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Intensified Alternative for Sustainable Gamma-Valerolactone Production from Levulinic Acid

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ABSTRACT

An intensified approach to γ-valerolactone (GVL) production is achieved using a reactive distillation column. Conventional methods require multiple units, leading to high energy consumption, costs, and limited scalability. The proposed technology integrates reaction and separation into a single unit, enhancing process efficiency for biomass-derived chemicals. A multiobjective optimization framework balances economic, environmental, and operational goals, reducing total annual cost (TAC) by 43% and environmental impact (EI99) by 45% compared to conventional processes. Additionally, energy consumption drops by 63%, while GVL production increases by 25%, highlighting the potential of reactive distillation for improved efficiency and sustainability.

Keywords: Process Intensification, Optimization, Distillation, Life Cycle Analysis, Biomass

INTRODUCTION

The rise of Industry 4.0 is transforming manufacturing through digital integration, automation, and smart systems, fostering sustainability and efficiency [1]. Traditional biofuel production, such as bioethanol and biobutanol, faces challenges in cost and energy efficiency, prompting a shift towards high-value bio-based chemicals like γ-valerolactone (GVL) [2]. GVL, derived from levulinic acid via catalytic hydrogenation, serves as a green solvent, biofuel additive, and precursor for biofuels [2]. Despite its potential, conventional GVL production methods are energy-intensive and costly, requiring high pressures and temperatures, limiting scalability [2-3]. Process Intensification (PI) offers a solution by integrating chemical reactions and separation, reducing energy consumption and enhancing efficiency [5]. Reactive distillation, which combines reaction and distillation into a single unit, has successfully improved processes like biodiesel production, reducing energy use by 40% [6]. This study proposes a sustainable, intensified approach to GVL production using reactive distillation, compared with conventional methods under a multi-objective optimization framework evaluating total annual cost (TAC) and environmental impact [7]. This novel strategy aligns with Industry 4.0 and sustainability goals, enhancing GVL production efficiency and viability.

PROBLEM STATEMENT AND CASE STUDY

Biocompounds derived from renewable biomass present a sustainable alternative to petrochemical-based products. However, conventional production methods are highly energy-intensive, often diminishing their environmental advantages. Typical processes involve multiple stages, including feedstock pretreatment, chemical or biochemical conversion, and product purification. Each stage contributes significantly to energy demand, with steam explosion consuming up to 15% of the total process energy, fermentation requiring 10-15%, and distillation accounting for 35-40% in ethanol production [7].

To address these inefficiencies, Process Intensification (PI) has emerged as a promising strategy, integrating multiple unit operations to enhance mass and heat transfer, reduce equipment size, and minimize energy consumption. By leveraging PI, biocompound production can achieve improved economic feasibility and environmental performance [8].

In the case of γ-valerolactone (GVL) production, catalytic hydrogenation of levulinic acid (LA) has been widely studied [8]. demonstrated that a Cu–ZrO_2 nanocomposite catalyst achieves over 90% selectivity under optimal conditions (473 K, 3–4 MPa H_2 pressure), with excellent recyclability and low metal leaching, making it suitable for industrial applications. Later, [7]. implemented this process in a multi-product biorefinery, producing GVL alongside levulinic acid, furfural, and hydroxymethylfurfural using conventional reaction and separation technologies. However, their study revealed that GVL production accounted for 41% of the total energy demand of the process, highlighting a need for further optimization.

This study proposes the integration of a reactive distillation column as an intensified alternative to replace conventional reactor-separation schemes. By merging reaction and separation into a single unit, energy consumption is reduced, operational efficiency is enhanced, and process sustainability is improved. The proposed intensified process will be systematically compared against its conventional counterpart using multi-objective optimization, evaluating total annual cost (TAC) and environmental impact (EI99) as key performance indicators. The conceptual approach for process intensification applied to GVL production is illustrated in Figure 1.

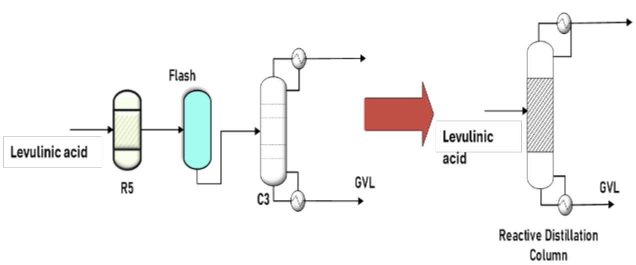

Figure 1: Process intensification applied to GVL production.

PERFORMANCE ASSESSMENT

Economic and Environmental Evaluation

A multi-objective optimization framework is used to evaluate both economic and environmental performance. The total annual cost (TAC) [9]. and environmental impact (EI99) [1]. serve as key indicators:

TAC Calculation:

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

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

Environmental Impact Evaluation (EI99):

To ensure a robust assessment, the system boundaries were carefully defined to encompass the entire life cycle of the process, from raw material input to product output. The analysis considers both direct and indirect environmental impacts associated with the production and operation of the proposed technology. Specifically, it includes the environmental footprint of the materials used for equipment construction, the energy required for heating, and the utilities needed for process operation. In particular, the impact of steel used for the fabrication of the equipment is incorporated into the analysis, considering its extraction, processing, and eventual disposal. Additionally, the steam utilized for process heating is accounted for, as it represents a major contributor to energy consumption. The evaluation also includes the electricity required for pumping operations, which reflects the indirect energy demand necessary for fluid transport and process continuity.

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

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.

METHODOLOGY

Kinetic Parameter Determination

The kinetic model for GVL production was developed using experimental data from [8]. with reaction kinetics adapted for a Cu–ZrO_2 catalyst. The catalyst parameters were optimized using the kinetic parameter estimation framework proposed by [9]. The process follows a two-step hydrogenation reaction: first, hydrogen peroxide decomposes into hydrogen and carbon dioxide. Then, levulinic acid undergoes hydrogenation in the presence of hydrogen gas, yielding γ-valerolactone (GVL) and water. Finally, an intramolecular cyclization step completes the formation of GVL, a high-value bio-based chemical with diverse industrial applications:

$$CH_2O_2 \rightarrow H_2 + CO_2 \tag{3}$$

$$C_5H_8O_3 + H_2 \rightarrow C_5H_8O_2 + H_2O \tag{4}$$

Process Simulation and Modeling

The intensified alternatives were developed based on the optimization of the conventional GVL production process. The previously reported scheme [7]. was replicated to ensure a fair comparison, as detailed in Table 1 and illustrated in Figure 2, which highlights the key process stages. At the inlet of reactor R5, the feed stream rich in levulinic acid undergoes conversion, primarily yielding γ-valerolactone (GVL). The Aspen Plus process simulator was used to model both conventional and intensified processes, ensuring accurate process representation. Thermodynamic modeling was performed using the Non-Random Two-Liquid (NRTL) model for phase equilibrium, providing reliable predictions of separation efficiencies and component interactions.

Table 1: Design parameters conventional design [7].

Column C3	Value	Reactor R5	Value
Stages	39	Flow rate (l/min)	12.188
Feed Stage	22	Volume (m³)	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		

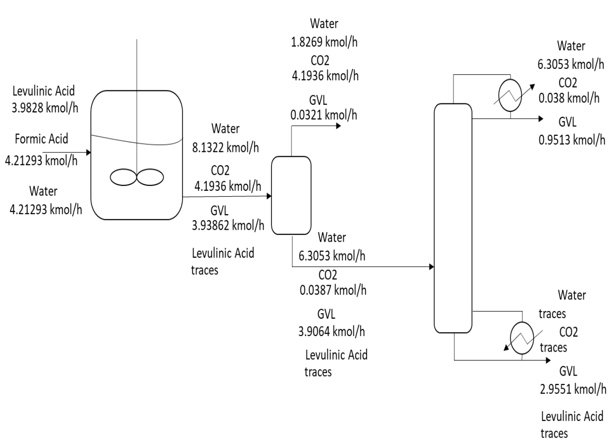

Figure 2: Mole balance of the conventional technology for GVL production.

Reactive Distillation Design and Optimization

The optimization of the reactive distillation column design combines empirical heuristics with a hybrid optimization approach, integrating Aspen Plus with Differential Evolution with Tabu List (DETL) [12]. This method effectively handles nonlinear, nonconvex processes by preventing the re-evaluation of previously assessed points, enhancing search efficiency. The objective function minimizes both total annual cost (TAC) and environmental impact (EI99), ensuring an optimal balance between economic and environmental performance.

The design process starts with defining key parameters such as column dimensions, catalyst type, number of stages, and feed conditions, which are initialized using empirical rules and refined through Aspen Plus simulations. To ensure feasibility, the operating conditions of reaction and separation must align. Factors such as temperature, pressure, and relative volatility are critical, as mismatches between reaction kinetics and separation efficiency can compromise performance [11].

The multi-objective optimization integrates Aspen Plus with Excel via Dynamic Data Exchange (DDE). The DETL algorithm, implemented in Visual Basic, iteratively adjusts decision variables (e.g., reflux ratio, reboiler duty, and feed stage locations) based on process simulations. Optimization parameters include 200 individuals, 1000 generations, a tabu list size of 50%, a tabu radius of 1×10^{-6}, and crossover/mutation rates of 0.8 and 0.6, derived from previous studies [12]. The objective function minimizes both TAC and EI99:

$$Min(TAC, EI99) = f(N_{tn}, N_{fn}, R_{rn}, F_{rn}, R_{sn}, D_{cn}) \quad (5)$$

$$\text{Subject to} \quad \vec{x_m} > \vec{y_m}$$

where N_{tn} is the total number of column stages, N_{fn} is the feed stages in the column, R_{rn} is the reflux ratio, F_{rn} 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.

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 2).

Table 2: Decision Variables in the multi-objective optimization problem

Variable	Type	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)

RESULTS AND DISCUSSION

Kinetic Model Validation

Figure 3 shows a strong correlation between experimental and predicted outflows in the reactor, with a **99.9% GVL yield**. The close agreement between red (experimental) and blue (predicted) bars across all components validates the kinetic model's accuracy, confirming its reliability for process optimization.

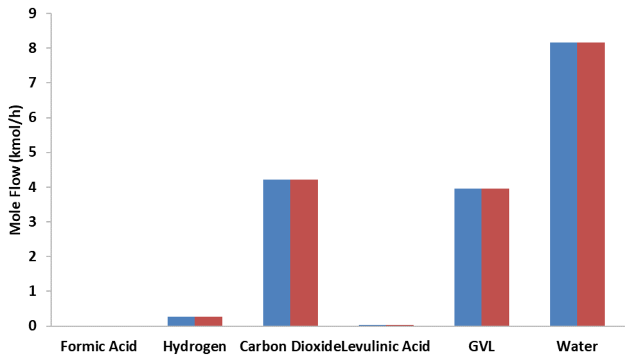

Figure 3: Experimental (red) and predicted (blue) outflows in the reactor

Table 3 presents the kinetic parameters for key reactions in GVL production. The decomposition of **formic acid ($CH_2O_2 \rightarrow H_2 + CO_2$)** has a high rate constant and activation energy, indicating a fast, energy-intensive step. In contrast, the **hydrogenation of levulinic acid to GVL** occurs at a slower rate, suggesting it is the limiting step. These findings emphasize the need for optimized catalysts and conditions to enhance conversion efficiency

Table 3: Caption for the table. Multi-line table captions will be fully justified. The style is **PSE_TableCaption**.

Reaction	k	E (cal/mol)
$CH_2O_2 \rightarrow H_2 + CO_2$	29513.430	3399.005
$C_5H_8O_3 + H_2 \rightarrow C_5H_8O_2 + H_2O$	552.581	1703.585

Process Optimization and Comparison

Reactive distillation column for GVL production was optimized using Differential Evolution with Tabu List (DETL), minimizing total annual cost (TAC) and environmental impact (EI99). The Pareto front (Figure 4) highlights designs that meet GVL purity constraints, demonstrating the trade-off between economic and environmental objectives.

Reducing equipment costs favors smaller, compact designs, but these require higher reflux ratios or reboiler duties, increasing operational costs. Conversely, minimizing steel usage reduces environmental impact but can lead to higher energy consumption. The optimal design, marked in Figure 4, balances TAC and EI99, ensuring an efficient and sustainable reactive distillation process.:

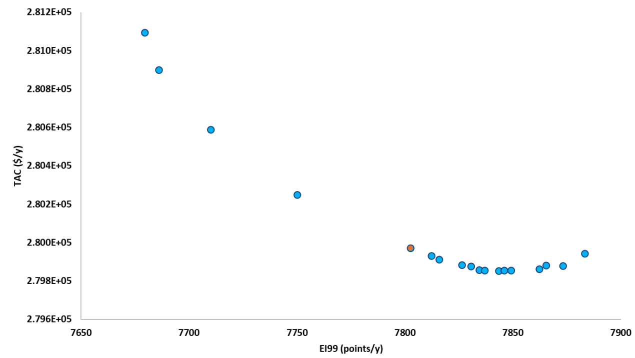

Figure 4. Pareto front for the reactive distillation column for GVL production.

A Pareto front analysis identified optimal designs that balance total annual cost (TAC) and environmental impact (EI99), demonstrating the advantages of the intensified process over the conventional approach. The intensified design achieved a 43% reduction in TAC, a 45% decrease in EI99, and a 63% reduction in energy consumption, while increasing GVL production by 25%. Compared to the conventional process, these improvements highlight the effectiveness of integrating reaction and separation into a single unit, significantly enhancing efficiency and sustainability.

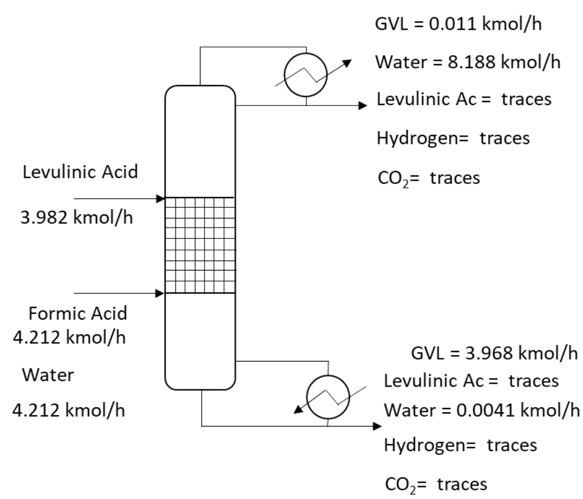

Figure 5: Flowsheet of the reactive distillation column.

Figure 5 presents the complete flowsheet of the intensified process, emphasizing the integration of reaction and separation within a single unit to enhance efficiency and sustainability. When contrasted with the Pareto front shown in Figure 4, the optimized design achieves a significant reduction in total annual cost (TAC) and environmental impact (EI99). The highlighted optimal point in the Pareto front confirms that the intensified process configuration successfully balances economic and environmental objectives, reinforcing the advantages of reactive distillation over conventional multi-unit approaches.

Table 4: Optimal design parameter of the reactive distillation for GVL production.

Reactive Column			
Number of stages	12	Distillate flowrate (kmol h-1)	12.64
Reflux ratio	0.322	Condenser duty (kcal h-1)	-15.66
Feed stage	5 and 9	Reboiler duty (Watt)	9.89
Reactive stages	5 to 9	Operative pressure (kPa)	101.32
Hold Up (cum)	0.668	GVL production (kmol/h)	3.968

Table 4 presents the complete flowsheet of the intensified process, emphasizing the integration of reaction and separation within a single unit to enhance efficiency and sustainability. This optimized design, when contrasted with the Pareto front in Figure 5, demonstrates a substantial reduction in total annual cost (TAC) and environmental impact (EI99). The highlighted optimal point in the Pareto front confirms that the intensified configuration effectively balances economic and environmental objectives. The key design parameters, such as the number of stages, reflux ratio, and reboiler duty, were optimized to maximize GVL yield while minimizing energy consumption. This reinforces the advantages of reactive distillation over conventional multi-unit approaches, offering a more sustainable and cost-effective alternative for GVL production.

The results clearly demonstrate the advantages of process intensification in γ-valerolactone (GVL) production. As shown in **Figure 6**, the intensified process significantly reduces Total Annual Cost (TAC) and environmental impact (EI99) while maintaining a lower heat duty compared to the conventional approach. This indicates improved energy efficiency and economic feasibility. Furthermore, **Figure 7** illustrates the molar composition profile along the reactive distillation column, where levulinic acid is effectively converted into GVL, with water as a major byproduct. The presence of formic acid and carbon dioxide suggests minor side reactions, while hydrogen formation in intermediate stages aligns with catalytic hydrogenation mechanisms. Overall, these findings validate the effectiveness of reactive distillation in optimizing GVL production, offering a more sustainable and cost-efficient alternative to conventional multi-unit processes.

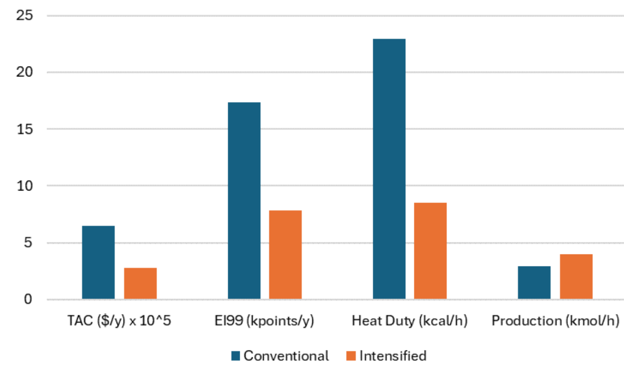

Figure 6: Comparison of the performance of technologies in GVL production

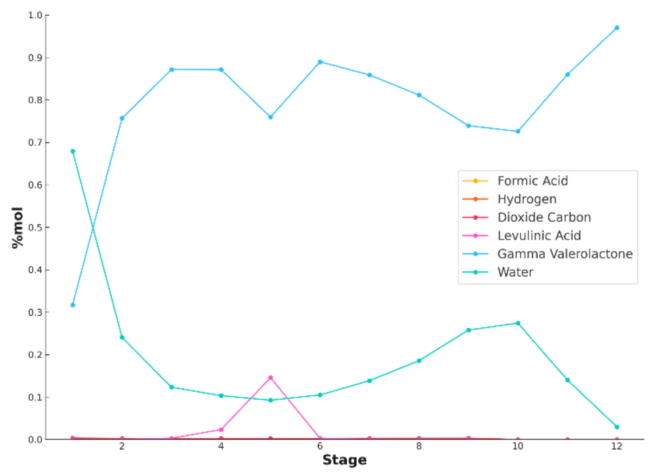

Figure 7: Molar composition profile at the reactive distillation column for GVL production

CONCLUSION

This study introduces an intensified reactive distillation process for γ-valerolactone (GVL) production, significantly improving efficiency over conventional methods. By integrating reaction and separation in a single unit, energy consumption is reduced to 37% of the traditional process, enhancing sustainability. The approach aligns with Industry 4.0 principles, emphasizing process integration, automation, and resource efficiency, demonstrating its potential to drive economic and environmental benefits in modern industrial practices.

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