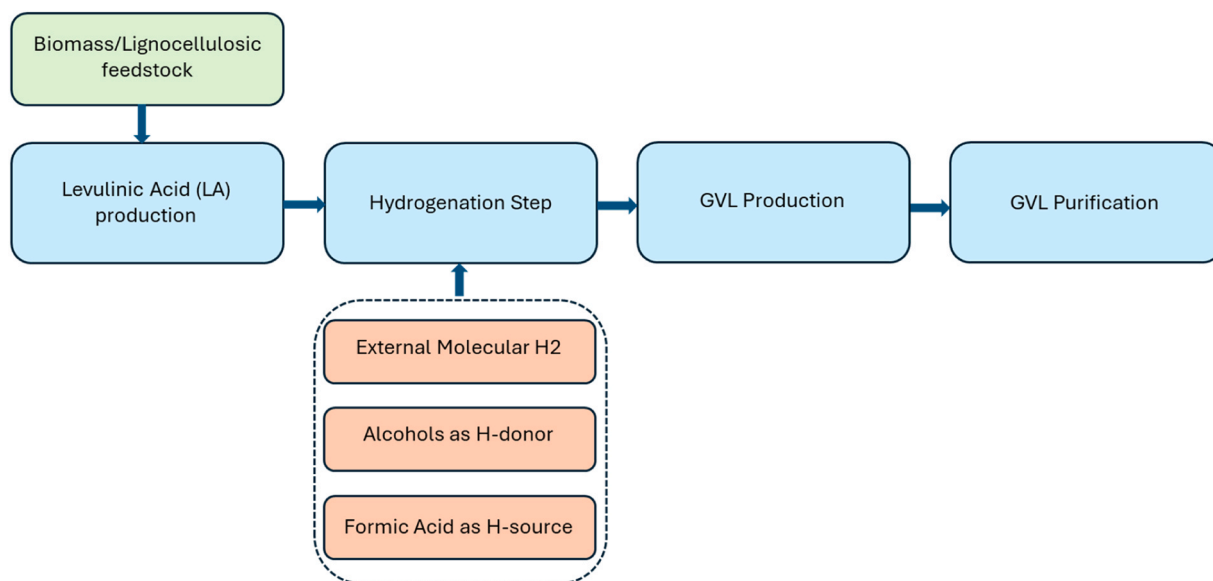


Fig. 1. Simplified flowsheet for GVL production considering different hydrogen sources.

components through catalytic hydrogenation of levulinic acid. In 2023, the Gamma Valerolactone market was valued at USD 535 million, and it is anticipated to grow to USD 590 million by 2030, with a compound annual growth rate (CAGR) of 1.3 % throughout the forecast period of 2024–2030 (Verified Market Reports, 2023). GVL has garnered significant attention for its applications as a biofuel additive, solvent, and precursor for various chemicals, making it an attractive candidate within the framework of Industry 4.0 (Kumaravel et al., 2021). For instance, GVL is used as a green solvent in the pharmaceutical and fine chemical industries, providing a more sustainable alternative to traditional solvents. As a biofuel additive, it enhances fuel stability and energy density, contributing to improved fuel performance. Additionally, GVL serves as a precursor for the production of pentanoic acid and valeric biofuels, which are highly valued for their energy content and compatibility with existing fuel infrastructure (Arias et al., 2023).

γ -Valerolactone (GVL), a renewable bio-based compound, has gained significant attention due to its versatility as both a solvent and a precursor for biofuels. Its broad applicability in various sectors, including chemical synthesis and energy production, underscores the growing need for efficient methods to produce GVL from biomass. This section explores the role of GVL as a solvent and its potential as a biofuel, highlighting the importance of GVL in addressing the challenges of sustainability and the reduction of fossil fuel dependency.

GVL has shown considerable promise as a green solvent due to its renewable nature, low toxicity, and excellent solvency properties for a range of organic and inorganic compounds. It has been recognized for its ability to replace more harmful organic solvents commonly used in industrial applications. (Horváth et al., 2008) first proposed the use of GVL as a sustainable solvent in biomass conversion processes, noting its biodegradability, stability, and low toxicity, which make it an ideal candidate for a variety of chemical reactions. Furthermore, GVL has been found to effectively dissolve a wide range of biomass feedstocks, which makes it particularly useful in biomass conversion to valuable chemicals. Recent research has expanded on this idea, with (Fegyverneki et al., 2010) exploring several GVL-derived chemicals that could be utilized as solvents in various industrial applications, such as alkyl 4-alkoxyvalerates and GVL-derived ionic liquids. These GVL-based solvents exhibit higher performance in reactions like olefin hydrogenation compared to traditional ionic liquids, significantly improving reaction selectivity and catalyst turnover rates. In addition, (Strádi et al., 2013) demonstrated that the hydrogenation of olefins in GVL-based ionic liquids offers a faster and more efficient reaction process,

highlighting the solvent's utility in advanced chemical processing. The potential applications of GVL as a solvent are vast, ranging from the extraction of valuable bio-based chemicals to facilitating catalytic reactions that are vital for green chemistry. As an alternative to conventional solvents, GVL's ability to enhance reaction rates and improve catalyst stability positions it as a key player in the transition toward more sustainable chemical processes.

Beyond its role as a solvent, GVL also serves as a precursor for biofuels, particularly in the context of renewable and sustainable energy. GVL can be converted into high-energy fuels and fuel additives, offering a promising alternative to traditional fossil-based fuels. Horváth et al. (2008) first recognized GVL as a potential oxygenate for gasoline and diesel fuels, noting its favorable properties such as lower vapor pressure and higher energy density compared to ethanol, which is commonly used as a fuel additive. GVL's potential as a fuel additive has been further demonstrated by (Bruno et al., 2010), who investigated the distillation characteristics of GVL in gasoline and found that it could be blended effectively to improve fuel properties. GVL not only enhances fuel stability but also reduces emissions, such as CO and smoke, in automobile exhaust. Furthermore, (Lange et al., 2012) explored the conversion of GVL to methyl tetrahydrofuran (MTHF), a biofuel that can be blended with gasoline, achieving a high octane number and making it suitable for use as a renewable fuel.

In addition to GVL, its derivatives, such as valeric acids and valerates, have also been studied as potential biofuels. Lange et al. (2012) demonstrated that these compounds, derived from GVL, can be used as oxygenates in gasoline and diesel fuels, enhancing fuel performance and combustion efficiency. Their high energy content and ability to be tailored for specific applications (e.g., by adjusting their alkyl chain length) make them valuable for the biofuel industry. For instance, ethyl valerate has shown promising results as a gasoline additive, and pentyl valerate is more suitable for diesel applications due to its better volatility and cold-flow properties. The catalytic upgrading of GVL to various fuel products, such as butenes and C8 + alkenes, has also been explored. Alonso et al. (2013) developed an integrated catalytic system where GVL is first converted to unsaturated pentenoic acids and then to butenes, which can be further oligomerized into high-value jet fuels. This process, which eliminates the need for high-pressure hydrogen, demonstrates the feasibility of producing liquid fuels directly from biomass-derived GVL.

As the demand for sustainable and renewable energy sources continues to rise, the role of GVL in both chemical synthesis and fuel production becomes increasingly critical. GVL's versatility as a solvent and

as a precursor for biofuels positions it as a key building block for future sustainable chemical processes. Its potential to replace fossil fuels in various applications, combined with its environmentally friendly properties, makes GVL an attractive option for industries looking to reduce their carbon footprint and transition to greener alternatives.

γ -Valerolactone (GVL) has emerged as a promising platform chemical derived from biomass, with applications in green solvents, biofuels, and other chemical industries. The production of GVL involves the selective hydrogenation of levulinic acid (LA) or its esters, with various hydrogen sources being employed to drive the reduction reactions. These hydrogen sources can be categorized into three main types: external molecular hydrogen (H_2), alcohols, and formic acid (FA). Each of these sources has its own advantages and disadvantages, particularly in terms of efficiency, cost, and the complexity of the reaction system.

The use of external molecular hydrogen (H_2) as a hydrogen source for the production of GVL is the most common method (See Fig. 1). Several studies have explored this approach using heterogeneous and homogeneous catalytic systems. For instance, (Braca et al., 1991) employed $Ru(CO)_4I_2$ as a catalyst for the hydrogenation of LA to GVL, achieving a GVL yield of 39.5 % starting from glucose. Similarly, (Starodubtseva et al., 2005) used a $RuII$ -BINAP- HCl system for the conversion of ethyl levulinate to GVL, reaching an impressive yield of 95 %. More recently, (Delhomme et al., 2013) investigated the effect of various phosphine ligands on the catalytic activity, demonstrating a maximum GVL yield of 95 % under aqueous conditions.

Despite its effectiveness, the use of external H_2 presents several drawbacks. Firstly, the requirement for a hydrogen gas supply under elevated pressures often results in higher operational costs. Additionally, the hydrogenation process may lead to the formation of unwanted by-products, which require further separation and purification steps. As a result, the process often demands high energy consumption for product recovery, especially if yields are low.

An alternative hydrogen source for GVL production involves the use of alcohols as H-donors. This approach, known as catalytic transfer hydrogenation (CTH), has gained attention for its potential to operate under milder reaction conditions compared to H_2 . Chia and Dumesic (2011) first reported the conversion of LA to GVL using ZrO_2 as a catalyst, achieving GVL yields over 80 % from alkyl levulinates. Yang et al. (2013) demonstrated the use of Raney Ni as a catalyst for the CTH of ethyl levulinate to GVL, with a yield of 99 % at room temperature using 2-propanol as the hydrogen donor. The main advantages of alcohols as hydrogen sources are the relatively mild reaction conditions and the easier handling of alcohols compared to H_2 . However, one significant limitation of this approach is the potential for side reactions, such as over-hydrogenation, which can reduce the selectivity to GVL. Additionally, alcohols tend to have lower hydrogenation potentials than molecular H_2 , which may require longer reaction times or higher temperatures to achieve comparable yields. Furthermore, the separation of alcohols from the reaction mixture can be challenging, particularly when dealing with large volumes of solvent.

The use of formic acid (FA) as a hydrogen source is an emerging strategy that has been identified as a promising alternative due to its high hydrogen content and the fact that it decomposes to produce hydrogen and CO_2 . FA can act as an in situ hydrogen donor, making the process more atom-efficient. For example, (Horváth et al., 2008) demonstrated a homogeneous catalytic system using $[(\eta^5-C_5Me_5)Ru(bpy)(H_2O)](SO_4)$ in an aqueous solution, which converted LA to GVL with a yield of 25 %. More recent developments have shown that FA can also be used in combination with other catalysts such as Ru/C to achieve complete conversions of LA to GVL, with yields up to 100 %. One of the key advantages of using FA is its ability to provide hydrogen in situ, eliminating the need for a separate hydrogenation step. This method is particularly advantageous in terms of cost and simplicity, as it does not require the use of high-pressure hydrogen gas. Additionally, FA can be directly derived from biomass, making it a renewable and sustainable hydrogen source. However, the presence of CO_2 as a by-product can

interfere with the reaction, reducing the overall efficiency of the process. Nevertheless, FA's ability to serve as both a hydrogen donor and a carbon source for subsequent reactions makes it a highly versatile and efficient alternative.

Process Intensification (PI) offers a pathway to enhance the efficiency of GVL production by improving catalyst performance and reducing energy consumption, which are key objectives within the sustainability framework (López-Guajardo et al., 2022). Strategies such as the use of high-efficiency reactive distillation columns can significantly lower energy requirements while optimizing reaction conditions and heat transfer, making GVL production more compatible with the goals of smart manufacturing (Demirel and Rosen, 2023). This technique combines chemical reaction and distillation into a single unit operation, allowing for continuous product removal and driving reactions to completion. The integration of these processes into a smart, automated system is particularly beneficial for equilibrium-limited reactions and processes involving volatile reactants and products. Reactive distillation has shown substantial advantages in various applications, such as biodiesel production and the synthesis of bio-compounds, by increasing conversion rates and reducing energy consumption.

In several research reports, reactive distillation has shown significant advantages. For example, the production of biodiesel via the transesterification of vegetable oils or animal fats with methanol is greatly improved by reactive distillation. Traditional methods require separate reaction and purification steps, leading to higher energy consumption and lower yields. Reactive distillation, on the other hand, can increase the overall conversion rate by 20–30 % while reducing energy consumption by approximately 40 % compared to conventional technologies (Kiss et al., 2006). Given the energy-intensive nature of GVL production, implementing reactive distillation could similarly yield substantial improvements in efficiency and sustainability. While several catalytic strategies for GVL production have been proposed, a common challenge remains the need for an efficient and integrated process that combines production and purification in a single unit. Currently, the production of GVL is followed by a separate purification step, which is energy-intensive, especially when the yields are low. Distillation, for instance, is often used to separate GVL from the reaction mixture, but this step requires significant energy input to overcome the boiling point differences between GVL and other components. To date, no published study has demonstrated the use of a reactive distillation column for the simultaneous production and purification of GVL in a single unit operation. This represents a significant gap in the literature and highlights the novelty of the current work, which aims to integrate both production and purification into a single, energy-efficient step using reactive distillation.

Although the development of a reactive distillation model may appear straightforward, a crucial aspect from a process design perspective is identifying the valid operating window for the column and determining the appropriate design parameters. These parameters must be carefully selected to ensure that the reactive distillation column operates within a temperature and pressure range similar to those in a conventional reactor. Additionally, the operating conditions must be established in such a way that allows for the purification of the components obtained in a distinct region of the column. In other words, the design parameters and operating conditions must guarantee both the desired chemical reaction and the purification of at least one of the components produced. Furthermore, in this design exercise, experimental data presented in the literature were modeled to derive the kinetic parameters necessary for replicating the behavior observed under experimental conditions. This approach ensures that the model can accurately simulate the process under realistic operational conditions and provide valuable insights for optimizing the reactive distillation process for GVL production.

Thus, the purpose of this article is to propose a sustainable and intensified process alternative for the production of GVL. This proposal

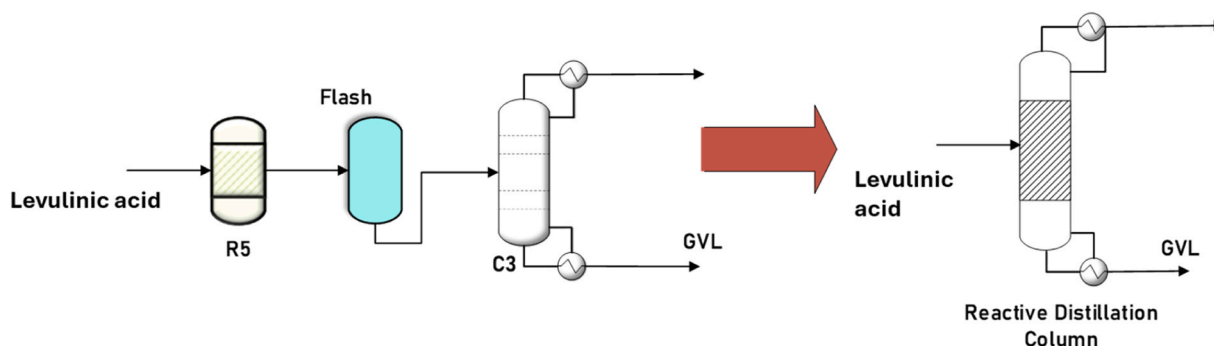


Fig. 2. Process intensification applied to GVL production.

has as its core process a reactive distillation column, an intensified process that has not been previously used for GVL production. To generate a fair comparison, the intensified scheme will be compared with its previously reported conventional counterpart (Caceres et al., 2024). This work was developed under a multi-objective optimization scheme to evaluate objective functions that promote the generation of sustainable schemes, for example, the total annual cost (TAC), and an environmental impact indicator (Eco Indicator 99).

2. Problem statement

Biocompounds, derived from renewable biomass, offer a promising alternative to petrochemical-based products. However, the production of biocompounds using conventional processes is often energy-intensive, which can diminish their environmental benefits. Typically, this kind of process involves several stages, including feedstock pretreatment, chemical or biochemical conversion, and product separation and purification.

For example, biomass feedstocks require pretreatment to enhance their convertibility. Methods such as steam explosion, acid hydrolysis, and mechanical grinding are commonly employed. For example, the steam explosion of lignocellulosic biomass can consume up to 15 % of the total process energy (Alvira et al., 2010). In chemical or biochemical conversion, the pretreated biomass is converted into desired biocompounds through chemical reactions or microbial fermentation. Maintaining optimal conditions for these reactions, such as temperature, pressure, and pH, involves significant energy use. The fermentation of glucose to ethanol, for instance, consumes around 10–15 % of the total process energy (Gnansounou and Dauriat, 2005). Regarding the purification step, distillation is a widely used method for the separation and purification of biocompounds. This step is particularly energy-intensive due to the need to vaporize large volumes of liquid. In the case of ethanol production, distillation accounts for approximately 35–40 % of the total energy consumption (MacRelli et al., 2012).

PI involves the development and implementation of innovative apparatuses and techniques that lead to significant improvements in manufacturing and processing efficiency. By integrating operations and enhancing process phenomena, PI can dramatically reduce equipment size, energy consumption, and waste production. There is an urgent need to explore intensified production strategies for various biocompounds that are currently economically feasible only through conventional methods or the use of non-renewable raw materials. The successful implementation of PI not only supports the transition to renewable feedstocks but also aligns with the broader goals of sustainable development by promoting energy efficiency, reducing environmental impact, and enhancing the economic viability of bio-based products (Charpentier, 2010).

3. Case study

In the context of GVL production, several production alternatives have been explored at different scales. Recently, Hegne and Rode (Hengne and Rode, 2012) proposed a study focusing on the production of γ -valerolactone (GVL) from levulinic acid (LA) using a Cu–ZrO₂ nanocomposite catalyst. The catalyst demonstrated impressive performance, achieving complete conversion of LA with over 90 % selectivity to GVL. The hydrogenation process was typically carried out under specific conditions: a temperature of 473 K, and a hydrogen pressure of 3–4 MPa. Cu–ZrO₂ catalyst was noted for its excellent recyclability, showing minimal metal leaching, which enhances its sustainability for commercial applications.

Due to its high conversion and performance, in a later work, Caceres-Barrera et al. (2024) reported on its implementation in a multi-product production plant of GVL as a stage of the overall process using biomass to generate levulinic acid, furfural, and hydroxymethylfurfural. In the case of this work, the production of all biocompounds is carried out using conventional technologies (reactors and columns), so there is a latent opportunity for process improvement using process intensification strategies. Previously, the work presented by Caceres-Barrera et al. proposed the production of GVL from a feed stream of 3.98 kmol/h of levulinic acid, 4.21 kmol/h of formic acid, and 4.21 kmol/h of water; to obtain 2.95 kmol/h of GVL (see Fig. 3). As reported by Caceres et al. (2024), the energy consumption of the equipment involved in the production of GVL is 22.964 kcal/h, which represents 41 % of the total energy consumption of the process. Thus, based on the process step where GVL is produced previously reported by Caceres et al. (2024), a process intensification strategy will be applied to generate a reactive distillation column (Fig. 2) as an intensified alternative as an immediate substitute to the reactor and column shown in Fig. 1. Note that a feed similar to the work of Caceres et al. (2024) will be considered, however the operation in the proposal of this work will be performed only on a single reactive distillation column, not in three as previously proposed.

3.1. Performance assessment

To generate a fair evaluation, it is necessary to evaluate both production alternatives (conventional and intensified) in a similar framework. The previous proposal (Caceres et al., 2024) evaluated the entire process using two indicators, one economic and the other environmental impact. This assessment was developed in a stochastic optimization framework. In the same way, in this work, the intensified proposal will be evaluated using a similar strategy. This stochastic optimization strategy will be explained in more detail in Section 4.

Evaluating the Total Annual Cost (TAC) is a key aspect in assessing the financial performance of a process, particularly in the context of Industry 4.0. This framework, which integrates advanced technologies, automation, and data analytics, calls for a deeper understanding of long-

Table 1

Unit eco-indicator used to measure the eco-indicator 99 in both case studies (Goedkoop and Spruiensma, 2000).

Impact category	Steel (points/kg)	Steam (points/kg)	Electricity (points/kWh)
Carcinogenics	6.32E-03	1.18E-04	4.36E-04
Climate change	1.31E-02	1.60E-03	3.61E-06
Ionizing radiation	4.51E-04	1.13E-03	8.24E-04
Ozone depletion	4.55E-06	2.10E-06	1.21E-04
Respiratory effects	8.01E-02	7.87E-07	1.35E-06
Acidification	2.71E-03	1.21E-02	2.81E-04
Ecotoxicity	7.45E-02	2.80E-03	1.67E-04
Land Occupation	3.73E-03	8.58E-05	4.68E-04
Fossil fuels	5.93E-02	1.25E-02	1.20E-03
Mineral extraction	7.42E-02	8.82E-06	5.7E-6

Table 2

Design parameters conventional design (Caceres et al., 2024).

Column C3	Reactor R5		
Stages	39	Flow rate (l/min)	12.188
Feed Stage	22	Volume (m ³)	0.731
Reflux ratio	0.039	Diameter (m)	0.677
Distillate flow (kmol/h)	7.296	Pressure (kPa)	101.32
Diameter (m)	0.992	Temperature (°K)	473
Condenser Duty (Watt)	−91280		
Reboiler duty(Watt)	138022		
Height (m)	22.55		

term financial implications. TAC analysis goes beyond the initial capital investment, offering insights into operational efficiencies and potential savings over time. By examining TAC, businesses can optimize resource management, reduce operational inefficiencies, and improve profitability in a more sustainable manner. For this study, we employed the cost estimation methodology proposed by Guthrie (1969) and applied the formula outlined by Turton (2001) to calculate the total cost of industrial plant operations. The formula used is:

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

Where TAC represents the total annual cost, C_{TM} stands for the capital cost of the plant, n signifies the payback period, and C_{ut} represents the utility cost.

In parallel to TAC, the Eco-Indicator 99 (EI99) provides a comprehensive tool for evaluating the environmental impacts of a process, which is essential in the Industry 4.0 paradigm focused on sustainability. EI99, a life cycle assessment (LCA) methodology, assesses environmental consequences across multiple categories such as global warming potential, resource depletion, and ecotoxicity. By integrating EI99 in the evaluation process, we ensure that the implementation of advanced technologies aligns with sustainability goals. The EI99 is calculated using the following equation:

$$EI99 = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (2)$$

Here, β_b denotes the total quantity of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ represents the damage caused by category k per unit of chemical b released into the environment, ω_d is the weighting factor for damage in category d , and δ_d is the normalization factor for damage in category d . This approach considers the impact of steel used for construction, steam used for heating, and electricity used for pumping. The weighting factors are presented in Table 1.

4. Methodology

This section will describe the design and optimization strategy followed for the development of the intensified alternatives. In the particular case of the conventional alternative, the previous work reported an optimal scheme for the production and separation of GVL (Caceres et al., 2024). Thus, in such a proposal, the proposal previously presented was reproduced according to Table 2 and Fig. 3. Fig. 3 highlights the section of the process where the generation of GVL is carried out. Please note that at the inlet of reactor R5, the feed contains a high proportion of levulinic acid and this reacts to produce mostly GVL.

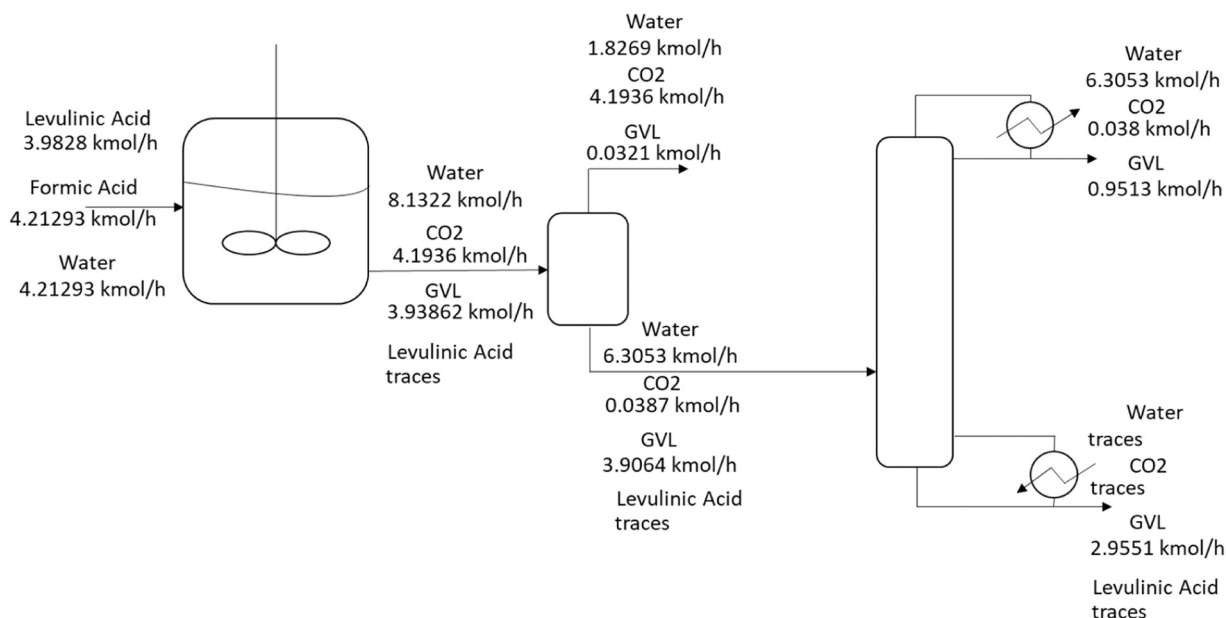


Fig. 3. Mole balance of the conventional technology for GVL production.

4.1. Determination of the kinetic parameters involved in the production of GVL

The production of GVL has been studied in several previous studies. Currently, there are several reports on experimental work where GVL is produced from levulinic acid. Particularly, in the work presented by [Hengne and Rode \(2012\)](#) the production of γ -valerolactone (GVL) from levulinic acid (LA) involves a two-step catalytic process:

1. Hydrogenation of Levulinic Acid: The first step is the hydrogenation of levulinic acid to form 4-hydroxylevulinic acid (4-HLA). This reaction typically requires a catalyst, and various catalysts have been studied, including noble metals like ruthenium (Ru) and non-noble metal nanocomposites like Cu–ZrO₂. The hydrogenation is performed under specific conditions, such as elevated temperatures and pressures, to facilitate the reaction.
2. Cyclization of 4-Hydroxylevulinic Acid: The second step involves the cyclization of 4-hydroxylevulinic acid to form γ -valerolactone. This step can occur either homogeneously or heterogeneously, depending on the catalyst used. The cyclization process typically involves the removal of water, leading to the formation of the lactone structure of GVL.

The process is reported to be highly efficient, with a high percentage yield (99.9 %), and can be represented by the following equations.



As mentioned, there is experimental support describing in detail the production of GVL in the work of ([Hengne and Rode, 2012](#)). However, no explicit kinetic data are reported.

In Process System Engineering (PSE), simulation plays a vital role. It involves both the creation of models and their refinement using experimental data. A simulation model is employed to perform ‘virtual experiments.’ Modeling is a key component of any simulation, often embedded within software technology, making it almost invisible. It’s important to note that simulation provides an approximation of reality with a certain level of realism, but it is not reality itself ([Thomé, 1993](#)). One significant benefit is the capability to represent complex chemical reactions within an appropriate simulation framework. Several studies have recently been published where complex chemical reactions were modeled ([Liu et al., 2022](#); [Romero-Izquierdo et al., 2021](#)). However, due to the challenges of fitting experimental data to reaction kinetics in a commercial simulation environment, simplified reactor models have been used. Given the kinetic complexity of many reactions, within the Aspen Plus simulator, there are a few alternatives to simulate reactions without detailed chemical kinetics data.

The study by [Sánchez-Ramírez et al.\(2022\)](#) introduced a general sequential optimization framework to address kinetic parameter estimation for simulating chemical reactions in the Aspen Plus process simulator. The primary goal was to identify the kinetic parameters E and K that accurately represent the experimentally observed behavior. The optimization problem focused on minimizing the discrepancy between the experimental data and the simulation results obtained from Aspen Plus.

Table 3
Decision variables in the multiobjective optimization problem.

Type of Variable		Search Range
Number of Stages	Discrete	5–100
Feed Stages	Discrete	4–99
Reactive stages range	Discrete	4–99
Reflux Ratio	Continuous	0.1–5
Bottoms Rate	Continuous	3.5–4 (kmol h ^{−1})
Diameter	Continuous	0.9–5 (meters)

4.2. Design and optimization of a reactive distillation column for GVL production

The methodology for optimizing reactive distillation column design combines empirical design heuristics with a robust stochastic optimization approach, specifically the Differential Evolution with Tabu List (DETL) algorithm. This algorithm has shown its capabilities to adequately design and optimize highly nonlinear, potentially non-convex, multiple local minima process schemes. This evolutionary approach incorporates the traditional steps of Differential Evolution but enhances the search process through the use of a Tabu List (TL). Essentially, the integration of DE with TL prevents the algorithm from re-evaluating previously assessed points. A detailed explanation of the DETL algorithm is available in the work by [Srinivas and Rangaiah \(2017\)](#). A complete and wide description can be found at ([Srinivas and Rangaiah, 2007a](#)).

The process begins with a clear definition of the design objectives, which may include maximizing product purity, minimizing the total annual cost, and the environmental load. All this task was developed while also considering physical limits and constraints. Key design parameters, such as column dimensions, catalyst type, number of stages, and feed conditions, are initially defined based on empirical heuristics and prior experience. Initial values for these parameters are set using well-established rules of thumb, which provide practical starting boundaries for the optimization process. The process design is developed in Aspen Plus, ensuring that the model accurately captures both the kinetic and thermodynamic behavior of the system. As mentioned, initial simulations are conducted using the empirically derived design values, serving as a baseline for subsequent optimization.

To achieve an effective design, it’s essential to have fundamental information about the chemical process. It’s important to remember that the primary benefits of reactive distillation (RD) lie in overcoming equilibrium constraints and improving selectivity for the desired product. Since both reaction and separation occur simultaneously within the same unit, the temperatures required for each process must be properly aligned. If there is no significant overlap between the operating conditions of reaction and separation, then combining these processes is not feasible (e.g., a high-pressure reaction cannot be paired with vacuum distillation). Additionally, working within the narrow window where reaction and separation conditions overlap is often a compromise rather than an optimal solution. Furthermore, the operating pressure and temperature should be kept away from the critical region of key components to avoid the formation of a supercritical phase. If the column operates near the critical pressure of key components, they may exist in the vapor phase, whereas, in most RD processes, the reaction occurs in the liquid phase. The relative volatility of key components is also a vital factor in determining the feasibility of RD. The temperature dependence of the vapor pressure of individual components can lead to reduced relative volatility as temperature increases in multicomponent systems, potentially creating a mismatch between the favorable temperatures for reaction kinetics and relative volatilities, making the RD process less attractive ([Shah et al., 2012](#)).

The multi-objective optimization is carried out using a hybrid system that integrates Aspen Plus with Microsoft Excel, a method developed by Srinivas and Rangaiah ([Srinivas and Rangaiah, 2007b](#)). In this setup, the DETL algorithm is programmed in Visual Basic within Excel, while the separation process model is simulated using Aspen Plus. Initially, decision variable vectors are transferred from Excel to Aspen Plus via Dynamic Data Exchange (DDE). These variables are then applied to the process model in Aspen Plus. Once the simulation is complete, Aspen Plus sends the resulting output data—such as flow rates, purity levels, and reboiler heat duty—back to Excel. Excel then evaluates these outputs against the objective function and adjusts the decision variables based on the DETL algorithm. For the optimization, the following parameters were used: 200 individuals, a maximum of 1000 generations, a tabu list size of 50 % of the total population, a tabu radius of 1×10^{-6} ,

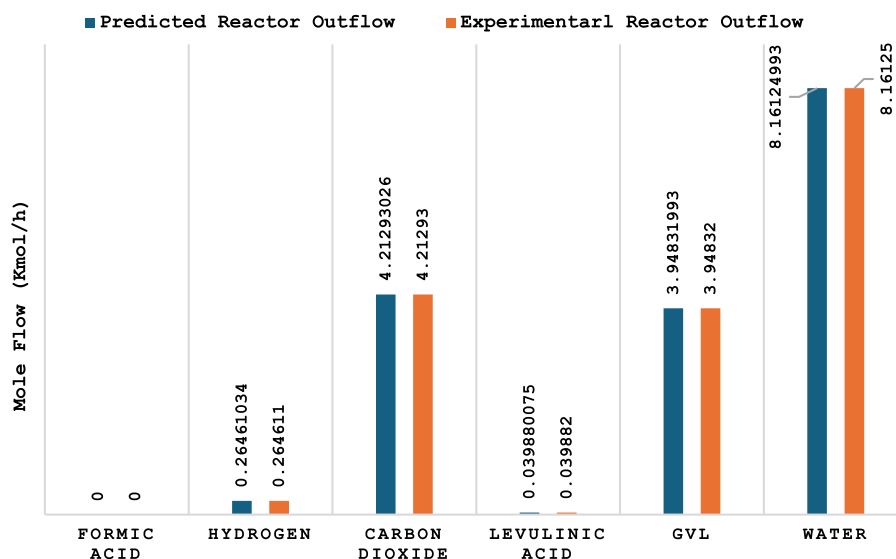


Fig. 4. Experimental (red) and predicted (blue) outflows in the reactor.

and crossover and mutation rates of 0.8 and 0.6, respectively. These settings were derived from existing literature and preliminary tuning studies (Srinivas and Rangaiah, 2017). Decision variables such as reflux ratio, reboiler duty, feed stage locations, and catalyst distribution are identified and optimized with respect to a multi-objective function that incorporates economic, environmental, and operational goals (See Table 3).

The search ranges for the optimization algorithm were established based on several key considerations. For the equipment topology, including stages and diameter, the ranges were informed by recommendations found in the literature (Douglas, 1988; Górák and Olujic, 2014). These values are commonly used in industry and have been adapted to the context of this study. For the mass and energy balance parameters, such as top and bottom flows and reflux ratio, the search limits were determined by considering the characteristics of the feed streams and the performance metrics of conventional GVL production processes, with an extension of the ranges to allow for potential improvements in performance.

Using a narrower range of variables could have resulted in the optimization algorithm finding suboptimal solutions, as it might have limited the search space and prevented the identification of improvements in the GVL production process. On the other hand, expanding the search range excessively could lead to a larger, more complex search space, increasing the risk of the optimization failing to converge to a feasible and efficient solution. Therefore, the selected search range strikes a balance between providing sufficient flexibility to explore improvements and maintaining the focus on a feasible solution space that ensures the model converges effectively.

To calculate the hold-up in cubic meters of a reactive distillation column as a function of its diameter, the model represented in Eq. (5) is used.

$$\text{Hold up} = \frac{\pi}{4} * d^2 * 0.1524 * 0.9 \quad (5)$$

This equation is used to estimate the volume of liquid retained in the column, where d is the diameter of the column in meters, 0.1524 is a conversion factor that converts the diameter to the cross-sectional area in square feet, 0.9 represents the fraction of the column's volume occupied by the liquid (Kong et al., 2025; Sánchez-Ramírez et al., 2024).

The optimization process begins with the empirically derived values as the initial population, guiding the algorithm toward feasible regions of the design space. Through iterative steps of mutation, crossover, and the application of the tabu list, the DETL algorithm explores the design

space comprehensively, ensuring a robust search for the global optimum while avoiding local minima.

Then, considering the performance indicators previously shown, the objective function was defined as follows (Eq. (6)).

$$\text{Min}(TAC, EI99) = f(N_m, N_{fn}, R_m, F_m, R_{sn}, D_{cn}) \quad (6)$$

$$\text{Subject to } x_m^- > y_m^-$$

Where N_{tn} is the total number of column stages, N_{fn} is the feed stages in the column, R_m is the reflux ratio, F_m is the distillate/bottoms flux, R_{sn} is the reactive stages, and D_{cn} is the column diameter. y_m and x_m are the vectors of both obtained and required purities for the m_{th} components, respectively. The minimum purity targets were fixed as 98.5 %wt for GVL. The parameters used for the optimization process were: 200 individuals, 1000 maximum number of generations, a taboo list of 50 % of total individuals, a taboo radius of 1×10^{-6} , 0.8 and 0.6 for crossover probability and mutation factor, respectively. These parameters were obtained from the literature and tuning process via preliminary calculations for this kind of complex models (Sánchez-Ramírez et al., 2024; Srinivas and Rangaiah, 2007a; Vázquez-Castillo et al., 2019).

In the optimization process, penalties are applied to ensure the feasibility and robustness of the results. These penalties are incorporated at various stages of the stochastic optimization algorithm to address potential issues that may arise during the simulation. One of the primary penalties is applied when violations of material or energy balances are detected, leading to convergence errors. Such issues typically arise when the simulator identifies discrepancies in the results, signaling the need for corrections. Additionally, penalties are imposed when the purity requirements for specific components are not met. Even in cases where the model converges without errors, failure to meet these purity specifications results in a penalty, emphasizing the importance of achieving the desired product quality. Moreover, hydraulic-related issues, such as pressure errors or plate flooding, are also considered in the optimization process. When the simulator detects such hydraulic anomalies, corresponding penalties are applied to prevent the optimization from converging to unfeasible operating conditions. This ensures that the process is not only optimized for economic and environmental performance but also adheres to the necessary hydraulic constraints.

Thus, the optimization process guarantees that the resulting design solutions are both reproducible and feasible, meeting the established recovery and purity requirements while avoiding unfeasible operating conditions related to the internal hydraulics and pressure profiles of the system.

Table 4

Kinetic parameters for GVL production process.

Reaction	k	E (cal/mol)
$\text{CH}_2\text{O}_2 \rightarrow \text{H}_2 + \text{CO}_2$	29,513.430	3399.005
$\text{C}_5\text{H}_8\text{O}_3 + \text{H}_2 \rightarrow \text{C}_5\text{H}_8\text{O}_2 + \text{H}_2\text{O}$	552.581	1703.585

5. Results

The following section will show the results ordered according to the methodology shown. We will start with the results obtained concerning the reaction kinetics and continue with the results obtained in the design and optimization of the reactive distillation column. Finally, a comparison will be made between the data previously reported for the conventional technology and the results obtained in this proposal.

5.1. Kinetic results

Following the methodology previously published by Sánchez-Ramírez et al. (2022), and aided by the experimental data published by (Hengne and Rode, 2012), the behavior presented in Fig. 4 and Table 4 was obtained.

According to Fig. 3, the difference between the results predicted with the help of the simulator compared to the experimental results is imperceptible. In that sense, it can be considered that the kinetic data found using the methodology of section 4.1 are adequate. In that sense, Table 4 shows the kinetic data for both modeled reactions.

5.2. Process optimization

As mentioned in section 4.2, using the stochastic hybrid optimization method Differential Evolution with Tabu List, a reactive column alternative for GVL production was obtained. As a result of minimizing the total annual cost (TAC), and the Eco Indicator 99 (EI99), a Pareto front was achieved as shown in Fig. 4. Note that all the designs present in the Pareto front of Fig. 5, satisfactorily comply with the GVL purity constraints.

In the optimization process, both the Total Annual Cost (TAC) and the Environmental Impact (EI99) are minimized, reflecting a clear trade-off between these two objectives. Several authors have reported this tendency when this kind of objective are considered (Berhane et al., 2009; Carvalho et al., 2012; Ponce-Ortega et al., 2011; van Elzakker et al., 2017; Wu et al., 2015). Minimizing capital costs often leads to the selection of smaller equipment designs, such as columns with fewer stages and smaller diameters. While this reduces upfront costs, it can

lead to higher operational demands, such as increased reflux ratios or reboiler duties, increasing services cost. Similarly, minimizing environmental impact, as represented by the EI99 metric, requires balancing the energy and material use, particularly the steel required for construction. A process designed to minimize steel usage may lead to an increase in energy consumption, which in turn raises the environmental impact, and vice versa.

The Pareto front reflects this trade-off, presenting a range of optimal solutions where both objectives are minimized, even though improving one objective may result in an increase in the other. However, a small region at the bottom-right of the Pareto front shows an increase in both TAC and EI99 simultaneously. Although this region may appear to present a trivial solution, it is important to emphasize that the lowest values of EI99 do not occur in this area. This suggests that while this region does not represent an optimal solution, it still contains non-dominated solutions, which is consistent with the nature of the Pareto front.

The apparent trivial behavior observed in this region is likely due to its proximity to the optimal zone. The optimization model, which incorporates complex equations for material balances, thermodynamic equilibrium, energy balances, and chemical reaction modeling, is highly nonlinear and potentially non-convex. As a result, multiple local optima may exist, and it is not unexpected to encounter regions with different behaviors, particularly near the optimal solution. Therefore, although the region where both TAC and EI99 increase does not exhibit the same clear trade-off as other regions of the Pareto front, it remains a valid, non-dominated solution. It is part of the front because it reflects the complexity of the model and the inherent trade-offs captured during the optimization process.

On the Pareto front of Fig. 2, only non-dominated solutions are presented. The Pareto fronts are shown in 2D for better understanding and to be able to observe the trends of the objective functions. In most cases, the presence of a minimum in any objective function is present within the highest values of another function and vice versa. Broadly speaking, within a multi-objective optimization framework, determining the optimal sequence can pose challenges. Hence, the objective of this study is to offer a more comprehensive perspective on selecting the optimal design using a normalization technique. By normalizing the various objective, it becomes feasible to pinpoint the sequence that aligns best with sustainability principles. Koski (1985) proposed the following method for normalizing the objective functions:

$$f_i(x) = \frac{F_i(x) - \min F_i(x)}{\max F_i(x) - \min F_i(x)} \quad i = \text{funcion objetivo}, \quad X \in NP \quad (7)$$

When considering points as vectors originating from the origin

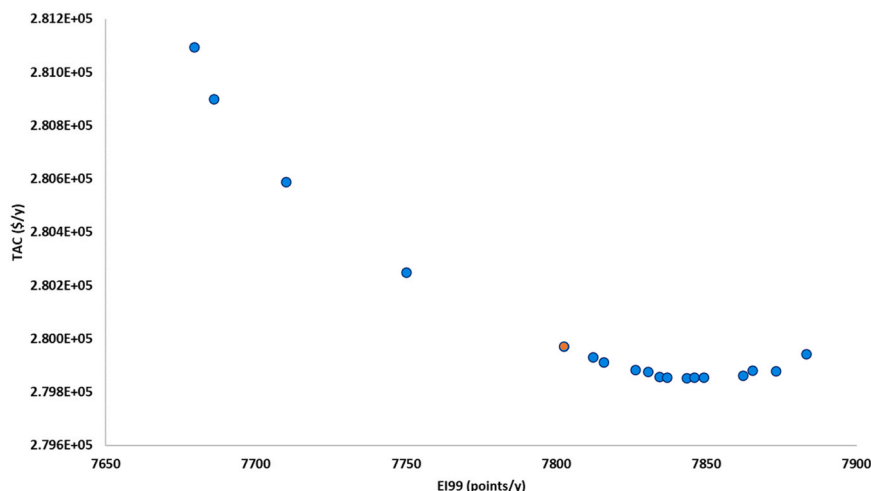


Fig. 5. Pareto front for the reactive distillation column for GVL production.

Table 5
Optimal design parameter of the reactive distillation for GVL production.

Reactive Column			
Number of stages	12	Distillate flowrate (kmol h ⁻¹)	12.645
Reflux ratio	0.322	Bottoms flowrate (kmol h ⁻¹)	3.981
Feed stage	5 and 9	Condenser duty (kcal h ⁻¹)	-15.664
Reactive stages	5–9	Reboiler duty (Watt)	9.893
Hold Up (cum)	0.668	Operative pressure (kPa)	101.32
Overall Efficiency	0.83	GVL production (kmol/h)	3.9688

within a plane or space, it becomes feasible to compute the magnitude of these vectors to identify the one that approaches the minimization of both coordinates. By utilizing the Pythagorean Theorem, the Euclidean distance can be generally computed as follows:

$$Distance = \sqrt{\sum_{i=1}^{NF} f_i^2}, NF = \text{Number of objective functions.} \quad (8)$$

By employing this approach of overarching selection criteria, the multiobjective optimization challenge transforms into refining a scalar value to pick the most optimal solution. The advantage of employing normalization lies in its ability to indicate the extent of separation between the optimum of an objective function in one sequence compared to the optimum of the same objective function in another sequence. In essence, it quantifies the deviation from the ideals of a sustainable process.

From the resulting Pareto front, it is possible to select a balanced solution for both objectives. That is, it is possible to select a design in the zone where the lowest values are found for the total annual cost (TAC) and for eco-indicator 99 (EI99). In this sense, Fig. 5 shows a red dot, which represents a design with these characteristics whose design parameters can be seen in Table 5. For the distillation columns the number of theoretical stages was converted to actual stages using the overall efficiency expression developed by Peters et al. (2002).

The search ranges for the optimization algorithm were established based on several key considerations. For the equipment topology, including stages and diameter, the ranges were informed by recommendations found in the literature (Douglas, 1988; Górak and Olujic, 2014). These values are commonly used in industry and have been

adapted to the context of this study. For the mass and energy balance parameters, such as top and bottom flows and reflux ratio, the search limits were determined by considering the characteristics of the feed streams and the performance metrics of conventional GVL production processes, with an extension of the ranges to allow for potential improvements in performance.

Using a narrower range of variables could have resulted in the optimization algorithm finding suboptimal solutions, as it might have limited the search space and prevented the identification of improvements in the GVL production process. On the other hand, expanding the search range excessively could lead to a larger, more complex search space, increasing the risk of the optimization failing to converge to a feasible and efficient solution. Therefore, the selected search range strikes a balance between providing sufficient flexibility to explore improvements and maintaining the focus on a feasible solution space that ensures the model converges effectively.

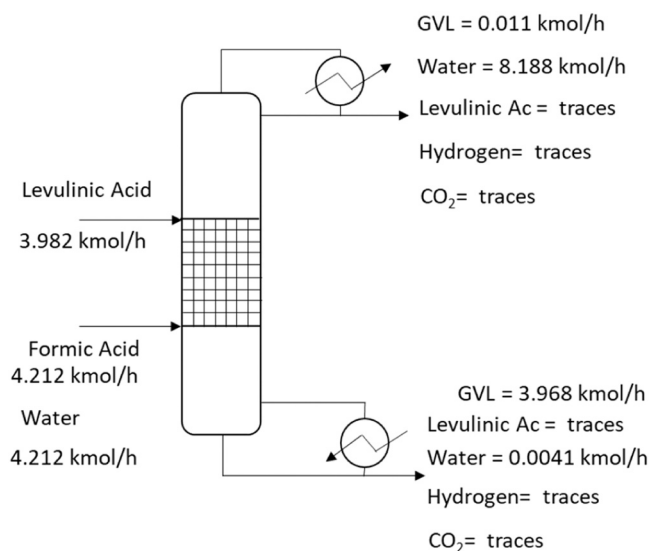


Fig. 7. Flowsheet of the reactive distillation column.

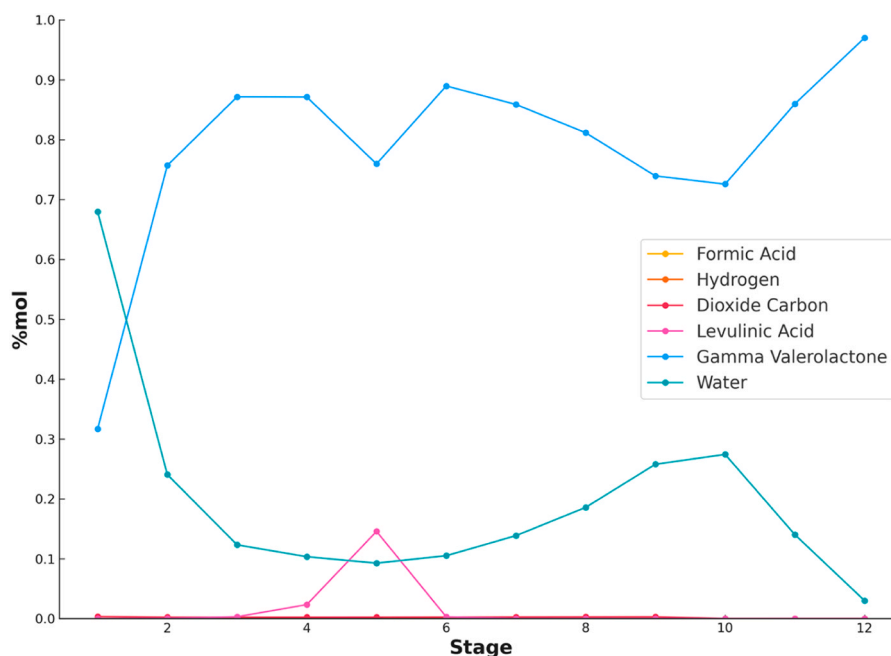


Fig. 6. Molar composition profile at the reactive distillation column for GVL production.

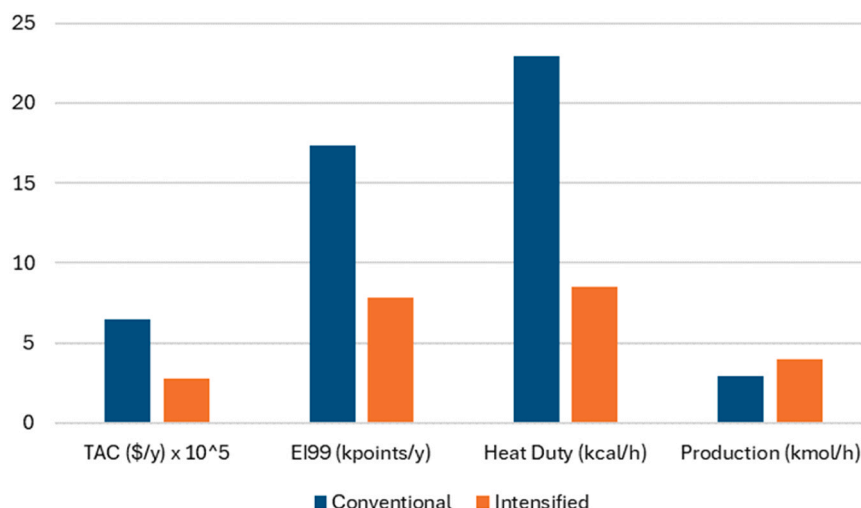


Fig. 8. Comparison of the performance of technologies in GVL production.

Likewise, the composition profile in Fig. 6 shows the molar composition profile that was presented inside the reactive distillation column, and Fig. 7a complete flowsheet of the intensified alternative.

5.3. Comparison of technologies for GVL production

Immediately, it is possible to make a comparison in terms of the indicators evaluated in the objective function. However, it is also possible to make a comparison on some other indicators, e.g. the amount of GVL produced, the thermal load of the process, etc. Initially, an important difference is the amount of equipment involved in the production of GVL. In the process published by Cáceres et al. (2024), three pieces of equipment are required to produce GVL, a reactor, a flash distiller, and a conventional distillation column. On the other hand, in the proposal presented in this work, the production of GVL is carried out using only a reactive distillation column. In this sense, Fig. 8 shows the comparison between the different types.

Fig. 8 shows a significant improvement in all performance indexes between conventional and intensified technology. The improvement could be expected considering that in the conventional production sequence, three pieces of equipment are involved, while in the intensified sequence only one. Thus, the improvement between the two alternatives can be quantitatively compared. For example, the TAC of the intensified sequence represents 43 % of the TAC of the conventional scheme. The EI99 of the intensified scheme represents only 45 % of the conventional scheme. Finally, the energy demand of the intensified scheme represents 37 % of the demand of the conventional process. A highly relevant aspect is the amount of GVL generated with the required purity. Although at the outlet of the reactor of the conventional scheme a quantity of GVL is obtained just below that obtained in the intensified scheme, this effluent still has to be purified. Thus, the production of GVL in the intensified scheme is considerably higher (25 %) than that obtained in the conventional design.

6. Conclusions

This study has successfully introduced an intensified process for the production of γ -valerolactone (GVL) through the use of a reactive distillation column. The analysis, conducted within a multi-objective optimization framework, demonstrates that this advanced approach yields significant improvements over a previously established conventional scheme.

The intensified process, characterized by its integration of a single unit operation as opposed to the conventional three-equipment setup, achieved noteworthy enhancements in GVL production efficiency and

overall performance. Notably, the energy consumption of the intensified process is reduced to just 37 % of that required by the conventional scheme. This reduction is a direct testament to the process's efficiency and sustainability. These results reflect a successful application of Industry 4.0 principles, particularly in terms of process integration and optimization. By leveraging advanced technologies such as reactive distillation, the study aligns with the goals of Industry 4.0, which emphasize increased automation, enhanced efficiency, and reduced resource consumption. The findings underscore the potential for such intensified processes to drive significant advancements in industrial practices, promoting both economic and environmental benefits in line with modern industrial paradigms.

CRedit authorship contribution statement

Quiroz-Ramírez Juan José: Supervision, Investigation, Conceptualization. **Coronel-Muñoz Melanie:** Software, Investigation, Data curation. **Contreras-Zarazúa Gabriel:** Writing – original draft, Methodology, Investigation, Conceptualization. **Cáceres-Barrera Carlos Rodrigo:** Software, Investigation, Formal analysis. **Huerta-Rosas Brenda:** Writing – original draft, Investigation, Data curation. **Sánchez-Ramírez Eduardo:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Conceptualization. **Segovia-Hernández Juan Gabriel:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT in order to homogenize the writing style. After using this tool, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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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References

- Alonso, D.M., Wettstein, S.G., Dumesic, J.A., 2013. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. *Green. Chem.* 15, 584–595. <https://doi.org/10.1039/C3GC37065H>.
- Alvira, P., Tomás-Pejó, E., Ballesteros, M., Negro, M.J., 2010. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. *Bioresour. Technol.* 101, 4851–4861. <https://doi.org/10.1016/j.biortech.2009.11.093>.
- Arias, A., Feijoo, G., Moreira, M.T., 2023. Biorefineries as a driver for sustainability: key aspects, actual development and future prospects. *J. Clean. Prod.* 418, 137925. <https://doi.org/10.1016/j.jclepro.2023.137925>.
- Berhane, H.G., Gonzalo, G.G., Laureano, J., Dieter, B., 2009. Design of environmentally conscious absorption cooling systems via multi-objective optimization and life cycle assessment. *Appl. Energy* 86, 1712–1722. <https://doi.org/10.1016/j.apenergy.2008.11.019>.
- Braca, G., Raspolli Galletti, A.M., Sbrana, G., 1991. Anionic ruthenium iodorcarbonyl complexes as selective dehydroxylation catalysts in aqueous solution. *J. Organomet. Chem.* 417, 41–49. [https://doi.org/10.1016/0022-328X\(91\)80159-H](https://doi.org/10.1016/0022-328X(91)80159-H).
- Bruno, T.J., Wolk, A., Naydich, A., 2010. Composition-explicit distillation curves for mixtures of gasoline and diesel fuel with γ -valerolactone. *Energy Fuels* 24, 2758–2767. <https://doi.org/10.1021/EF100133A/ASSET/IMAGES/LARGE/EF-2010-00133A.0003.JPEG>.
- Caceres, C.R., Sánchez-Ramírez, E., Segovia-Hernández, J.G., 2024. Design and optimization of a sustainable process for the transformation of glucose into high added value products. *Comput. Aided Chem. Eng.* 53, 73–78. <https://doi.org/10.1016/B978-0-443-28824-1.50013-2>.
- Carvalho, M., Lozano, M.A., Serra, L.M., 2012. Multicriteria synthesis of trigeneration systems considering economic and environmental aspects. *Appl. Energy*. <https://doi.org/10.1016/j.apenergy.2011.09.029>.
- Charpentier, J.C., 2010. Among the trends for a modern chemical engineering, the third paradigm: The time and length multiscale approach as an efficient tool for process intensification and product design and engineering. *Chem. Eng. Res. Des.* 88, 248–254. <https://doi.org/10.1016/j.cherd.2009.03.008>.
- Chia, M., Dumesic, J.A., 2011. Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to γ -valerolactone over metal oxide catalysts. *Chem. Commun.* 47, 12233–12235. <https://doi.org/10.1039/C1CC14748J>.
- Delhomme, C., Schaper, L.A., Zhang-Preße, M., Raudaschl-Sieber, G., Weuster-Botz, D., Kühn, F.E., 2013. Catalytic hydrogenation of levulinic acid in aqueous phase. *J. Organomet. Chem.* 724, 297–299. <https://doi.org/10.1016/j.jorganchem.2012.10.030>.
- Demirel, Y., Rosen, M.A., 2023. Process intensification, energy analysis, and artificial intelligence. *Sustain. Eng.* <https://doi.org/10.1201/9781003191124>.
- Douglas, J., 1988. *Conceptual Design of Chemical Processes*. McGraw Hill.
- van Elzakker, M.A.H., Maia, L.K.K., Grossmann, I.E., Zondervan, E., 2017. Optimizing environmental and economic impacts in supply chains in the FMCG industry. *Sustain. Prod. Consum.* 11, 68–79. <https://doi.org/10.1016/j.spc.2016.04.004>.
- Fegyvermeki, D., Orha, L., Láng, G., Horváth, I.T., 2010. Gamma-valerolactone-based solvents. *Tetrahedron* 66, 1078–1081. <https://doi.org/10.1016/j.tet.2009.11.013>.
- Gnansounou, E., Dauriat, A., 2005. Ethanol fuel from biomass: A review. *JSIR* 64 (11), 809–821 [November 2005] 64.
- Goedkoop, M., Spriensma, R., 2000. *Eco-indicator 99 Manual for Designers*. PRE Consultants, Amersfoort, The Netherlands.
- Górák, A., & Olujic, Z., 2014. Distillation: Equipment and Processes.
- Guthrie, K., 1969. Capital cost estimating. *Chem. Eng.* 114.
- Hengne, A.M., Rode, C.V., 2012. Cu–ZrO₂ nanocomposite catalyst for selective hydrogenation of levulinic acid and its ester to γ -valerolactone. *Green. Chem.* 14, 1064–1072. <https://doi.org/10.1039/C2GC16558A>.
- Horváth, I.T., Mehdi, H., Fábos, V., Boda, L., Mika, L.T., 2008. γ -Valerolactone—a sustainable liquid for energy and carbon-based chemicals. *Green. Chem.* 10, 238–242. <https://doi.org/10.1039/B712863K>.
- Kabugo, J.C., Jämsä-Jounela, S.L., Schiemann, R., Binder, C., 2020. Industry 4.0 based process data analytics platform: A waste-to-energy plant case study. *Int. J. Electr. Power Energy Syst.* 115, 105508. <https://doi.org/10.1016/j.jepes.2019.105508>.
- Kiss, A.A., Omota, F., Dimian, A.C., Rothenberg, G., 2006. The heterogeneous advantage: Biodiesel by catalytic reactive distillation. *Top. Catal.* 40, 141–150. <https://doi.org/10.1007/S11244-006-0116-4/METRICS>.
- Kong, Z.Y., Sánchez-Ramírez, E., Yang, A., Li, Y., Segovia-Hernández, J.G., Wong, B.T., Sunarso, J., 2025. A new alternative route for achieving energy saving in intensified reactive-extractive distillation system with a surprise discovery. *Chem. Eng. J.* 503, 158498. <https://doi.org/10.1016/j.cej.2024.158498>.
- Koski, J., 1985. Effectiveness of weighting method in multicriterion optimization of structures. *Commun. Numer. Methods Eng.* 1, 333–337. <https://doi.org/10.1002/cnm.1630010613>.
- Kumaravel, S., Thiruvengadam, P., Kundu, S., 2021. Biosolvents as green solvents in the pharmaceutical industry. *Green Sustainable Process for Chemical and Environmental Engineering and Science. Solvents for the Pharmaceutical Industry*, pp. 105–149. <https://doi.org/10.1016/B978-0-12-821885-3.00007-4>.
- Lange, J.P., Van Der Heide, E., Van Buijtenen, J., Price, R., 2012. Furfural—a promising platform for lignocellulosic biofuels. *ChemSusChem* 5, 150–166. <https://doi.org/10.1002/CSCE.201100648>.
- Lasi, H., Fettke, P., Kemper, H.G., Feld, T., Hoffmann, M., 2014. Industry 4.0. *Bus. Inf. Syst. Eng.* 6, 239–242. <https://doi.org/10.1007/S12599-014-0334-4/FIGURES/1>.
- Liu, Y., Yang, X., Zhang, J., Zhu, Z., 2022. Process simulation of preparing biochar by biomass pyrolysis via aspen plus and its economic evaluation. *Waste Biomass. Valoriz.* 2022 13 (5), 2609–2622. <https://doi.org/10.1007/S12649-021-01671-Z>.
- López-Guajardo, E.A., Delgado-Licona, F., Álvarez, A.J., Nigam, K.D.P., Montesinos-Castellanos, A., Morales-Menendez, R., 2022. Process intensification 4.0: a new approach for attaining new, sustainable and circular processes enabled by machine learning. *Chem. Eng. Process. - Process. Intensif.* 180, 108671. <https://doi.org/10.1016/j.cep.2021.108671>.
- MacRelli, S., Mogensen, J., Zacchi, G., 2012. Techno-economic evaluation of 2 nd generation bioethanol production from sugar cane bagasse and leaves integrated with the sugar-based ethanol process. *Biotechnol. Biofuels* 5, 1–18. <https://doi.org/10.1186/1754-6834-5-22/TABLES/9>.
- Pereira, A.A., Vera, F.P.S., Coelho, H.C.P., Tessaro, I., Chandel, A.K., 2024. Renewable carbon in industry 4.0: toward the sustainable bioeconomy. *Biorefinery and Industry 4.0: Empowering Sustainability*, pp. 1–27. https://doi.org/10.1007/978-3-031-51601-6_1. Green Energy and Technology Part F2511.
- Peters, M., Timmerhaus, K., West, R., 2002. *Plant Design and Economics for Chemical Engineers*, Plant Design and Economics for Chemical Engineers. McGraw-Hill Education.
- Ponce-Ortega, J.M., Mosqueda-Jiménez, F.W., Serna-González, M., Jiménez-Gutiérrez, A., El-Halwagi, M.M., 2011. A property-based approach to the synthesis of material conservation networks with economic and environmental objectives. *AIChE J.* 57, 2369–2387. <https://doi.org/10.1002/aic.12444>.
- Romero-Izquierdo, A.G., Gómez-Castro, F.I., Gutiérrez-Antonio, C., Hernández, S., Errico, M., 2021. Intensification of the alcohol-to-jet process to produce renewable aviation fuel. *Chem. Eng. Process. Process. Intensif.* 160, 108270. <https://doi.org/10.1016/J.CEP.2020.108270>.
- Sánchez-Ramírez, E., Huerta-Rosas, B., Quiroz-Ramírez, J.J., Suárez-Toriello, V.A., Contreras-Zarazua, G., Segovia-Hernández, J.G., 2022. Optimization-based framework for modeling and kinetic parameter estimation. *Chem. Eng. Res. Des.* 186, 647–660. <https://doi.org/10.1016/J.CHERD.2022.08.040>.
- Sánchez-Ramírez, E., Sun, S., Sim, J.Y., Yang, A., Kong, Z.Y., Segovia-Hernández, J.G., 2024. A more appropriate way to optimize the hybrid reactive-extractive distillation system. *Sep. Purif. Technol.* 344, 127184. <https://doi.org/10.1016/J.SEPUR.2024.127184>.
- Shah, M., Kiss, A.A., Zondervan, E., De Haan, A.B., 2012. A systematic framework for the feasibility and technical evaluation of reactive distillation processes. *Chem. Eng. Process.* 60, 55–64. <https://doi.org/10.1016/j.cep.2012.05.007>.
- Srinivas, M., Rangaiah, G.P., 2007a. Differential evolution with tabu list for solving nonlinear and mixed-integer nonlinear programming problems. *Ind. Eng. Chem. Res.* 46, 7126–7135. <https://doi.org/10.1021/ie070007q>.
- Srinivas, M., Rangaiah, G.P., 2007b. Differential Evolution with Tabu List for Solving Nonlinear and Mixed-Integer Nonlinear Programming Problems 7126–7135.
- Srinivas, M., Rangaiah, G.P., 2017. Differential evolution with tabu list for global optimization: evaluation of two versions on benchmark and phase stability problems. *Differ. Evol. Chem. Eng. Dev. Appl. Process Syst. Eng.* 6 6, 91–127. https://doi.org/10.1142/9789813207523_0004.
- Starodubtseva, E.V., Turova, O.V., Vinogradov, M.G., Gorshkova, L.S., Ferapontov, V.A., 2005. Enantioselective hydrogenation of levulinic acid esters in the presence of the RuII-BINAP-HCl catalytic system. *Russ. Chem. Bull.* 54, 2374–2378. <https://doi.org/10.1007/S11172-006-0125-2/METRICS>.
- Strádi, A., Molnár, M., Óvári, M., Dibó, G., Richter, F.U., Mika, L.T., 2013. Rhodium-catalyzed hydrogenation of olefins in γ -valerolactone-based ionic liquids. *Green. Chem.* 15, 1857–1862. <https://doi.org/10.1039/C3GC40360B>.
- Thomé, B., 1993. *Systems engineering: principles and practice of computer-based systems engineering*. John Wiley and Sons Ltd.
- Turton, R., 2001. *Analysis, Synthesis and Design of Chemical Process*. Prentice Hall.
- Vázquez-Castillo, J.A., Contreras-Zarazúa, G., Segovia-Hernández, J.G., Kiss, A.A., 2019. Optimally designed reactive distillation processes for eco-efficient production of ethyl levulinate. *J. Chem. Technol. Biotechnol.* 94, 2131–2140. <https://doi.org/10.1002/jctb.6033>.
- Verified Market Reports, 2023. Global Gamma Valerolactone Market By Type (Food Grade, Industrial Grade), By Application (Food Flavors, Solvent), By Geographic Scope And Forecast [WWW Document]. URL (<https://www.verifiedmarketreports.com/product/gamma-valerolactone-market/>) (Accessed 9.9.24).
- Wu, L., Liu, Y., Kang, L., 2015. Multi-objective optimization on driving options for rotating equipment in process industries to make trade-offs between economy and environmental impacts. *Chem. Eng. Trans.* 45, 1093–1098. <https://doi.org/10.3303/CET1545183>.
- Yang, Z., Huang, Y.B., Guo, Q.X., Fu, Y., 2013. RANEY® Ni catalyzed transfer hydrogenation of levulinic acid esters to γ -valerolactone at room temperature. *Chem. Commun.* 49, 5328–5330. <https://doi.org/10.1039/C3CC40980E>.