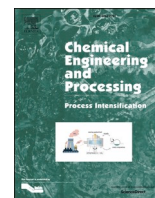




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Design and optimization of an intensified sustainable plant to produce biojet fuel using the ATJ process

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ABSTRACT

The study considers the pressing need to explore alternatives to alleviate the environmental burdens associated with the air transport sector, which contributes significantly to global CO₂ emissions. Biojet fuel, produced through the Alcohol to Jet (ATJ) process, emerges as a promising solution aligned with sustainable development goals. Process intensification is implemented in the pretreatment stage through a saccharification-fermentation (SSF) reactor, in ethanol purification via a divided wall column, and in biojet fuel production using a reactive distillation column for oligomerization and hydrogenation reactions. This intensified strategy led to notable reductions in Total Annual Cost (TAC) and Eco-Indicator 99 (EI99) impact, including a 39 % decrease in pretreatment costs, a 4 % reduction in ethanol purification costs, and a remarkable 49 % decrease in biojet fuel production costs compared to conventional processes. Moreover, there was an 18 % reduction in the global environmental impact and a 20 % reduction in overall TAC. These findings underscore the potential of intensified technology in mitigating the environmental impact of biofuel production processes.

1. Introduction

In 2017, global transportation involved over 4.1 billion individuals and 539 million metric tons of goods, representing 35 % of global trade value. Aviation, emitting 781 million metric tons of CO₂ over 2017–2018, surpassed emissions from other transportation sectors by 12 % and various human activities by 2 % [30]. The growing demand for aviation services is exacerbating this issue, with passenger numbers expected to rise by 2036 [3,11,38], although predictions have been impacted by the COVID-19 pandemic. Biofuels, derived from renewable sources like crops and algae, are being explored as alternatives to traditional fossil fuels. Aviation biofuels, or biojet fuels, are specifically targeted to reduce the carbon footprint of air travel, sourced from diverse materials including algae, plant oils, and waste.

The Alcohol-to-Jet (ATJ) process offers a sustainable option by utilizing lignocellulosic agro-industrial waste, avoiding interference with food production and excessive water usage. However, it is currently expensive and lacks competitiveness compared to traditional jet fuel production. ATJ involves multiple stages, including ethanol conversion,

dehydration, oligomerization, hydrogenation, and purification, consuming substantial energy. Research indicates that up to 80 % of total energy consumption in the ATJ process can occur during specific segments, highlighting the need to explore viable alternatives for sustainable jet fuel production [23].

Process Intensification (PI) offers a promising strategy for enhancing biojet fuel production efficiency. PI involves redesigning chemical, biological, or physical processes to improve performance, reduce resource consumption, and minimize waste generation [25]. The goal is to achieve outcomes comparable to or better than conventional methods while significantly reducing energy, raw materials, and environmental impact. PI can also lead to more compact and modular process designs, saving space and facilitating easier scalability in manufacturing [16].

In their study, Rivas-Interian et al. [22] proposed a process scheme using the Alcohol-to-Jet (ATJ) method for biojet fuel production. They focused on intensifying the ethanol purification section and compared it to a conventional process without intensification. Their findings showed that applying Process Intensification (PI) reduced total annual costs, environmental impact, and lowered the minimum sale price for the

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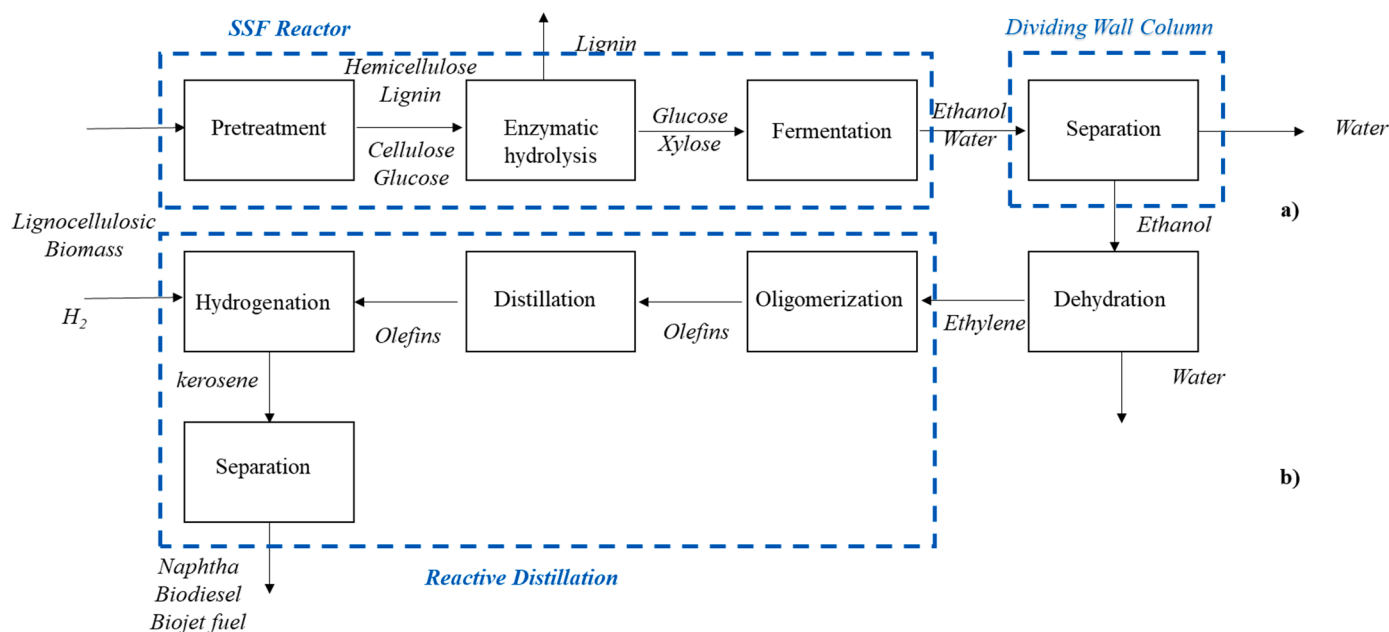


Fig. 1. ATJ conventional process, and the proposed sections as intensified processes (green).

intensified scheme. This study demonstrated the feasibility of the intensified process and identified areas for improvement, suggesting that both pre-ethanol purification processes (fermentation, saccharification, etc.) and post-alcohol purification processes (hydrogenation, oligomerization, etc.) could benefit from intensification to reduce costs, operational expenses, and environmental impact.

Thus, it is projected that the implementation of process intensification strategies can make a substantial contribution to the sustainable development objectives presented in the United Nations (UN) 2030 agenda. Specifically, SDG 7 targets energy access and the transition to clean and sustainable energy sources; SDG 12 focuses on sustainable consumption and production patterns, while SDG 13 dedicates itself to climate action [13]. Therefore, the production of biojet fuel through intensified production processes could generate a clean source of energy, which can generate production patterns based on renewable and sustainable raw materials, and therefore, generate a direct impact on the effects of industrial processes on the environment.

In their study, Romero-Izquierdo et al. [23] proposed a method for obtaining biojet fuel using the Alcohol-to-Jet (ATJ) process, focusing on intensified columns for effluent purification. However, their approach begins with an ethanol stream rather than biomass. They highlighted the opportunity to address the high energy consumption in the ATJ purification section. Building upon this, the objective of the current study is to propose an intensified process for biojet fuel production from biomass via the ATJ route. Taking inspiration from the proposal by Rivas-Interian et al. [22], the study aims to develop an intensified production scheme where the three main process steps (biomass-ethanol, ethanol purification, ethanol-biojet fuel) are intensified. Specifically, ethanol production will utilize a saccharification fermentation reactor (SSF), ethanol purification will employ an intensified separation scheme (dividing wall column), and oligomerization and hydrogenation will occur in a reactive distillation column. The application of intensification aims to create a more compact biojet fuel production plant, reducing capital and service costs. Ultimately, the goal is to present this intensified alternative as a feasible and competitive option in the market compared to conventional methods.

The structure of this work is organized as follows: initially, the case study will be discussed, highlighting the sections where the process will be intensified. Subsequently, the indicators used to evaluate the performance of the proposed process will be presented. Following that, we

will outline the methodology employed to generate the intensified proposal, along with the optimization framework consistently applied. Lastly, the results obtained, and the conclusions drawn from the study will be presented.

2. Case study

The ATJ process gained American Society for Testing and Materials (ASTM) approval in April 2016, allowing the production of biojet fuel from alcohol through various technological pathways. This biojet fuel, suitable for commercial aviation, can be blended with traditional fossil jet fuel at levels up to 30%. Originating from the conversion of short-chain alcohols like methanol, ethanol, and butanol from diverse feedstocks, the biojet fuel undergoes a four-step upgrading procedure to yield aviation-appropriate hydrocarbons. This includes catalytic dehydration, oligomerization, hydrogenation, and distillation. In this study, intensified schemes will be developed for three sections: biomass-ethanol, ethanol purification, and biojet fuel production. In previous works it has been observed the feasibility of performing the saccharification and fermentation operation in a single equipment in an intensified way [12]. Additionally, ethanol separation using intensified separation schemes has demonstrated energy savings [6,31], and substituting three operations with a single reactive distillation column for biojet fuel separation, hydrogenation, and oligomerization is feasible based on thermodynamics [14]. Thus, observing the conventional process of Fig. 1, this implementation can be feasible to apply.

The bioethanol production process begins with pretreatment, involving physical, chemical, physicochemical, or biological methods. Ethanol production relies on crops rich in sugar or starch. Despite the theoretical fermentation yield being 0.511 g of ethanol per gram of glucose, achieving this ideal yield is challenging due to glucose diversion by yeast, resulting in experimental yields typically ranging from 90 to 95% of the theoretical maximum. Industrial yields usually fall between 87 and 93% of the theoretical maximum [33].

After obtaining ethanol, the ATJ route initiates with dehydration, catalytically removing water to produce olefins at temperatures of 300–500 °C. Oligomerization follows, where short-chain molecules combine to form longer-chain molecules, generating alkenes. The reaction conditions vary based on catalysts and input materials. Moderate temperature and pressure conditions (150–250 °C, 30–40 bar) facilitate

Table 1
Unit eco-indicator used to measure the eco-indicator 99 in both case studies [7].

Impact category	Steel (points/kg)	Steam (points/kg)	Electricity (points/kWh)
Carcinogenics	6.32×10^{-3}	1.18×10^{-4}	4.36×10^{-4}
Climate change	1.31×10^{-2}	1.60×10^{-3}	3.61×10^{-6}
Ionizing radiation	4.51×10^{-4}	1.13×10^{-3}	8.24×10^{-4}
Ozone depletion	4.55×10^{-6}	2.10×10^{-6}	1.21×10^{-4}
Respiratory effects	8.01×10^{-2}	7.87×10^{-7}	1.35×10^{-6}
Acidification	2.71×10^{-3}	1.21×10^{-2}	2.81×10^{-4}
Ecotoxicity	7.45×10^{-2}	2.80×10^{-3}	1.67×10^{-4}
Land Occupation	3.73×10^{-3}	8.58×10^{-5}	4.68×10^{-4}
Fossil fuels	5.93×10^{-2}	1.25×10^{-2}	1.20×10^{-3}
Mineral extraction	7.42×10^{-2}	8.82×10^{-6}	5.7×10^{-6}

the conversion of olefins into a distillate containing unsaturated hydrocarbons suitable for aviation fuels, typically within the C₆–C₁₆ range. Industrial oligomerization processes yield broader carbon number ranges, including 5 % of C₄; 50 % of C₆–C₁₀; 30 % of C₁₂ and C₁₄; 12 % of C₁₆ and C₁₈; and 3 % of C₂₀ and beyond [21].

The resulting olefins are distilled to obtain diesel, jet fuels, and light olefins. Jet fuel products then undergo hydrogenation at 370 °C and varying space velocities with hydrogen feed to convert alkenes into alkanes, as unsaturated compounds are considered unstable in jet fuel. Product stream purification for naphtha, kerosene, and diesel fractions involves traditional distillation columns, where the product is introduced in a gaseous state. Separation occurs through condensation at different levels within the column, based on distinct boiling points. Lighter fractions condense on upper levels, while heavier fractions concentrate closer to the lower section. This method is the industry standard, globally utilized for many years.

3. Indicators for performance assessment

In the next decade, carbon-neutral innovations will emerge in emission-heavy sectors. The UN's 2030 Agenda, promoting sustainability, includes 17 Sustainable Development Goals (SDGs) targeting improved quality of life. These goals prioritize sustainable production, emphasizing eco-friendly energy, industry, innovation, and climate action. When evaluating process sustainability, various aspects and metrics require consideration, including economic and environmental factors. Assessing total annual cost is crucial as it offers a holistic understanding of environmental, social, and economic implications. Stakeholders can make informed decisions by weighing direct and indirect financial expenses, environmental impacts, social implications, and potential externalities, ensuring long-term sustainability. This proposal focuses on determining the Total Annual Cost (TAC) computed using Guthrie's approach [10]. Cost estimation for the industrial plant is conducted following equations outlined by Turton et al. [32], facilitating expense approximation across various plant units for cost assessment (Eq. (1)).

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

In the given context, TAC represents the total annual cost, C_{TM} stands for the capital cost of the plant, n signifies the payback period, C_{ut} represents the utility cost, and F_k denotes the product flow.

On the other hand, Eco-Indicator 99 (EI99) is a vital tool for assessing the environmental impact of processes, aligning with the UN's 2030 Agenda. It covers various impact categories like resource depletion, global warming potential, and human toxicity, offering a comprehensive evaluation. EI99 supports SDGs such as Responsible Consumption and Production (Goal 12), Climate Action (Goal 13), and Life on Land (Goal 15), promoting sustainable practices and informing consumer choices.

The scale of EI99 quantifies the environmental burden (Eq. (2)), with 1 Pt representing one-thousandth of the annual burden of an average European resident.

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

Where β_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, α_{b,k} is the damage caused by category k per unit of chemical b released to the environment, ω_d is a weighting factor for damage in categories d, and δ_d is the normalization factor for damage of category d. In this approach, it has been considered the impact of steel for building, steam for heating, and electricity for pumping. The weight factors are shown in Table 1.

4. Methodology

Ethanol production from lignocellulosic biomass was structured using a superstructure framework, considering two biomass types and pretreatment methods. It comprises saccharification and fermentation (SSF), and separation zones. Sugarcane bagasse and corn stover were identified as the main biomass sources in Mexico, with steam explosion and dilute acid found to be the most effective pretreatment methods [22].

4.1. Simultaneous saccharification and fermentation (SSF) modeling

The modeling of the intensified configurations was conducted within the saccharification and fermentation zones using MATLAB 2017 software. The modeling framework for enzymatic hydrolysis was adopted based on the approach outlined by Kaddam et al. [12]. This approach has demonstrated strong predictive capabilities in estimating enzymatic hydrolysis patterns within and beyond the designated parameter estimation design space, rendering it suitable for process optimization.

The heterogeneous nature of the substrate and the presence of various enzyme activity confound kinetic modeling of enzymatic hydrolysis. Enzyme adsorption, sugar inhibition, temperature effects, and substrate reactivity are all phenomena that rigorous models need to take into account. Nonetheless, the model and prediction of this event provided by Kadam et al. [12] is quite successful.

The effectiveness of the model presented by Kadam et al. [12] is mainly due to the inclusion of several previous proposals, and to the effective complement of the areas of opportunity of those models. For example, Kadam et al. [12] proposition encompasses the kinetic model of enzymatic hydrolysis introduced by Wald et al. [36], which integrates enzyme adsorption, product inhibition, and a multi-enzyme system. The concurrent adsorption of cellulase components, each characterized by distinct adsorption properties, governs the hydrolytic process, an aspect that had not been adequately addressed previously. Unlike earlier modeling endeavors employing the Michaelis-Menten model, which is applicable primarily to low substrate concentrations far from saturation, Wald et al. [36] depiction relates enzyme adsorption to the availability of sorption sites and, consequently, to the accessible surface area through a Langmuir-type isotherm relationship.

The proposal by Gusakov et al. [[8,9]a] is also suitably incorporated. This model describes the kinetics of glucose and cellobiose formation from cellulose for both batch and plug-flow processes for enzymatic cellulose hydrolysis. It also accounts for the structural complexity of cellulose, the composition of the cellulase complex, inhibition by reaction products, and enzyme inactivation during enzymatic hydrolysis.

Lastly, suggestions from South et al. [27] and Philippidis and Hatzis [19], who created SSF-based models to explain the conversion of lignocellulose to ethanol, are also included in the Kadam et al. model. The South et al. [27] model includes a hydrolysis rate equation and is applicable to both batch and continuous processes. As a result, Kadam et al.'s proposal details the creation and verification of a kinetic model for enzymatic cellulose hydrolysis that can forecast performance under a

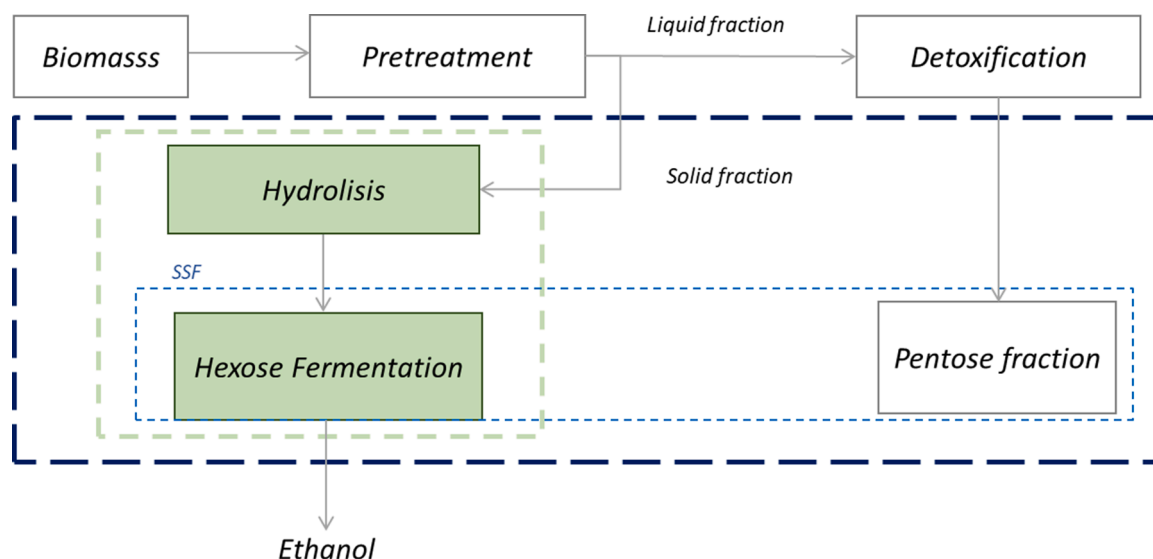


Fig. 2. SSF process to generate ethanol.

variety of operational circumstances, including changes in temperature, mixing regime, and background sugar content.

The Simultaneous Saccharification and Fermentation (SSF) process facilitates prompt glucose utilization by yeast (Fig. 2), reducing the risk of bacterial contamination and lowering capital costs. Traditionally, ethanol production involves separate stages like biomass treatment, detoxification, hydrolysis, and fermentation, where only hexoses are fermented. Integrated processes allow for joint fermentation of both hexoses and pentoses, promoting intensification. SSF operates at lower temperatures, reducing energy costs and enabling diverse product creation, including biofuels and chemicals. The biorefinery concept integrates biomass conversion processes to produce a range of products [18]. The model by Kadam et al. [12] describes enzymatic hydrolysis kinetics of lignocellulosic biomass, considering enzyme adsorption, sugar inhibition, and substrate reactivity. Detailed kinetics for SSF reactor reproduction are available in the **Supplementary Material**.

4.2. Ethanol purification

Once ethanol is obtained from the step described in 4.1, it is necessary to purify the alcohol. The modeling for the ethanol separation segment involved the adoption of a dividing wall column sequence as the optimal approach. Glycerol was employed as the extracting agent, with careful consideration of both equipment expenses and energy demands, in line with the recommendations provided by Conde-Mejía et al. [2]. The process begins with the introduction of ethanol and water in substantial quantities, followed by purification through the dividing wall column, resulting in the attainment of highly pure ethanol with a 99.8 % purity level, alongside glycerol [22]. This modeling endeavor was executed within the Aspen Plus software, leveraging the RADFRAC modules.

4.3. Biojet fuel production through a double reactive distillation column

After ethanol purification, the subsequent stages include dehydration, oligomerization, and hydrogenation. Dehydration achieves a remarkable ethylene conversion rate of 98.8 %. Oligomerization and hydrogenation occur in a Reactive Distillation column (RD), functioning as both a reactor and a separator. RD technology overcomes limitations related to conversion and phase equilibrium, offering significant cost savings of around 20 % compared to conventional sequential processes [25].

In RD column, a series of reactions occurs, as indicated by the

transformations outlined in **Supplementary Material**. In the work reported by [35], it is assumed that the reactions have a first-order behavior and the values of k and E were modeled with an optimization-based strategy to adequately predict the experimental results. This assumption holds true for the majority of reactions conducted in both laboratory and industrial settings [5]. Typically, the relationship between the rate constant and temperature can be expressed using Arrhenius' equation, presented as follows:

$$k = k_0 * \exp(-E / RT) \quad (3)$$

where: k represents the rate constant, denoting the frequency of collisions resulting in a chemical reaction. In chemical kinetics, this rate constant or coefficient (k) quantifies the speed and direction of the reaction. T is the absolute temperature, measured in degrees Kelvin or Rankine. k_0 is the pre-exponential factor, also known as the frequency factor. According to collision theory, k_0 relies on the frequency of molecular collisions when all concentrations are at 1 mol/L and the proper orientation of molecules during these collisions. E stands for the activation energy of the reaction. In the realms of chemistry and physics, activation energy represents the minimum energy required for compounds to undergo a chemical reaction. It can be conceptualized as the height of the potential barrier, often referred to as the energy barrier, that separates the minima of the potential energy surface corresponding to the initial and final thermodynamic states. R denotes the universal gas constant [15].

Wang et al. [37] noted the lack of a standardized approach for constructing reactive distillation columns. In response, the authors incorporated heuristics from Subawalla and Fair [29] into an algorithm to estimate critical parameters for jet fuel production. These parameters, including column pressure, reactive zone location, theoretical stage count, reflux ratio, and diameter, were systematically adjusted to improve yield and efficiency. Holdup magnitude was determined based on recommendations from Barbosa and Doherty [1] for accuracy. The study followed the strategy outlined by Subawalla and Fair for initial product compositions and reflux ratios, although it's acknowledged that this approach may not ensure optimal design. Despite this, the authors successfully designed a reactive distillation column for jet fuel production, considering prerequisites from Shah et al. [26] to confirm feasibility, including multiple products, aligned reaction and separation temperatures, and absence of azeotropes.

Table 2
Optimization variables.

Optimized Variables	
Yeast	Reboiler Heat Duty
Glucose concentration at fermentation	Reactive stages
Cellulose concentration at saccharification	Distillate-to-feed ratio
Glucose concentration at saccharification	Diameter
Residence Time	Solvent/Feed ratio
Xylose Concentration	Side stream
Enzyme concentration	Number of stages
Solvent Temperature	Interconnection flows
Feed Stage	Reflux Ratio
Solvent Stage	

4.4. Multiobjective optimization process

For multi-objective optimization, a hybrid approach called Differential Evolution with Tabu List (DETL) was utilized, integrating stochastic techniques known for their effectiveness in complex optimization problems [4,24,34]. DETL, an extension of the Differential Evolution (DE) algorithm, is rooted in natural selection theory and was adapted by Madavan and Field for multi-objective problems [17]. The optimization process involved a hybrid system combining Aspen Plus and Microsoft Excel, following a method previously established by Zhang and Rangaiah [39]. DETL was implemented in Microsoft Excel using Visual Basic, while the separation scheme model ran in Aspen Plus. Decision variables were transferred from Excel to Aspen Plus using dynamic data exchange (DDE), where they were assigned to relevant process variables.

After completing the simulation, output data containing parameters like flow streams, purities, and reboiler heat duty was transmitted back to Microsoft Excel. Excel then analyzed objective function values and proposed new decision variable values using the DETL methodology [20]. DETL initializes the population within specified bounds on decision variables and computes objectives and constraints for each individual. A tabu list (TL) is randomly populated based on the initial population. In each generation, trial vectors are generated through mutation and crossover operations, with a tabu check executed during evaluation to reject trial individuals close to those in the tabu list. Accepted individuals are stored in the child population and added to the tabu list. Pareto dominance ranking and crowding distance calculations are then used to select individuals for subsequent generations until the Pareto front of the last evaluated generation is reached [28].

In the optimization process it was considered a population of 200 individuals and 1000 generations. A tabu list, comprising 50 % of the total individuals, was incorporated, with a taboo radius set at 1×10^{-6} . Additionally, a crossover probability of 0.8 and a mutation factor of 0.6 were applied. These parameters, initially guided by existing literature, were further refined through preliminary computations. The saccharification-fermentation section, based on the model by Kadam et al. [12], was optimized with 7 variables. Subsequently, the ethanol purification stage involved solving MESH equations with 8 variables to optimize the dividing wall column. Finally, in the last stage of the ATJ process, MESH equations with chemical reaction were utilized to optimize the reactive distillation column for the oligomerization and hydrogenation process, involving 10 variables. All variables and equipment were modeled in Aspen Plus and optimized using the hybrid stochastic algorithm DETL.

Within this approach, it is essential to establish the objective function for optimization. In this context, we have chosen to minimize the Total Annual Cost (TAC) and consider the environmental impact assessed using the Eco-Indicator (EI99) as well as the EI99 itself as indicators of process sustainability. The forthcoming objective function can be described as follows.

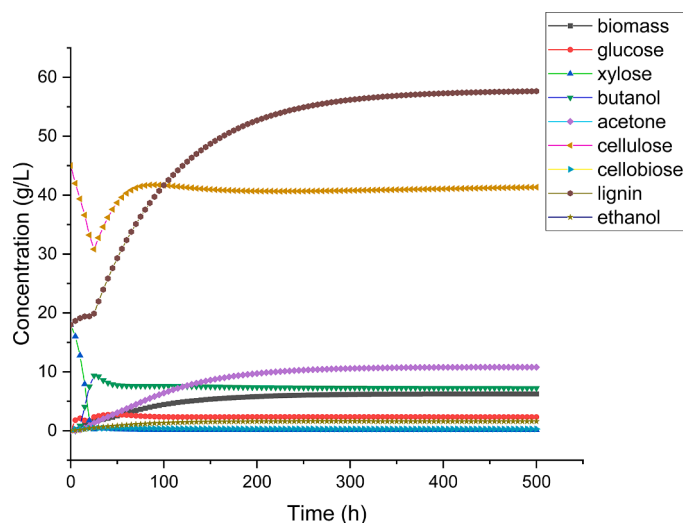


Fig. 3. Composition profiles in SSF reactor.

$$\begin{aligned} \text{Min} (TAC, EI99, \dots) &= f(w, t, z, \dots) \\ \text{Subject to } x_m^{\rightarrow} &> y_m^{\rightarrow} \end{aligned} \quad (4)$$

Where w , t , and z , are variables involved in the design of the process, and y_m and x_m are the vectors of both obtained and required flows and purities for the m th components, respectively. Thus, Table 2 shows the decision and constraint variables used for the optimization of the biojet fuel production process.

5. Results

This section will present the results obtained by intensifying the biojet fuel production process. The results will be presented in three main blocks. Initially, the results obtained from the intensified reactor, the composition profiles obtained from the SSF reactor, as well as its performance indexes will be shown. Subsequently, the results obtained from the intensified process for ethanol purification will be shown, and finally, the results obtained in the intensified process for biojet fuel production will be shown.

5.1. Intensified reactor SSF

Once equations S1-S9 of **Supplementary Material** were appropriately solved, it became possible to determine the composition profiles at the exit of the SSF intensified reactor. As observed in the graph, stable profiles were obtained over time. For instance, Fig. 3 illustrates the profile obtained when the reactor was fed with a concentration of 60 g/L of sugar, and with a continuous production of components. An example of the obtained profiles is shown in Figure 9.

Once the composition profiles have been obtained, a natural doubt arises regarding the generation of ethanol as feedstock for the ATJ process, compared to the conventional process.

In this context, Fig. 4 shows the immediate difference between ethanol generation by the conventional process and ethanol generation considering an intensified process. Thus, Figs. 4 and 5 shows the ethanol flow obtained, the concentration obtained, as well as the ethanol conversion obtained in the conventional previously reported by [22] and intensified process.

Figs. 6 and 7 show that in the processes using sugar cane with diluted acid there was a higher conversion, reaching 95 %, and likewise the % of ethanol is much higher than in the conventional process, with an increase of approximately 1.5 %. Concerning the volume of the reactors, in both cases, when the steam explosion and diluted acid were used, the volume decreased significantly. Thus, Table 3 shows the operative

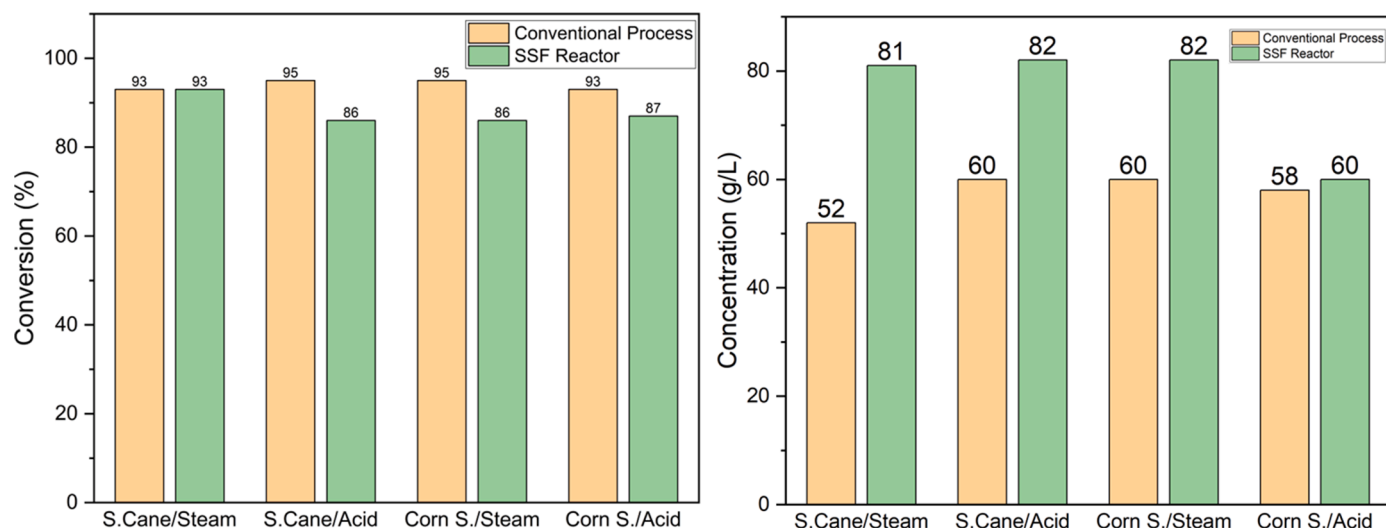


Fig. 4. Conversion and concentration of ethanol in conventional process and SSF reactor.

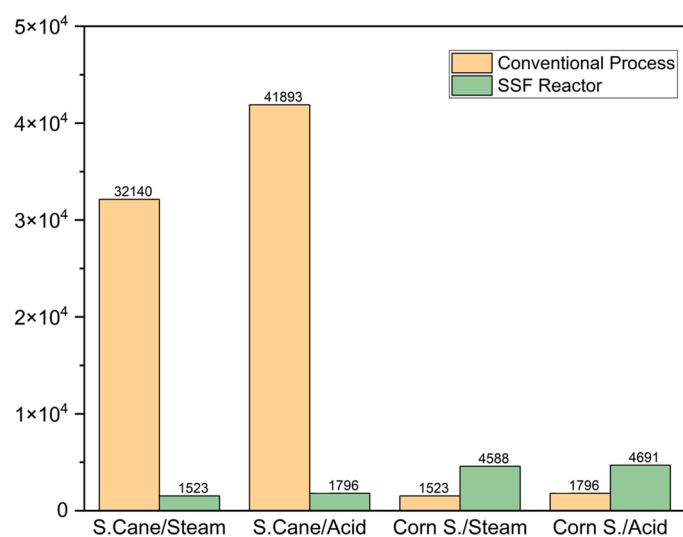


Fig. 5. Ethanol flow (kg/h) produced from both conventional process and SSF reactor.

conditions for both scenarios.

Regarding production costs, Figs. 6–9 show the breakdown of costs associated with the various items involved in the reaction zone.

Overall, ethanol production using sugarcane as feedstock is more expensive compared to production using corn stover. This increase in the cost of ethanol production using sugarcane is consistent with the amount of ethanol produced using this methodology. On the other hand, the use of corn stover for ethanol production does not represent an economic impact like that generated by the use of sugarcane. Thus, ethanol production using bagasse is more expensive than using corn stover. Particularly, the route that considers using steam as pretreatment is the most expensive and the most productive in both routes with bagasse. On the other hand, ethanol production using corn stover considering dilute acid or steam explosion generates a much lower economic impact than considering bagasse.

In general, the cost associated with the enzyme represents, in most cases, the major cost of the ethanol production process. In some case studies, due to the amount of solution treated, as well as the physicochemical characteristics of the solution, the cost of agitation presented a considerable cost. Overall, Table 4 presents the total cost of each case study, as well as the cost per kilogram of ethanol produced.

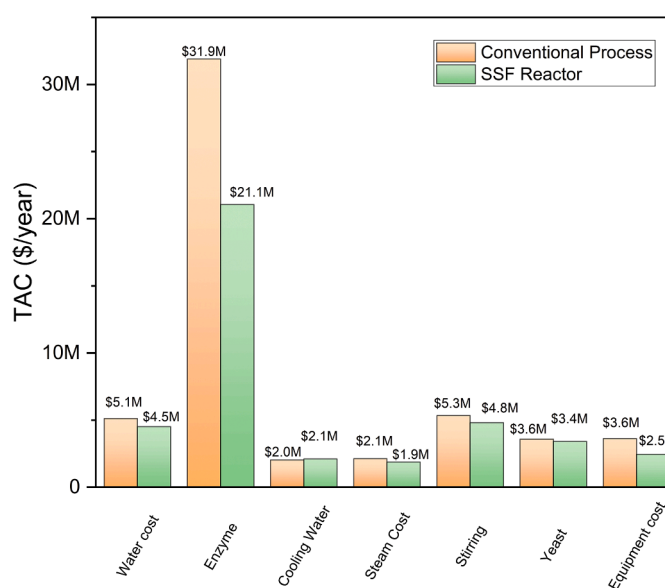


Fig. 6. Cost comparison of the conventional process and the intensified model (SSF) using steam explosion sugarcane as pretreatment.

It can be observed that, based on the earlier discussion, the cost of both technologies considered for sugarcane bagasse results in the highest Total Annual Cost (TAC). However, when this cost is weighted and evaluated against the amount of ethanol produced, the cost of the intensified technology has a lower economic impact than the other technologies. Thus, the intensified technology using sugarcane bagasse as raw material, and employing steam explosion, is the best alternative for the analyzed case studies.

Once the reaction process was modeled, the purification stage was performed, considering a dividing wall column sequence as the intensified technology, which was identified as the best alternative. Glycerol was used as the extractant agent, and equipment costs and energy requirements were taken into account, following the approach by Conde-Mejía et al. [2]. As observed in Table 6, the route that considered steam explosion and sugarcane bagasse was the most economically feasible. Therefore, the output stream from this section can be subsequently routed to an ethanol purification stage. Fig. 10 shows the Pareto front for the purification section when feeding the effluent from the intensified reactor process using bagasse and steam explosion. Fig. 10 and 11 are

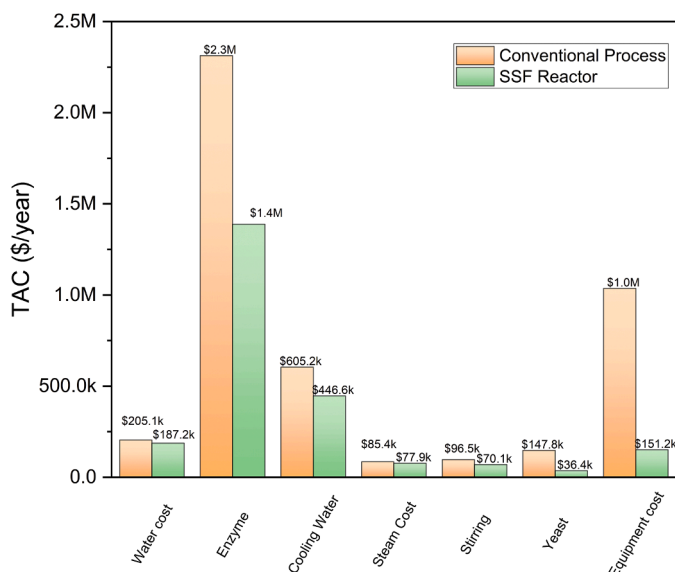


Fig. 7. Cost comparison of the conventional process and the intensified model (SSF), using corn stover dilute acid as pretreatment.

Table 3
Operative conditions for sugar cane and corn stover.

Production System	Residence time (h)	Volume (m ³)	Enzyme (FPU/g cellulose)	Yeast	RPM
Sugar C./ Steam	29.63	20,492	9.01	0.998	150.83
Corn S./ Steam	29.64	6633	18.75	0.995	200.81
Sugar C./Acid	32.82	62,528	10.00	1.003	150.03
Corn S./Acid	25.03	16,455	10.77	1.005	18,086

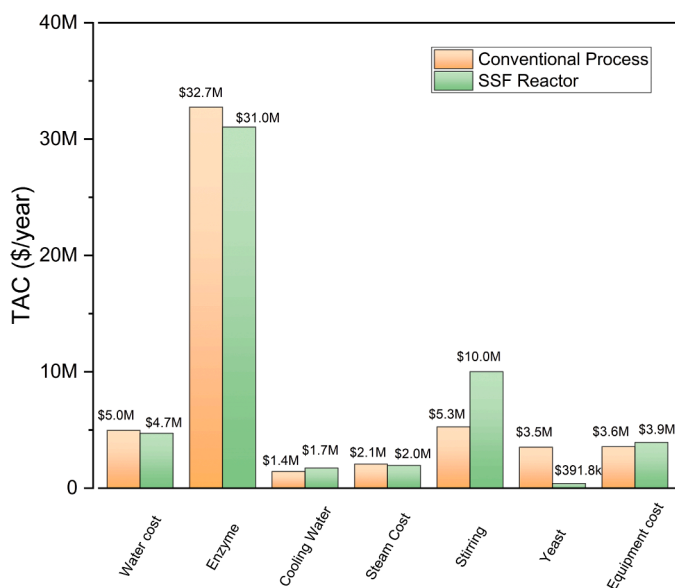


Fig. 8. Cost comparison of the conventional process and the intensified model (SSF), using sugar cane and steam explosion as pretreatment.

normalized. The normalization was performed by considering the largest value of the objective function in the Pareto front. Thus, the unnormalized value is obtained by simply multiplying the desired value by the upper limit of the Pareto front (highest number).

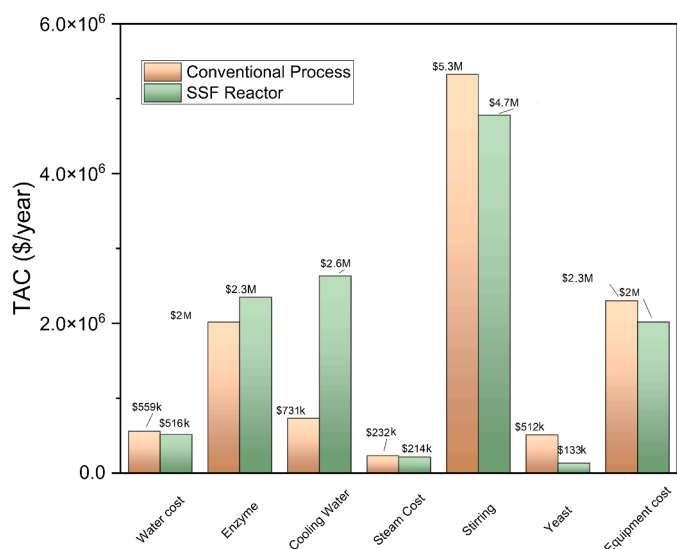


Fig. 9. Cost comparison of the conventional process and the intensified model (SSF), using dilute acid and corn stover as pretreatment.

The Pareto front shows a tradeoff between both objective functions. In the process of minimizing the objectives, both objective functions try to find a minimum value, so that as the total annual cost values decrease, it is easy to see that the TAC increases and vice versa.

This behavior is observed due to the continuous interaction between the design variables that have a direct impact on the total annual cost (TAC) and the eco indicator 99 (EI99). According to Eq. (1), the TAC is directly influenced by the cost associated with heating and cooling, as well as the cost of equipment. Thus, to reduce this objective function, it is necessary to generate small equipment designs with low energy consumption. Regarding EI99 on the other hand, according to Table 1, the value of the fossil fuel use category is the highest of all the categories. Thus, for the minimization of EI99, the design variables that may be associated with the fossil fuel category, for example, the reboiler duty, must be immediately minimized.

However, although from the perspective outlined in the previous paragraph, it would only be a matter of designing equipment with low reboiler duty and small dimensions, the design-optimization process is not that straightforward. That is, some design variables have a relationship between them that makes it impossible to generate a direct relationship. For example, it is possible to generate a design of a column that can have a small energy consumption, in exchange, the energy that is not provided directly from the reboiler duty to promote the liquid-vapor equilibrium must be compensated with equilibrium stages. Thus, it is possible to generate equipment with low energy consumption, but which is likely to be equipment with a large number of contact stages or with a considerable diameter.

This particular relationship between process variables generates a compensation between them. Therefore, in areas with lower TAC, it is possible to find equipment with low energy consumption, but with larger dimensions compared to the rest of the designs. On the other hand, in the regions with a higher TAC, there are designs with higher energy consumption, but with smaller dimensions. Therefore, the middle region of the Pareto front is a good region to select a feasible solution in the ethanol purification process. Table 5 shows the characteristics of the dividing wall.

Once high-purity ethanol is obtained, it can be fed to the ATJ process. Starting from ethanol, it is dehydrated in a conventional reactor to obtain ethylene. Subsequently, it is possible to make use of an intensified technology (reactive distillation column), to oligomerize ethylene in alkenes of chain plus C₄ to C₁₄ marks using the reactions described in the methodology section.

Table 4
Performance indicators for the pretreatment section.

	Conventional S. Cane - Steam	SSF	Conventional Corn Stover - Steam	SSF	Conventional S. Cane - D. Acid	SSF	Conventional Corn Stover - D. Acid	SSF
TAC (\$/year)	5.38×10^7	4.03×10^7	4.49×10^6	2.36×10^6	5.36×10^7	5.38×10^7	1.17×10^7	1.27×10^7
\$/kg product	1672.51	961.67	2949.14	1313.77	35,204.34	29,941.96	2546.01	2696.48
EI99 (points/y)	4.71	3.534	0.788	0.401	4.703	53.588	1.024	1.110

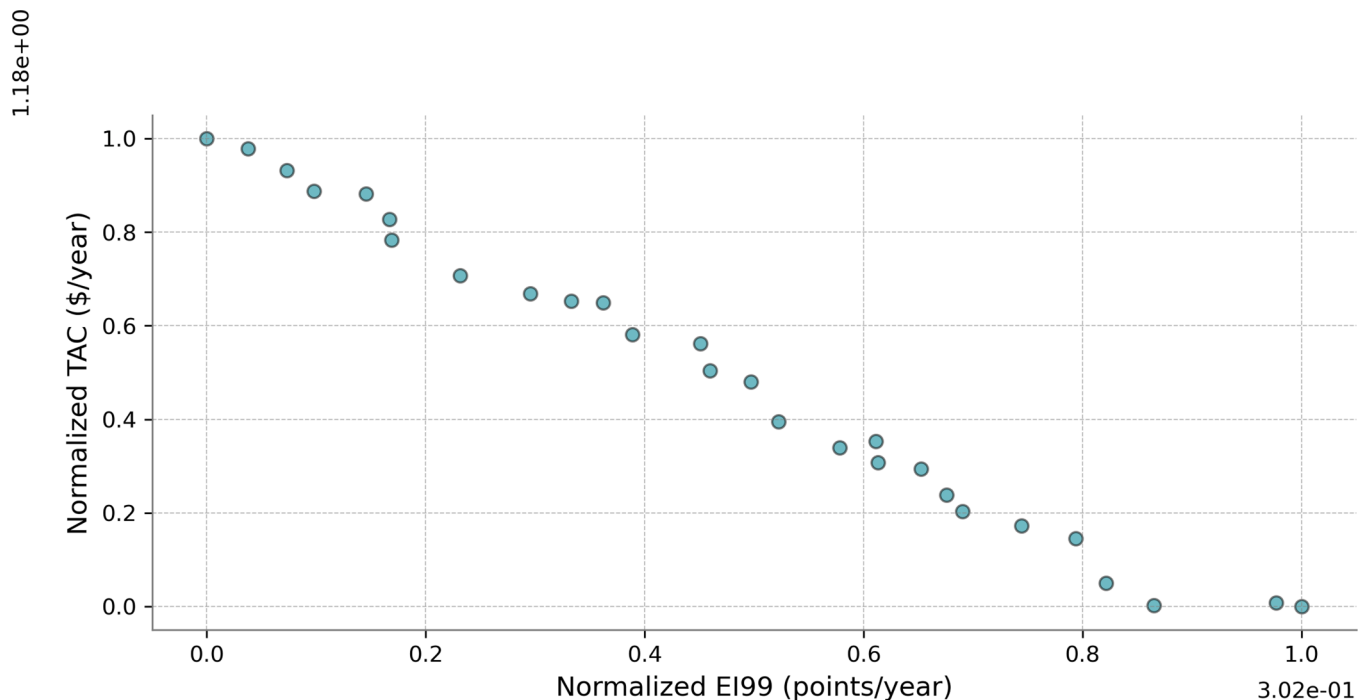


Fig. 10. Pareto front of ethanol purification stage.

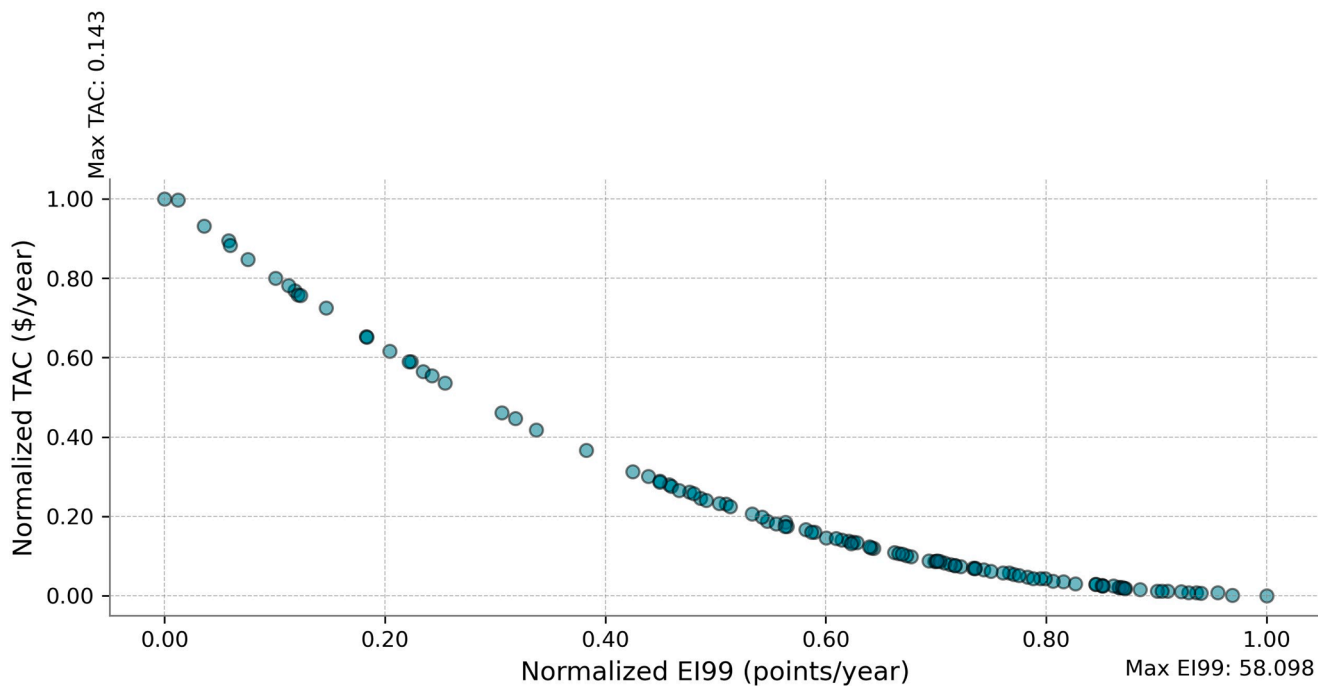


Fig. 11. Pareto front of ATJ process.

Table 5
Design parameters of dividing wall column for ethanol purification.

	Design Variable	
Column 1	Stage	51
	Feed Stage	27
	Reflux ratio	1.65
	Diameter	0.73
	Reboiler Heat Duty (MW)	160.67
	Stages	79
	Feed Stage	20
	Solvent Stage	4
	Side Stream	52
	Solvent/Feed ratio	0.52
Column 2	Reflux ratio	0.69
	Diameter	0.98
	Reboiler Heat Duty (MW)	20.73
	Carga total (MW)	181.40
	TAC (\$/kg ethanol)	1.80
	EI99 (points/kg ethanol)	0.302

Table 6
Design parameters of the reactive distillation columns with two reactive zones.

Oligomerization-Hydrogenation Reactive Column	
Number of stages	33
Reflux ratio	69
Feed stage	24 and 30
Side stream stage	33
Reactive stages	12–20, 21–29
Hold Up (l)	3.5, 48
Distillate flowrate (kg h^{-1})	5422.44
Condenser duty (kcal h^{-1})	9.56216×10^6
Reboiler duty (kcal h^{-1})	854,153
Operative Temperature ($^{\circ}\text{C}$)	
Operative pressure (atm)	21.71
Jet Fuel Production (kg/h)	19,935.82

According to the strategy outlined in the methodology section, the intensified ATJ process was optimized. The intensification strategy consisted of reducing the dehydration, oligomerization, and hydration reactors and subsequent purification to only one ethanol dehydration reactor and one distillation column with two reactive zones. Once the optimization strategy was applied to the ATJ process, the following Pareto fronts was obtained (Fig. 11).

It is important to remember that the Pareto front shows the best solutions. In this Pareto front, a trend similar to the one previously observed for the ethanol purification section is observed, since similar trends among the design variables of the ATJ process were presented. Thus, selecting a scheme with the best compromise between both objectives, Table 6 shows the design parameters of the distillation column with two reactive zones.

An important issue is to know the distribution of each of the components around the reactive column. The composition profiles shown below (Fig. 12) present the distribution of components within the reactive column.

Finally, it is important to make a comparison in terms of the cost and environmental impact of the intensified technology in direct comparison with the conventional technology. Thus, Table 7 shows a comparison of both technologies in terms of TAC and EI99 for the cheapest alternative for both conventional and intensified alternatives and Fig. 13 shows a summarized process diagram and its comparison with the conventional process diagram.

6. Conclusions

In this work, an intensified alternative for the production of biojet fuel using biomass as a starting point and then ethanol considering the ATJ route was presented. The conventional process involves several stages in biojet fuel production, including pretreatment, fermentation, ethanol purification, dehydration, oligomerization, hydrogenation, and biojet fuel purification. The intensification process allowed for a considerable reduction in the process by compacting the initial stages, incorporating an intensified Simultaneous Saccharification and Fermentation (SSF) reactor, a split-wall column for ethanol purification, and finally, a distillation column with two reactive zones.

As reported in a previous study, this intensification led to significant reductions in both Total Annual Cost (TAC) and Eco-Indicator 99 (EI99) impact in various process zones. For instance, the cost of the pretreatment zone was reduced by 39 % compared to the conventional process. The cost associated with ethanol purification saw a reduction of 4 %, and in the biojet fuel production area, costs were reduced by 49 %.

Furthermore, the environmental impact was also favorably affected. According to previous findings, the reduction in the global environmental impact was 18 %. This decrease in the environmental impact was mainly due to the reduction of equipment and the decrease in energy

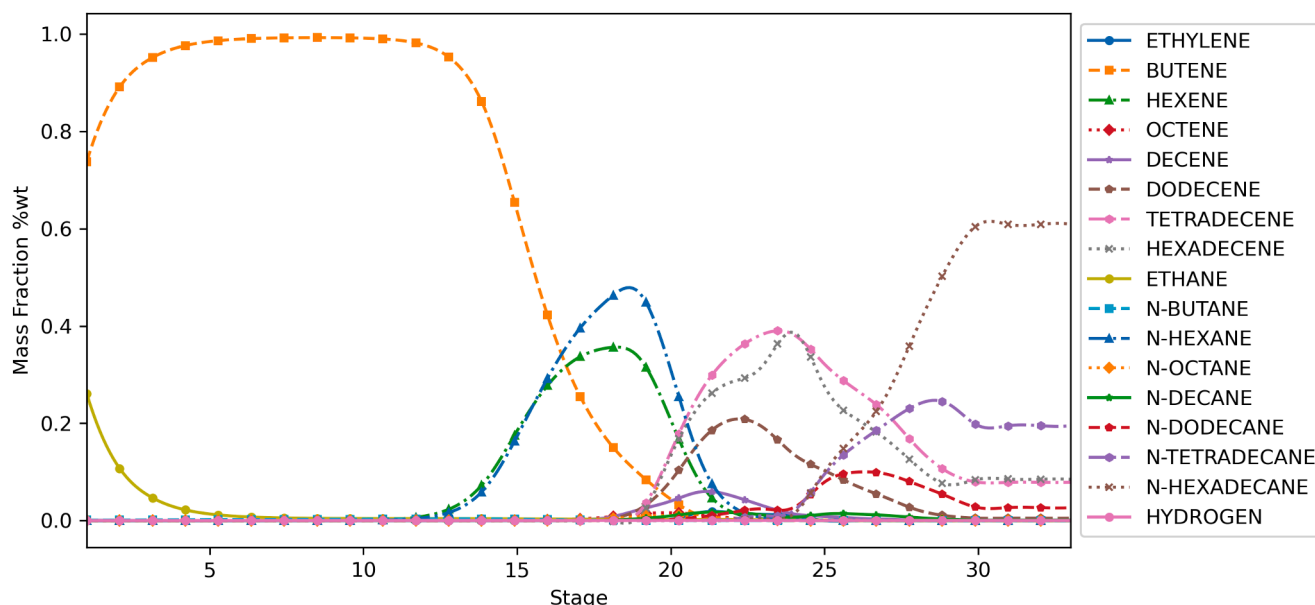


Fig. 12. Composition profile for the reactive distillation column.

Table 7
Performance indicator for both conventional and intensified processes to produce biojet fuel.

	TAC (\$/kg)			EI99 (points/kg)		
	pretreatment	ethanol separation	biojet production	pretreatment	ethanol separation	biojet production
Conventional	0.65	1.22	0.27	0.41	0.46	70.18
Intensified	0.40	1.18	0.14	0.25	0.30	58.09

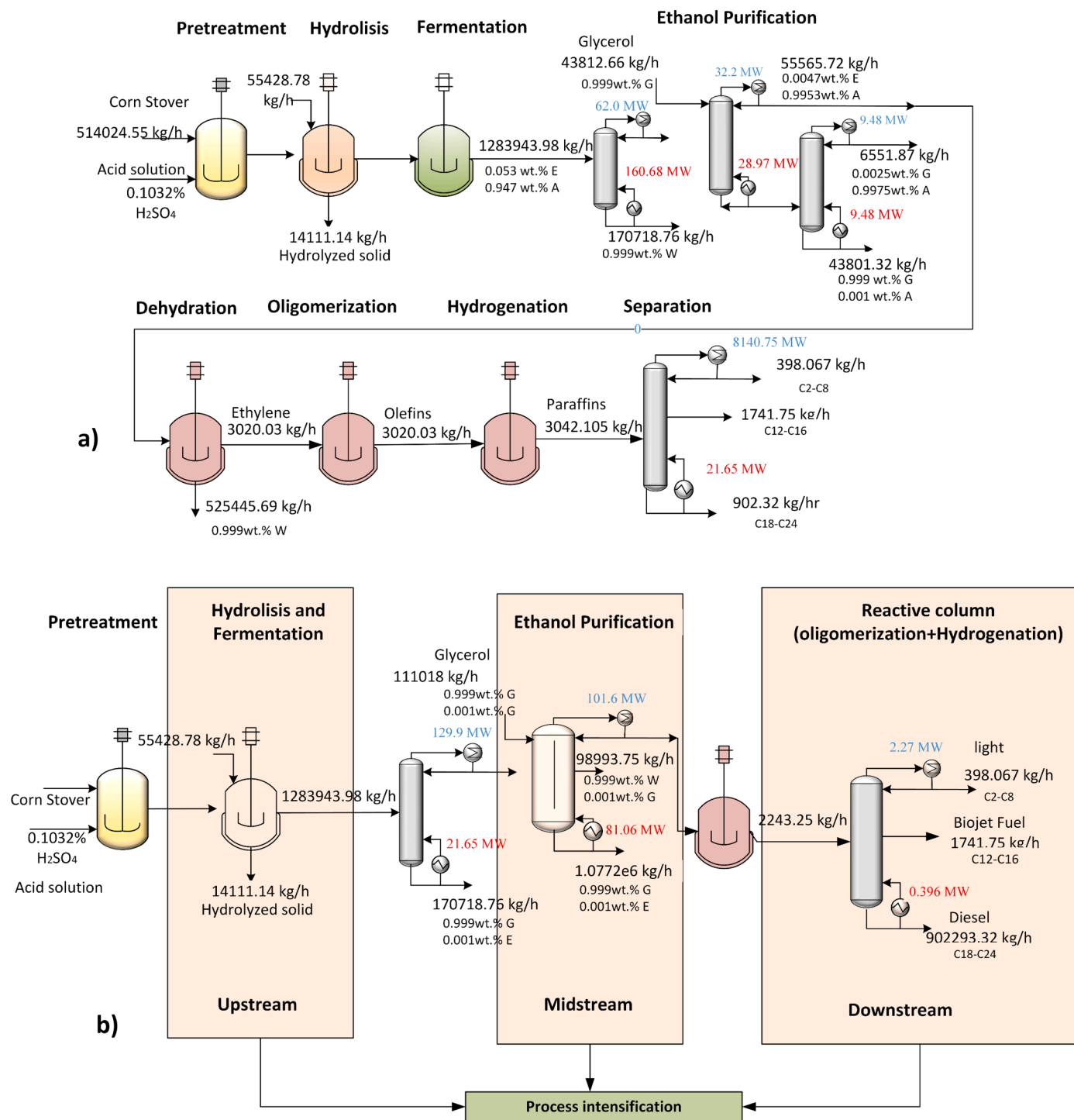


Fig. 13. Conventional (a), and intensified ATJ process diagram (b).

requirements. In other words, the reduction in the number of pieces of equipment meant that less material was used for their construction, and energy consumption decreased in a similar way. Thus, the process design presented in this work serves as an example of the potential application of intensified technology for reducing the impact generated in processes oriented toward the production of biofuels.

CRedit authorship contribution statement

Brenda Huerta-Rosas: Writing – original draft, Methodology, Conceptualization. **Eduardo Sánchez-Ramírez:** Writing – review & editing, Writing – original draft, Validation, Methodology, Conceptualization. **Gabriel Contreras-Zarazua:** Writing – original draft, Validation, Methodology, Conceptualization. **Juan José Quiroz-Ramírez:** Writing – original draft, Validation, Methodology, Conceptualization. **Oscar A. Luevano-Rivas:** Writing – original draft, Methodology, Conceptualization. **Juan Gabriel Segovia-Hernández:** Writing – original draft, Supervision, Methodology, Conceptualization.

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.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cep.2024.109774](https://doi.org/10.1016/j.cep.2024.109774).

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