

Desing and optimization of a multi-objective plant to obtain the best furfural derivates

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ABSTRACT

The valorization of lignocellulosic biomass represents a key pathway toward sustainable chemical production, as it enables the development of circular economy products with reduced dependence on fossil resources. Among the platform molecules derived from biomass, furfural stands out as a versatile intermediate that can be transformed into several high-value chemicals, such as furfuryl alcohol, 2-methylfuran, tetrahydrofurfuryl alcohol, furan, tetrahydrofuran, and maleic anhydride. In this work, an integrated biorefinery scheme for producing the main furfural derivatives is proposed and evaluated through process simulation and sustainability metrics. The process was modeled in Aspen Plus V14, using furfural obtained from lignocellulosic biomass (corn stover) as raw material, following hydrogenation and oxidation routes. The process is multi-product, meaning that the main furfural derivatives are produced simultaneously within the same plant. This was achieved by implementing splitters that work at 50% capacity in the division of raw materials. The mass and energy balances from the simulation were used to evaluate environmental, economic, energy, and efficiency performance using a set of indicators. Economic data were obtained from Aspen Economics, yielding a total capital cost of 7.65 MUSD and a total annual cost of 1.93 MUSD/year. The environmental assessment resulted in an EI99 of approximately 2.0×10^8 mPt/year, mainly influenced by hydrogen consumption and carbon monoxide emissions. From an efficiency perspective, the process shows favorable performance, with an MLI of 0.07 and an MCI of 69%, indicating high material efficiency despite the inherent complexity of multi-stage hydrogenation and oxidation pathways. Overall, the results demonstrate the technical and sustainability potential of an integrated furfural-based biorefinery, while highlighting opportunities for further improvement through process integration and hydrogen recovery.

Keywords: Furfural, Furfuryl alcohol, Biomass, Biorefinery, Performance Indexes

INTRODUCTION

Background

Sustainability, the need to generate circular economy products, furfural as a high-value product from biomass, a biorefinery scheme to produce all components for different applications, furfural as a versatile platform, explaining each of the products to be obtained.

The valorization of biomass as a sustainable alternative to its fossil counterpart, to create sustainable and profitable processes, is of great importance since lignocellulosic biomass is the only source that fixes carbon, is

especially abundant, relatively inexpensive, and has great potential to be transformed into high-value bio-based chemicals. Due to this great economic advantage offered by using biomass as a starting point for the creation of a complete process, process design is relevant to identifying the appropriate kinetic and thermodynamic conditions.

The concept of biorefinery has become popular in recent years, as it involves the general concept of a plant that processes raw materials from biomass and converts them into a platform product, from which products with higher market value can subsequently be extracted, but

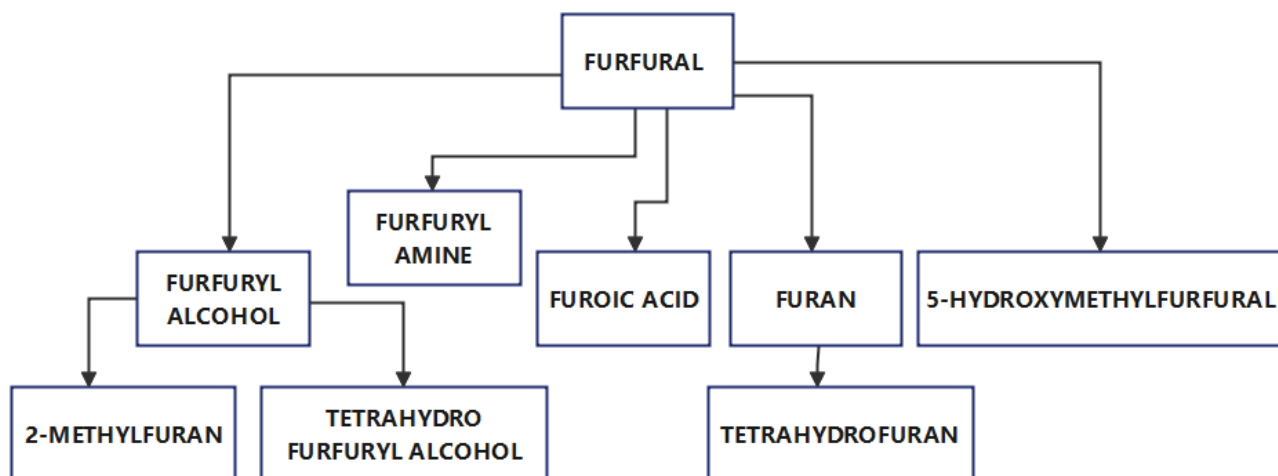


Figure 1. Primary products derived from the direct transformation of furfural [1].

which now have a more sustainable origin as they come from biomass.

This study considered integrated biorefinery processes by combining different processes to produce various products of interest. This was achieved by integrating mass and energy flows for the processing of furfural by-products, which can improve process efficiency in terms of yield, raw materials, and energy consumption, reducing waste generation and promoting economic and environmental performance. Since process integration provides a broader view of the use of products and by-products, through simple processes such as oxidation or hydrogenation, we can obtain a new product derived from the biorefinery. It is important to note that in previous cases, such as that carried out by Kabwe et al. (2025), scenarios are studied where production focuses only on some furfural derivatives. In this study, we carried out a multi-product process, meaning that all the main furfural derivatives are produced simultaneously within the same plant. This was achieved through the implementation of splitters that operate at 50% capacity and manage to divide the product flows that feed another sub-process.

The Chemistry of furfural and its derivatives

The chemistry of furfural and its derivatives is well developed. The main transformation of furfural is through hydrogenation and oxidation, resulting in primary families of derivatives that are more profitable than furfural, as most of them already have an established market, as can be seen in Figure 1. The different compounds obtained are widely used as solvents, transportation fuels, gasoline additives, lubricants, resins, additive and decolorizing agents, and flavor enhancers for food and beverages.

Furfuryl alcohol

Among the main furfuryl derivatives, furfuryl alcohol is the most established, due to its broad market with applications in the chemical industry, specifically in pharmaceuticals, polymers, and resin manufacturing. It is also an important chemical intermediate for the manufacture of fragrances [1].

2-Methylfuran

In addition to the production of furfuryl alcohol, alternative furfural derivatives of interest that show market potential include 2-methylfuran (MF), which is currently the focus of research because it is an alternative to fossil fuels. Since MF has physicochemical characteristics like gasoline, its implementation in internal combustion engines is a potential field of application [2].

Tetrahydrofurfuryl

Tetrahydrofurfuryl alcohol is a promising source of organic chemicals that are currently produced from fossil fuels [3].

Furan

Furan is commercially produced from furfural by decarbonylation, where the loss of carbon monoxide directly yields furan. From a general chemical perspective, furan is a 5-membered heterocyclic unsaturated ring compound containing oxygen; therefore, it is the basic ring structure found in all kinds of industrially important products [4].

Tetrahydrofuran

Tetrahydrofuran has established itself as an excellent solvent, with high volatility, a low freezing point, and

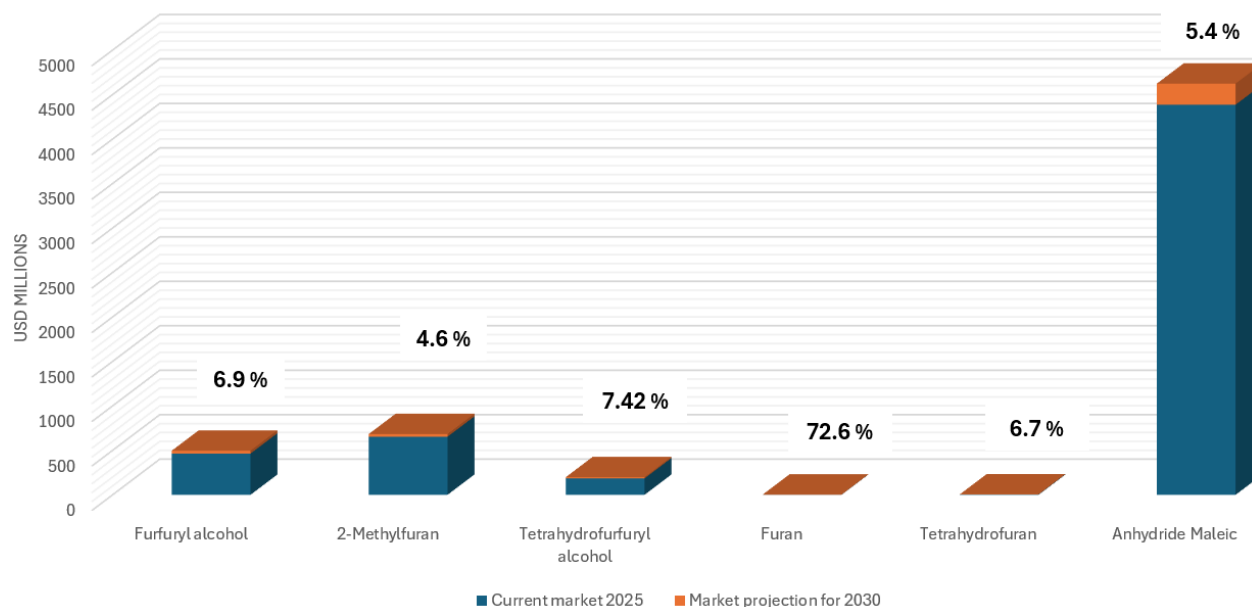


Figure 2. Growth projections for the main furfural derivatives for 2030 [8-13].

the ability to dissolve both polar and non-polar compounds. The applications of tetrahydrofuran are diverse, ranging from the production of polymer coatings and adhesives to pharmaceutical chemistry, where its presence reflects the use of a clean solvent that can be easily separated from the desired products [5]. Currently, THF is produced industrially from petroleum-derived intermediates, involving the hydrogenation of maleic anhydride or the dehydration of 1, 4-butanediol. Bio-based THF can be produced by direct catalytic hydrogenation of furfural or using furan as an intermediate, achieving typical yields of 52–100% [6].

Maleic anhydride

Finally, maleic anhydride is the anhydrous form of maleic acid and is currently produced on an industrial scale from fossil fuels, but there is another route for obtaining it from furan. Its main applications are in the pharmaceutical industry and in the manufacture of polyester resins. The largest percentage of maleic anhydride produced in the United States is used in the manufacture of polyester resins (52%). These applications are diverse, ranging from their use in reinforced plastics for automobiles, boats, and construction panels, among others [7]. However, the market for maleic anhydride resins is undoubtedly growing year after year, hence the importance of finding a new biosustainable production mechanism.

Market for the main furfural derivatives

The market for furfural derivatives, as shown in Figure 2, has become even more important than that for furfural itself as a base product, because it is these

transformed compounds that truly capture the greatest economic and technological value in industrial chains. While furfural is mainly used as a chemical platform and specialized solvent, its derivatives find direct and massive applications in resins, fuels, additives, polymers, coatings, and high-performance materials. This means that demand is driven more by the end markets for these derivatives than by the consumption of furfural itself, shifting the focus from simple intermediate production to the integration of higher value-added conversion processes. In this sense, furfural increasingly functions as a strategic “building block” within a biorefinery, while the real economic and growth engine of the sector lies in the diversification and expansion of its derivatives in larger-scale, higher-margin industrial markets.

Based on this, several researchers have focused their attention on conducting techno-economic analyses of furfural derivatives to compare production costs with prices established for different scenarios, such as Kabwe et al. (2025), who evaluated different scenarios for the conversion of furfural products, depending on the product of interest and the conditions established.

CASE STUDY

Furfural production

The background to furfural production is the design and optimization of a multi-product biorefinery aimed at obtaining furanic compounds proposed by Caceres-Barra et al. (2024) from lignocellulosic biomass, using corn stover as the main raw material. The proposed process is based on a pretreatment that allows the biomass to be

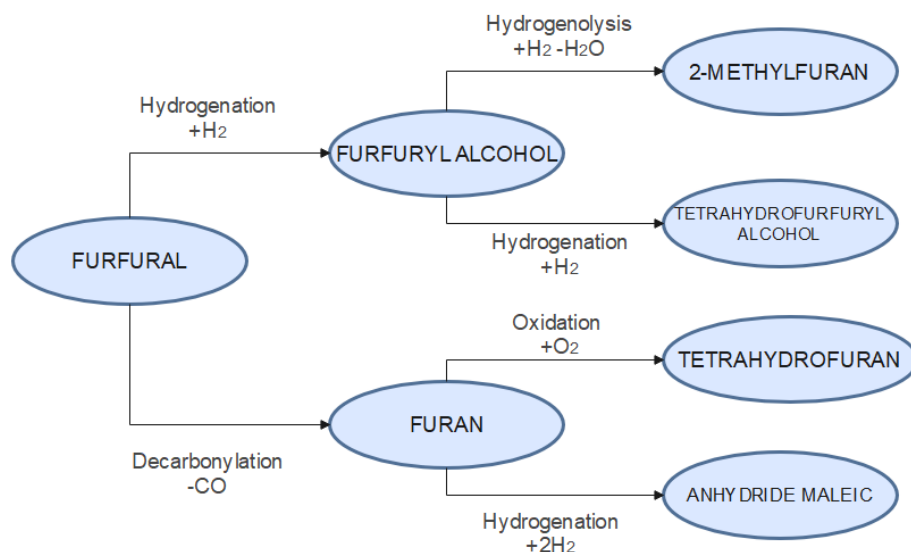


Figure 3. The main production routes for furfural derivatives.

broken down and the constituent sugars to be released, especially the pentoses from hemicellulose, which are subsequently converted into furfural through dehydration reactions. The design strategically integrates the reaction and separation stages to maximize the recovery of furfural and other valuable products such as HMF, levulinic acid, and γ -valerolactone. It is here that we segment the production route and take the final stream of the furfural product as feedstock for the biorefinery proposed in this study.

Process description

The production process was modeled in the Aspen Plus V14 process simulation tool using the diagram shown in Figure 3 to obtain mass and energy balances. The data retrieved from the simulation was used to perform multi-objective optimization using the mathematical model we constructed to estimate the quantity produced of each furfural derivative, maximizing profit. Assuming that the amount of furfural is fixed and predetermined (i.e., fixed plant size) retrieved from the article published by Cáceres-Barrera et al. (2024) [14].

The main production routes for furfural derivatives, as shown in Figure 3, are hydrogenation and oxidation. The reaction kinetics for each of the routes are shown in Table 1.

Finally, the process modeled in Aspen Plus follows the methodology shown in Figure 4. The process mainly consists of six reactive zones for obtaining the main products derived from furfural. The production of 2-Methylfuran includes an additional separation process through a distillation column for the purification of 2-

Methylfuran. The maleic anhydride production process includes a purification process through an absorber to include a solvent that separates water from maleic anhydride, which is then obtained through a distillation column.

Table 1: The reaction kinetics.

Kinetics	Reference
$C_5H_4O_2 + H_2 \rightarrow C_5H_6O_2$	[15]
$C_5H_4O_2 + 2H_2 \rightarrow C_5H_6O + H_2O$	[15]
$C_5H_4O_2 + 4H_2 \rightarrow C_5H_{10}O_2$	[16]
$C_5H_4O_2 \rightarrow C_4H_4O + CO$	[17]
$C_4H_4O + 2H_2 \rightarrow C_4H_8O_2$	[18]
$C_4H_4O + \frac{3}{2}O_2 \rightarrow C_2H_2O_3 + H_2O$	[17]

Optimization

The production process for the main furfural derivatives presents a suitable case for optimization, with the analysis of the process's economic, environmental, and safety properties serving as the objective function. This can be explained through the design parameters involved in the process that directly impact economic, environmental, and safety indicators. It is important to note that to achieve a process with a positive environmental impact, it is necessary to consider various external variables, such as the chosen solvent. To achieve a design with high recovery of the main furfural derivatives, low environmental impact, low operating costs, and safety, it is necessary to have an appropriate design for the separation and purification units of the main products. Likewise, the choice of the solvent used to purify maleic

anhydride and the appropriate operating conditions play a significant role in the process.

In this project, the objective function involves indicators and metrics necessary for optimizing the production process of the main furfural products, which are described below.

Eco-indicator 99 (EI99)

The advantages of incorporating EI99 in sustainability evaluations are manifold. Firstly, it offers a thorough perspective on the environmental performance of a product or system, enabling decision-makers to prioritize actions and investments in areas with the most substantial impacts. EI99 covers a broad spectrum of environmental categories, aligning with the multidimensional approach of the UN's 2030 Agenda that seeks to tackle interconnected global challenges. Eco-indicator 99 is one of the most widely used environmental impact estimation methods and consists of a quantitative analysis of the life cycle evaluated from beginning to end. The calculation is performed using Eq. (1). Where ω represents the damage weight factor (Pts/kg), C_i represents the impact value for each of the categories i , and α_j is the value of subcategory j (kg/year). This methodology accounts for the origin of raw material in processing and degradation. It is based on standard ecological indicators, which are numbers that express the total environmental burden of a product or a process. The higher the value of the indicator, the greater the environmental impact. Therefore, the best scenario is the lowest possible EI99.

$$EI99 = \sum_i \sum_j \omega \cdot C_i \cdot \alpha_j \quad (1)$$

Total annual cost (TAC)

Assessing the overall yearly expenses of a process is crucial within a sustainability framework. The evaluation of total annual costs is essential for various compelling reasons. Firstly, by quantifying these costs, organizations and policymakers can comprehensively grasp the environmental, social, and economic implications of their actions. Sustainability goes beyond minimizing immediate expenditure; it requires an evaluation of long-term consequences. Considering the comprehensive cost, which includes direct and indirect financial expenses, environmental impacts, social implications, and potential externalities, allows stakeholders to make well-informed decisions considering the entirety of sustainability factors. This approach fosters transparency and accountability, as it enables a clear evaluation of trade-offs between short-term economic gains and long-term sustainability objectives. The TAC assumes the annualization of the investment cost of the main process equipment over a 10-year amortization period. To calculate it, Eq. (2) is used. Where $C_{TM,i}$ is the capital cost of the equipment in dollars (\$), r represents the payback period in years, and $C_{ut,j}$ is the cost of cooling and heating services, in dollars

per year (\$/year). The objective function evaluates the lowest annual cost of the process while considering the utilities used by the plant and various units. The best scenario is a total annual cost as low as possible to recover the investment.

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

Individual risk (IR)

The Individual Risk (IR) metric is crucial for sustainability because it evaluates the likelihood of accidents or harmful events affecting individuals, thus supporting the design of safer industrial processes. By quantifying potential risks to human health and safety, IR ensures that processes prioritize safety, reducing the chance of incidents that could harm people or damage the environment [19]. This focus on minimizing risks aligns with the broader goals of sustainability, including regulatory compliance and social responsibility. Moreover, IR supports Sustainable Development Goals (SDGs) such as Good Health and Well-being (SDG 3) and Decent Work and Economic Growth (SDG 8) by promoting safe working conditions and protecting human health, which are essential components of sustainable development [19]. The IR identifies the risk that a person faces based on his position, including the likelihood of an accident resulting in death or serious injury. The IR is defined as shown in Eq. (3). Where, f_i represents the recurrence that one accident will occur, and $P_{x,y}$ is the likelihood that the accident will occur in a particular location.

$$IR = IR = \sum f_i P_{x,y} \quad (3)$$

In the methodology of this project, the instantaneous and continuous risk analysis was performed for each of the equipment involved in the CO₂ capture process that is in contact with the solvent of interest. Catastrophic events such as Boiling Liquid Expanding Vapor Explosion (BLEVE), Unconfined Vapor Cloud Explosion (UVCE), Jet Fire, Flash fire, and toxic explosion were evaluated using specific mathematical models for each case reported in the literature. The ideal scenario is the one with the lowest individual risk index (IR), as it would be a less risky process.

The objective function

In this study, the objective function encompasses three key areas: environmental, economic, and process safety. It is hoped that this work will contribute to selecting the optimal production route for the main furfural derivatives or to a specific analysis of a product of individual interest. Similar studies have been previously reported by Sanchez-Ramirez et al. [20] and Romero-Garcia et al. [21] for carbon capture cases, but a similar methodology is applied. Therefore, based on this prior information regarding the indicators, the general mathematical

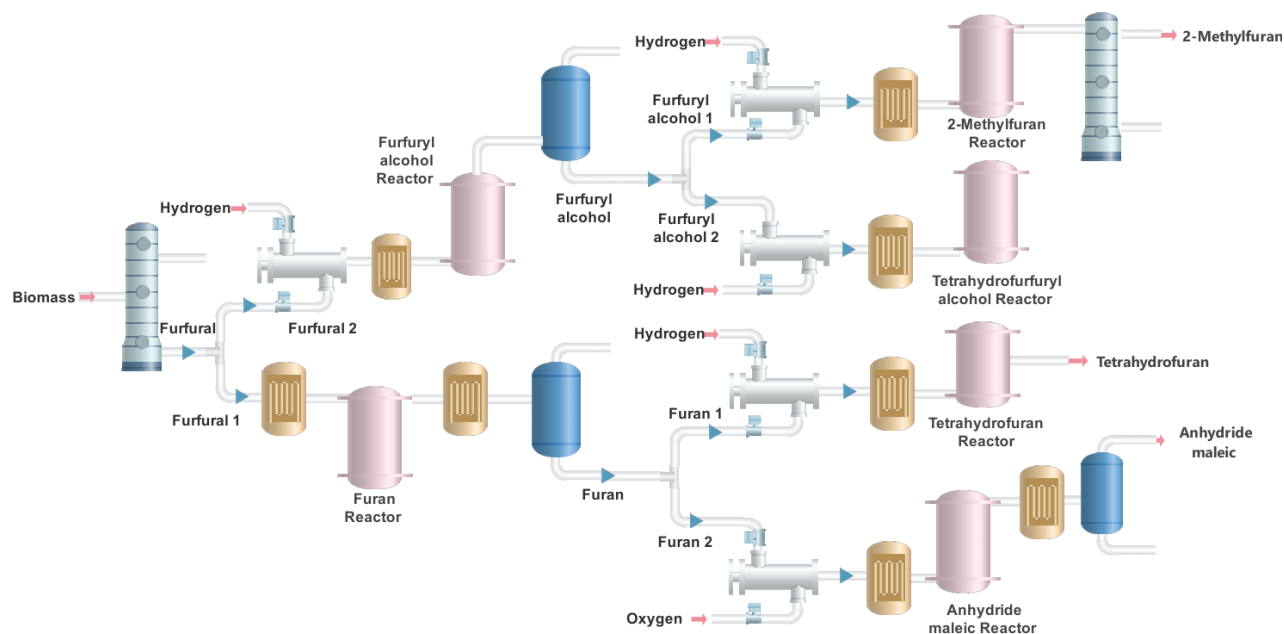


Figure 4. Process simulation diagram.

expression for the objective function, and the respective decision variables involved in the optimization process, are shown below in Equation (4).

$$\text{Min} [EI99, \text{TAC}, \text{IR}] = f(N_{i,j,k}, NF_{i,j}, D_{i,j,k}, \text{DBP}, \text{RR}, Q) \quad (4)$$

For the variables related to the capture process $N_{i,j,k}$ represents the number of stages, $NF_{i,j}$ represents the feed stage, $D_{i,j,k}$ represents the diameter where the i is specified for distillation column, absorber j and k corresponds to the desorber. DBP represents the solvent feed flow in the absorber, RR represents re reflux ratio and Q the reboiler duty, both in the desorber column.

The proposed model involves a significant number of variables that must be optimized to achieve an optimal design and operating conditions, with the goal of minimizing various performance metrics and maximizing the recovery of the main products of market interest. The implementation of the global optimization approach involved linking Aspen Plus with Microsoft Excel. To initiate the optimization process, the design variables were specified in Microsoft Excel using the stochastic optimization algorithm, Differential Evolution with Tabu List (DETL). During the optimization process, a vector of decision variables is created from Excel to Aspen; in Aspen, the process is evaluated under the parameters of the decision vector, then it is assessed whether the combination of variables is feasible; if not, the algorithm generates a new combination, the resulting data is returned from Aspen Plus and stored in Excel, to apply constraints based on the desired

purities or flows, evaluating the previously mentioned indicators, to minimize the objective function and find the optimal process design.

The parameters considered for the DETL method are: population size of 120 individuals, 1,000 generations, a tabu list size of 60, a tabu radius of 0.0001, a crossover rate of 0.9, and a mutation rate of 0.3. These parameters have been shown to work exceptionally well with nonlinear problems, yielding excellent results.

RESULTS

Analysis of the 3D Pareto Fronts

The scatter plot represents the system's solution space, highlighting the variability among the evaluated indicators. The blue points show all possible configurations, while the orange points represent the smoothed trend of the system's behavior. A nonlinear relationship is observed among the indicators, confirming the existence of a trade-off between them and the multi-objective nature of the problem.

Optimal Design

Table 2 provides a summary of the optimal design for the main purification units in the furfural production process; the optimal design is achieved when the objective functions are in equilibrium with one another and the trade-offs between the objectives are balanced.

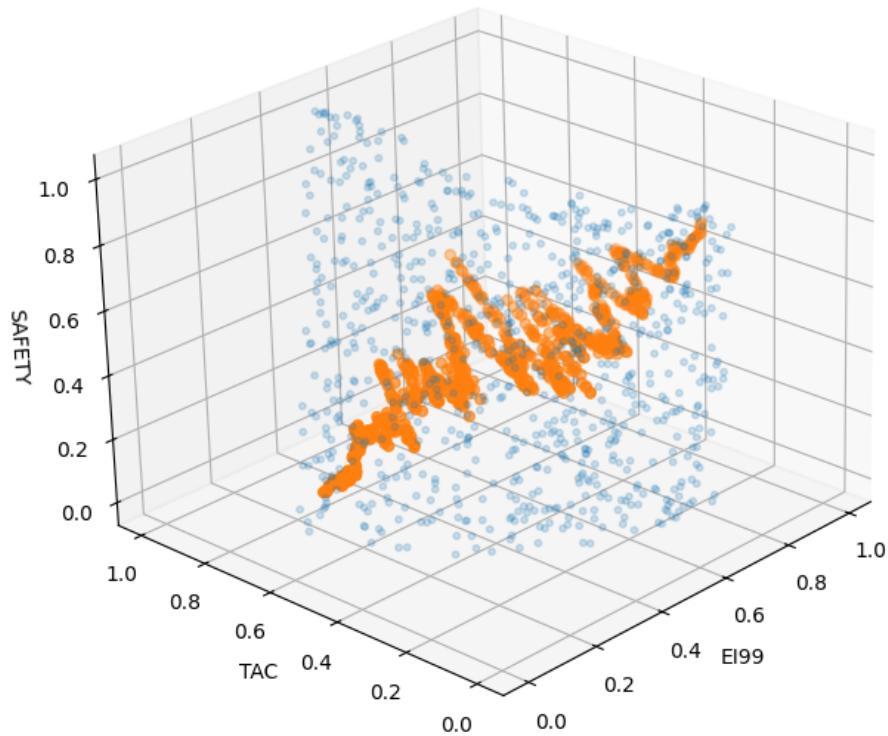


Figure 5. Pareto fronts between the Total annual cost (TAC), Ecoindicator 99 (EI99) and Safety.

Table 2: Design parameters for the best scenario.

Variables	Result
Column 1	
Number of stages	17
Feed stage	8
Diameter (m)	3.3163
Reflux ratio	3.1266
Reboiler duty (GJ/h)	0.6372
Adsorption	
Number of stages	17
Feed stage	1
Diameter (m)	1.9144
Desorption	
Number of stages	15
Feed stage	5
Diameter (m)	2.0566
Reflux ratio	2.6567
Reboiler duty (GJ/h)	1.4854
Objective function	
EI99	42896.24
TAC	4.3281E+10
SAFETY	3.2415E+09

It is possible to observe the impact of certain design parameters on process performance. In the case of the absorption unit, the solvent temperature plays an important role in achieving the adsorption of maleic anhydride and its subsequent separation, thus directly affecting the recovery efficiency of this main product. Furthermore, the reflux ratio is directly related to energy requirements. The higher the reflux ratio, the greater the energy requirements for capture. Regarding the analysis of sustainability indices, it is observed that the lowest EI99 is achieved when lower amounts of energy are used in the process, which is largely related to equipment sizes; this trend is related to the process topology. Energy efficiency

Figure 6 highlights an important perspective on efficiency by comparing the production rate (kg/h) with the energy consumption rate (MJ/h) for each component. It is evident that not all processes use energy with the same efficiency: for example, FURAN and FOL achieve relatively high production with low to moderate energy consumption, indicating efficient performance, while THF and THFA consume more energy without a proportional increase in production, making them less efficient. This contrast becomes more pronounced with MF and, especially, with MA, where energy consumption is significantly higher despite having production levels similar to those

of other components, revealing energy-intensive processes. Overall, the graph demonstrates that higher energy consumption does not necessarily translate to higher production, underscoring the importance of evaluating and optimizing energy efficiency in process design.

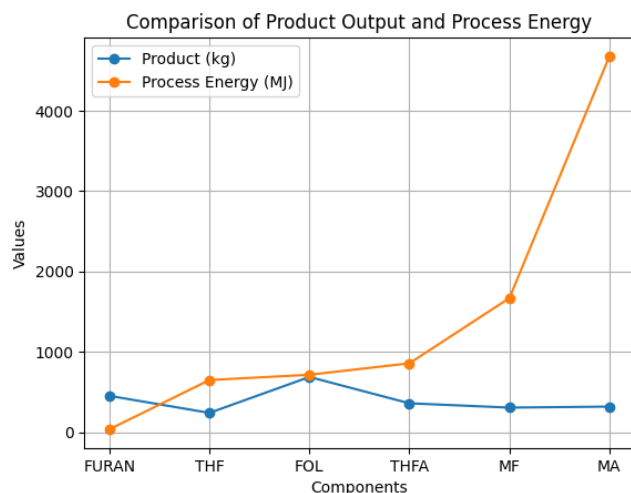


Figure 6. Energy efficiency.

CONCLUSIONS

This study proposes the design and optimization of a production plant for the main furfural derivatives. Simultaneous production is achieved through the implementation of flow separators for the main streams of first-generation furfural products, thereby enabling the simultaneous production of six of the main derivatives. The evaluation of metrics related to environmental impact, economic assessment, and process safety provides a broader perspective on how different variables can affect the sustainability of the process. Finally, the implementation of the multi-objective optimization algorithm provides a broader perspective on process control, with the objective function being to minimize these economic, environmental, and safety aspects of the process; this aims to achieve the optimal design that meets the established constraints and serves as the starting point for its implementation or scaling.

In conclusion, this work creates an opportunity for future research on the main furfural production routes. Considering the sustainability framework, there is significant potential for process improvement and adaptation, specifically regarding the implementation of new production routes based on this work or the implementation of a new solvent to recover maleic anhydride from the process.

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