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Intensification of the Oligomerization and Hydrogenation Stage for Biojet Fuel Production: Preliminary Outlines

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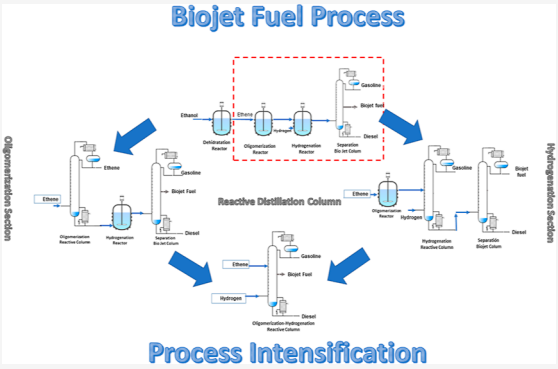
ABSTRACT: The environmental conditions generated by the consumption of fossil fuels have created a growing interest in alternative energy sources for various sectors of society. In the case of the aviation sector, one solution is biojet fuel as a sustainable fuel for direct application in flights. The alcohol to jet (ATJ) fuel process has high expectations due to its performance and for revalorizing alcohols from fermentation. Starting from ethanol, the ATJ process consists of four stages: dehydration, oligomerization, hydrogenation, and separation. On the other hand, process intensification philosophy promotes process efficiency, reducing the number of equipment used, reducing land use, and combining different phenomenologies. In this sense, this work researches the outlines of implementing intensification ideas to the ATJ process using reactive distillation (RD) to improve the sustainable performance of jet fuel production. Particularly, the oligomerization and hydrogenation stages will be subject to process intensification strategies. Both strategies were evaluated considering various sustainability indicators (global warming potential, mass intensity, energy intensity, economic impact, etc.). The most intensified alternative presented is an RD column with two reactive sections. Once a distillation column with two reactive zones was implemented, an improvement in the return on investment value of close to 50% and a decrease in the total annual cost of close to 90% were observed. The global warming potential value improved by 70%. Likewise, an improvement of close to 30% was observed in efficiency, mass intensity, and thermodynamic efficiency.



1. INTRODUCTION

The production and use of fossil fuels have been one of the key motors of the world economy for a long time. However, dependency on oil is more visible owing to its shortage and, subsequently, rising pricing. The usage of biofuels is capable of counteracting the detrimental impacts of conventional fuels on the economy and environment. Consequently, the design of biorefineries is a vital challenge in the route to the sustainability advocated by biofuels.

Despite the worldwide scenario created by COVID-19, the slow-growing demand for aviation fuel is predicted as a result of the global economic recovery. This occurs in a scenario where the price of fossil fuels grows while petroleum is scarcer. Additionally, the production and use of jet fuel are one of the reasons for the ongoing elevation of greenhouse gasses (GHGs) which adds to global warming. The aviation industry is one of the GHG sources where the rise in GHGs is quicker, at a pace of 5.7 percent per year, and it is responsible for 1.9 percent of such emissions. In 2018, this contribution expanded to 2.4 percent.[1]

Different ways of manufacturing biojet fuel provide varied advantages and downsides. Oil-based biojet fuel has been routinely manufactured, and numerous low-cost systems have been tested successfully. The most prevalent is the hydroprocessing of esters and fatty acids, the catalytic hydrothermolysis, and the hydroprocessing of depolymerized cellulosic jet. However, the raw material for the oil route may not be sustainable considering land use.[1−3] A possible reason is a lack of arable land for oilseeds and, if accessible, they compete with land for food crops. In the particular case of *Jatropha curcas* crops, although they are capable of growing in diverse agroclimatic conditions, they are accompanied by variations in important parameters such as seed yield, oil content, and nutrient requirements, which critically affect the economic viability of plantations.[4] In addition, it opposes the concepts of the circular economy since oil crops do not develop as a byproduct but as a primary feedstock.

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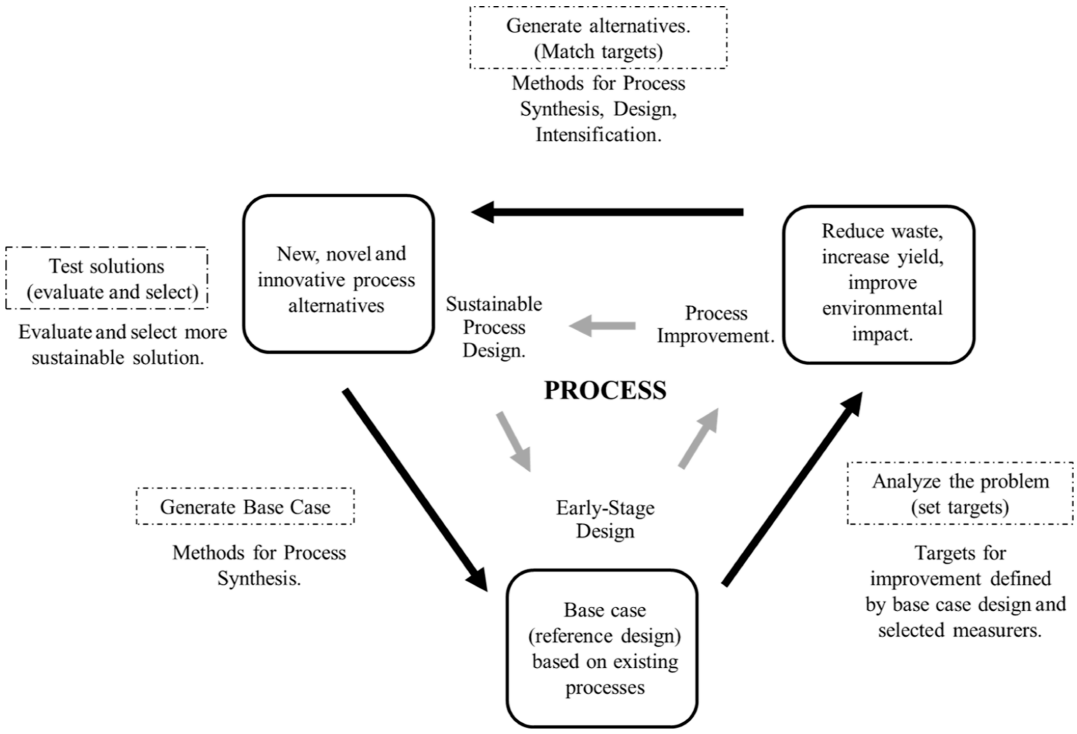

Figure 1. Development of sustainable and intensified processes.

A path that has not been investigated extensively is the alcohol route. Alcohols may be created from lignocellulosic biomass, which is recognized as the most potential renewable resource. Biomass is substantially available across the world and enables avoiding the food versus fuel issue connected to the usage of edible crops. The complete recycling and reuse of agro-industrial lignocellulosic wastes contribute to the circular economy as this renewable resource may be utilized again and again to develop value and marketable goods, replacing the exhaustible fossil-based resources.[5]

Through procedures of pretreatment, saccharification, and fermentation, agro-industrial lignocellulosic wastes may be transformed into short- and long-chain alcohols. Ethanol is continuing rise as a green and affordable alternative source to petrochemical fuels, the most frequent and employed liquid biofuel, and attracting significant attention thanks to the development of technological conversion that enhances its yield and performance.[5] Through phases of dehydration to create ethylene, oligomerization, and hydrogenation, biojet fuel may be easily manufactured from bioethanol. This upgrading is known as the ATJ process. The first renewable aviation fuel authorized by ASTM D7566 was biojet fuel made from isobutanol, permitting mixes of up to 30 percent with conventional jet fuel. On the other hand, ethanol has just been certified as a raw material allowing the biojet fuel created from it to be combined with conventional jet fuel up to 50 percent.[6]

Regardless of which process route is considered, the number of unit stages involved in all processes is quite large. In some works, it has been identified that starting from the use of ethanol, the dehydration, oligomerization, hydrogenation, and purification stages consume a significant amount of energy. For example, in the works published by Romero-Izquierdo et al.[7] and Arvidsson et al.,[8] it is reported that the purification stage consumes 80% of the total energy of the ATJ process. This represents an important area of opportunity to generate viable jet fuel production alternatives. Thus, a process alternative that is capable of decreasing the energy consumption in that section will be of vital importance in the path of sustainable jet fuel production in the ATJ process.

The reason for the high energy consumption in biojet fuel production is the need for several purification stages after the reactive stages. The use of separation columns in each stage leads to significant energy losses due to the nature of the separation process. Consequently, these energy and capital losses decrease the sustainability of the process and make it less competitive than technology based on non-renewable raw materials. To address this issue, the process intensification philosophy can be used to improve the yield of biojet fuel irrespective of the raw material used. The use of intensified equipment is still an opportunity area to reduce operating and investment costs and improve the efficiency of biojet fuel production.

Process intensification (PI), which refers to a wide range of tools capable of achieving dramatic improvements in manufacturing and processing by significantly reducing equipment size, waste production, and energy consumption, leads to smaller, cleaner, and more energy-efficient processes,[9] PI is one method to achieve a process that satisfies sustainable requirements. The use of PI principles has been able to demonstrate its value. For instance, using PI methodology, it has been feasible to cut some case studies' investment costs by 25%, operating expenses by 35%, and space needs costs by 40% in comparison to the traditional approach.[10] On the other hand, other authors emphasize that the PI concept allows for the development of unique and more sustainable procedures.[11] In other words, the development of sustainable designs, the synthesis of processes, and process intensification are all closely related (Figure 1).

The diagram in Figure 1 illustrates that sustainable design is achieved by making enhancements to the initial stage design, also known as the reference or base-case design. Process synthesis plays a crucial role in identifying the early-stage design

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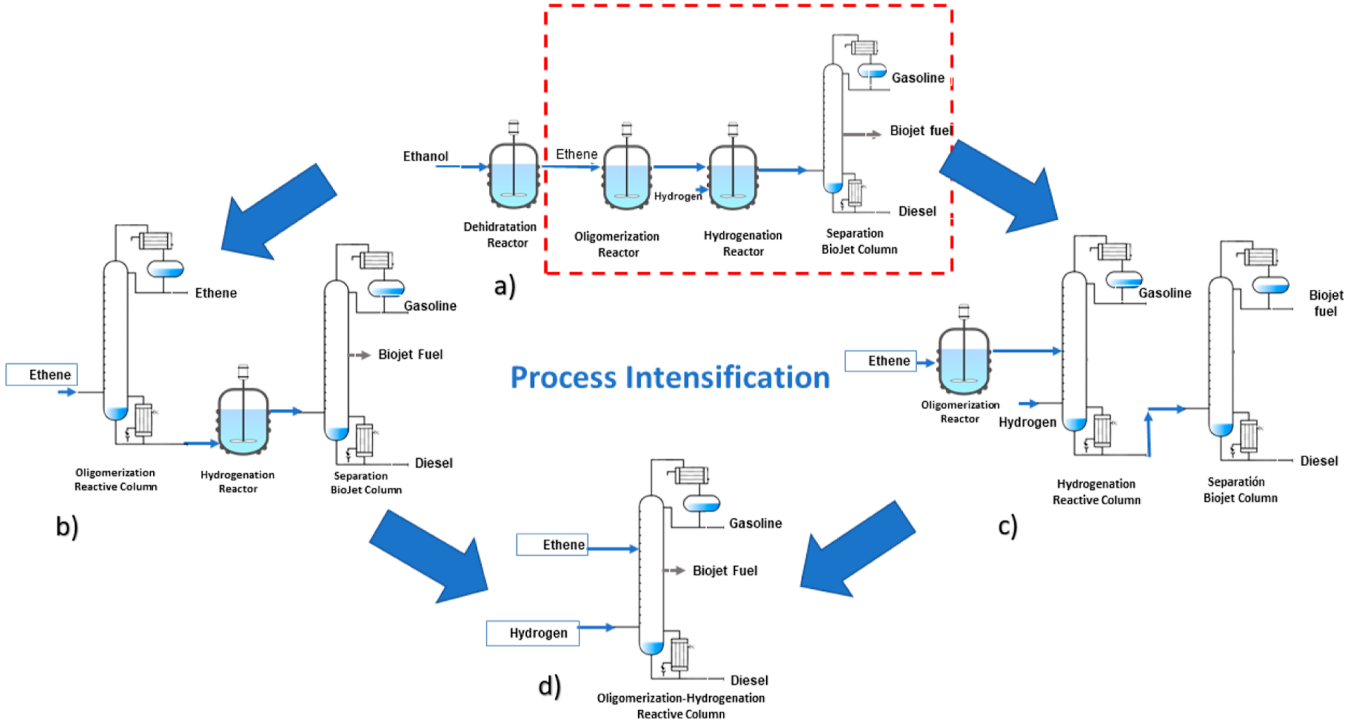

Figure 2. Process intensification methodology starts from ethene to jet fuel. (a) Conventional process of oligomerization, hydrogenation. and purification. (b) Intensified scheme including an oligomerization-reactive column. (c) Intensified scheme including a hydrogenation-reactive column. (d) Intensified scheme including a double oligomerization−hydrogenation reactive column.

and/or more sustainable design by creating viable process alternatives. Different methods can be used to generate these alternatives, such as trial and error, rule-based heuristics, process integration (mass and energy), process optimization, process intensification, and other approaches, Figure 2

Babi and colleagues[11] suggest that developing sustainable alternatives requires synthesizing processes with appropriate measurements. There are various methods to develop such alternatives, including optimization, rule-based heuristics, and trial and error. In the work of Jiménez-González et al.,[12] the authors propose a set of metrics to evaluate the degree of "greenness" of chemical processes and products in the industry. The proposed metrics are based on a set of twelve principles of green chemistry, including factors such as energy efficiency, waste minimization, use of renewable resources, and environmental impact. The authors suggest that these metrics should be used to assess and compare the environmental performance of different chemical processes and products. Although there have been efforts to apply process intensification strategies to the biojet production process, they have been limited to the purification section of the final effluents.[7,13] As a result, there is a significant potential for process intensification strategies to be applied to the reactive sections of the ATJ process, which have not yet been designed using intensified processes.

Therefore, this work researches an initial outline oriented to replace the conventional process for the production of biojet with intensified technology (RD columns). Specifically, the efforts will be oriented toward the oligomerization and hydrogenation processes. The columns will be designed and optimized parametrically to generate alternatives in a green process framework, evaluating them with various metrics to ensure the best performance and the smallest environmental footprint.

2. PROBLEM STATEMENT AND CASE STUDY

The whole process of producing biojet fuel using alcohols as intermediates necessitates the processing of lignocellulosic biomass to generate such alcohols. The general process of producing alcohols from lignocellulosic agro-industrial waste consists of four steps: pretreatment of biomass to break down cell walls into cellulose and hemicellulose and remove lignin; hydrolysis (or saccharification) of biomass; fermentation of produced monosaccharides to alcohols by the action of yeasts, bacteria, or other appropriate organisms; and alcohol purification.[14]

After obtaining the alcohols, they are transferred through the ATJ process to be converted to gasoline, biojet fuel, and diesel. The ATJ process is built on a concept that was designed to bridge the gap between alcohols that can be cheaply generated from renewable resources and the high-quality hydrocarbon fuels required in aircraft turbines. As seen in Figure 3, this method is based on three catalytic reactions: dehydration of alcohol, oligomerization of olefins, and hydrogenation, followed by separation of the synthetic paraffin product in the jet fuel range. The remaining cuttings are utilized in the production of gasoline and diesel.[15] Short-chain alcohols like ethanol, n-butanol, and isobutanol are particularly appealing as raw materials because they may be generated from lignocellulosic biomass or waste. Most ethylene is produced by steam cracking of hydrocarbons, such as natural gas, or naphtha. However, currently, one plant is operated by Braskem in Brazil that uses sugarcane-derived ethanol as a feedstock to produce ethylene through dehydration, and then converts the ethylene to polyethylene, a common plastic material.

Because of its technical maturity, ethanol was chosen the as the starting alcohol in this study over alternative bioalcohols. In the case of ethanol, its maximum usage as an addition in most

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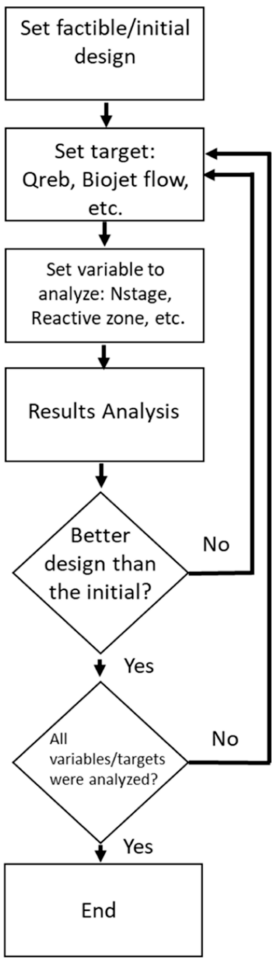

Figure 3. Sensitivity analysis flowsheet.

gasoline-powered cars is in mixes of 10 to 15%, creating a barrier to its market penetration as a gasoline additive. This, along with increases in production efficiency and raw material diversification, would result in surplus ethanol production at competitive pricing, with the ability to create a wide range of platform fuels and chemicals. As a result, its conversion into biojet fuel gives a chance to increase alcohol profitability.[2,6]

During oligomerization, short-chain molecules combine to form longer-chain molecules. There are several catalytic processes for the oligomerization of ethene to alkenes. The respective reaction conditions depend on the catalyst used and the feedstock; in addition, conversions for oligomerization and hydrogenation are favored at elevated pressure and temperature conditions.[16]

Once olefins are formed through alcohol dehydration, these intermediate compounds are converted under moderate temperature and pressure conditions (150−250 °C, 30−40 bar) into a distillate containing unsaturated hydrocarbons in the range of diesel and kerosene through oligomerization, with a range of C6−C16, which is typical for aviation fuels. Heterogeneous acid catalysts such as zeolites, solid phosphoric acid catalysts, mesoporous materials, and hetero polyacid compounds are generally used.

Long-chain alcohols need a low degree of oligomerization due to the different chemistry of oligomerization, which results in cheap costs for this procedure. Short-chain alcohols, on the other hand, have the advantage of achieving a more uniform distribution of the number of carbons in the final product, allowing the finished product to have a smoother distillation curve and be more comparable to conventional fuel obtained from petroleum.[15] There has been a lot of interest in switching out the homogeneous catalyst used in ethylene oligomerization for a more environmentally friendly and long-lasting heterogeneous catalyst. There have been several articles that recommend nickel-based heterogeneous catalysts for the ethylene oligomerization process.[17,18] Numerous solid supports have been characterized for the ethylene oligomerization of HZSM-5, MCM-41, SBA-15, Y-zeolite, and H-beta.[17−20] Several of these supports have acidic sites that play a role in the ethylene oligomerization process according to.[21]

On the other hand, the oligomerization products can undergo hydrogenation, which operates at temperatures of 370 °C and different space velocities with hydrogen feed on 5% by weight palladium or platinum on activated carbon (Patent US8378160B2).[22]

As alkenes are unsaturated and unstable hydrocarbons, and they are not desirable in jet fuel. Therefore, the goal of hydrogenation is to convert alkanes to alkenes by the addition of hydrogen. Since the dissociation is high, this process usually requires metal catalysts based on nickel, platinum, or palladium usually dispersed in activated carbon.[23] If Pt-, Pd-, or PtO2-catalysts are used, the reaction will already occur under standard conditions. However, depending on the catalyst and the application, higher temperatures may be necessary. On an industrial scale, low-cost Raney-Nickel catalysts are common.[24] Considering the design of the process to generate biojet fuel from ethanol and hydrogen, the process by which this gas is generated plays an important role in a sustainability framework. In that sense, the hydrogen that can be fed to this process can be generated from several sources. For example, the work of Malik and Tomer[25] provides a state-of-the-art review of morphological advancements in graphitic carbon nitride (g-CN) for sustainable hydrogen production. The production of hydrogen through water splitting using g-CN as a catalyst involves several steps. First, a source of renewable energy, such as solar or wind power, is used to generate electricity. This electricity is then used to power an electrolyzer, which uses the energy to split water molecules into hydrogen and oxygen. The g-CN catalyst is used to facilitate the reaction, lowering the energy required for the process to occur. In terms of the economic feasibility of the process, the authors note that while g-CN has significant potential as a catalyst for sustainable hydrogen production, there are still several challenges that must be addressed before it can be widely adopted. These challenges include improving the stability and durability of the catalyst, optimizing the efficiency of the water-splitting reaction, and reducing the cost of producing g-CN on a large scale.

On the other hand, L Cao et al.[26] explain the current state of research on biorenewable hydrogen production through biomass gasification. This process converts solid biomass into a gaseous fuel called syngas, which is composed of carbon monoxide (CO), hydrogen (H2), carbon dioxide (CO2), and other minor components. The process involves heating the biomass at high temperatures in the presence of a limited amount of oxygen or steam to produce the syngas. The syngas can then be purified to remove impurities such as tar and sulfur, and the hydrogen can be separated from the other components using various separation techniques. The authors note that the cost of producing hydrogen through biomass gasification is currently higher than that of traditional methods such as steam methane reforming. However, they also point out that the cost of

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hydrogen production through biomass gasification is expected to decrease as the technology advances and the scale of production increases.

Hydrogen also can be produced by plasma pyrolysis. As mentioned by Chen et al.,[27] this process uses high-energy plasma to decompose organic compounds into their constituent elements, including hydrogen. The process involves feeding a feedstock, such as waste biomass, into a reactor chamber, where it is exposed to high-temperature plasma. The plasma breaks down the feedstock into its constituent elements, including hydrogen, which can then be collected and purified. In that sense, there are alternatives for hydrogen production from sustainable sources. While there is not one alternative clearly more promising than the others, since a feasible production depends on several factors such as resource availability, costs, efficiency, scalability, and greenhouse gas emissions, several research work is being carried out to generate viable processes for hydrogen production. Thus, Figure 2 shows the diagram of biojet production from ethene.

Figure 2 shows initially the conventional process to convert ethylene to jet fuel considering an oligomerization reactor and a hydrogenation reactor to finally purify the biofuels obtained from the whole process. Consider that in Figure 2, it is possible to obtain ethylene that did not react in the light product stream (Note Figure 5). In the simulation work performed in this work, that stream is recirculated to the process feed. On the other hand, the hydrogen is almost entirely consumed and only traces are obtained at the process outlet. An important additional note to the intensification potential presented by the longer production scheme is the degradation of energy and various green process indicators. That is, some indicators such as mass intensity or energy efficiency degrade as the process includes a larger number of unit processes. In that sense, this work applies process intensification strategies to the conventional oligomerization−hydrogenation−purification process to finally generate a highly intensified process that considers only a reactive double column.

As intermediate schemes, in this work, two schemes were designed and analyzed where a reaction zone is substituted by a RD column to observe how the performance and the evaluated metrics change.

RD is a process that combines the chemical reaction and separation processes in a single unit. The book presented by Sundmacher and Kienle[28] covers various aspects of RD, including its principles, design, operation, benefits, and examples of industrial applications.

The improvements documented by the usage of RD are plenty, different, and in distinct case studies. For example, Souza et al.[29] describe a substantial increase in the purity gained by synthesizing Triacetin compared to the purity acquired in a conventional technique. On the other hand, Popken et al.[30] claim a decrease in energy consumption, enhanced selectivity, and conversion when methyl acetate is generated. In some cases, when the use of RD has been recorded, there are savings of 20 percent in the cost of capital and energy costs.[31]

The use of RD has not been left out of biofuel production; however, its application has been reported largely for biodiesel production. For example, Kiss et al.[32] proposed the manufacture of biodiesel using various heterogeneous catalysts (niobic acid, sulfated zirconia, sulfated titania, and sulfate tin oxide) (niobic acid, sulfated zirconia, sulfated titania, and sulfate tin oxide). Through the usage of RD, the reaction time was improved, productivity was increased, and the size of the equipment was lowered, gaining lower capital expenses. In the same approach, several writers have observed gains in productivity and production costs for biodiesel production.[33,34] On the other hand, the application of RD for other forms of biofuels, particularly ATJ, has not been researched.

3. PERFORMANCE EVALUATION INDICES

By 2030, zero-carbon solutions could be competitive in sectors that account for the largest percentage of global emissions. In addition, as part of the United Nations Agenda, the 2030 Agenda was created as a necessary continuity, which is a sustainability action plan taking into consideration the sustainable development goals, which are 17 goals that aim to improve life in a sustainable way for future generations.

Within this 2030 agenda, some objectives that can be focused on for the development of sustainable production schemes should be highlighted. For example, goal 7 is on affordable and clean energy, goal 9 is on industry, innovation, and infrastructure, goal 13 calls for urgent action to combat climate change and its impacts, etc.

Recently, Sheldon[35] published an interesting compendium in which several metrics oriented to the generation of green/sustainable processes are described, and it presents the metrics grouped by category. With this in mind, for the development and proper design of the technology presented in this work, several objectives grouped into 3 categories will be evaluated. 1. Economic objective, 2. Environmental objective, and 3. Energy and mass efficiency.

3.1. Economic Objectives. The inclusion of economic indicators at an early design stage can help to compare and evaluate performance indicators for more economical and cost-effective designs.

In order to calculate the total annual cost (TAC) used as the objective function, we used the method published by Guthrie.[36] Using equations presented by Turton et al.,[37] we carried out a cost approximation of the process using eq 1. It performs the cost estimation of an industrial plant divided into units.

$$\mathrm{TAC}\ (\$/\mathrm{kg}) = \frac{\frac{\sum_{i=1}^{n} C_{\mathrm{TM},i}}{\text{payback period}} + \sum_{j=1}^{n} C_{\mathrm{ut},j}}{F_k} \tag{1}$$

where TAC is the total annual cost, C_{TM} is the capital cost of the plant, and F_k is the product flow. The plant is assumed to run 8500 h/year with a payback period of 10 years. Besides, the following heating and cooling costs were taken into account: high-pressure steam (42 bar, 254 °C, \$9.88 GJ^{-1}), medium-pressure steam (11 bar, 184 °C, \$8.22 GJ^{-1}), low-pressure steam (6 bar, 160 °C, \$7.78 GJ^{-1}), and cooling water (\$0.72 GJ^{-1}).[38]

Additionally, it should be taken into account that engineering projects are evaluated using a variety of metrics in addition to the TAC, such as return on investment (ROI).[39] With this metric, the intricate process of cash flow that occurs throughout several periods in the future will be reduced to a single number. The simplest definition of ROI is as in eq 2

$$\mathrm{ROI} = \frac{(\sum_{i=1}^{N} \mathrm{CF}_i)/N}{I} \tag{2}$$

N represents the project's duration in years and the after-tax revenue average is used. One can calculate the rate of ROI by dividing it by the initial investment. The following average prices were considered: ethylene (1 \$/kg) and hydrogen gas (0.7 \$/kg)

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as well as the average prices of different fuels: jet fuel (0.55 \$/kg), diesel (\$/kg), and gasoline (1.13 0.7 \$/kg).[40−43]

3.2. Environmental Objective. The evaluation of the environmental impact in the design of processes is a determining factor in achieving the objectives of sustainable development. The comparison must be considered to determine and select the designs that have the least damage to the environment as well as the affectation on the society by the emission of pollutants.

The global warming potential (GWP) was created to allow for comparisons of the global warming effects of various gases. It is a measure of how much energy 1 ton of a gas will absorb over a given time in comparison to 1 ton of carbon dioxide emissions. The greater the GWP, the more a given gas heats the earth in comparison to CO2 throughout that time. The standard period for GWPs is 100 years ("Understanding Global Warming Potentials | US EPA"). GWPs provide a single unit of measurement, allowing scientists to add together estimates of multiple gases' emissions. The following is how GWP is defined and calculated (equation 3)

$$\mathrm{GWP} = \frac{\text{Total mass of } CO_2 \text{ equivalents (kg)}}{\text{Mass of Product (kg)}} \tag{3}$$

3.3. Energy and Mass Efficiency Objectives. Sustainable development guidelines include using resources as optimally and efficiently as possible and evaluating inputs and outputs of matter and energy contributing to the quantification of a baseline state for comparison with future states when modifications are made to the process design. To identify the mass and energy performance of the proposals in this work, the following performance metrics were used: (1) efficiency (ε) (equation 4), (2) mass intensity (equation 5) (MI), (3) resource energy efficiency (equation 6) (η_E), (4) energy intensity (equation 7) (R_{SEI}), and (5) thermodynamic efficiency (equation 8) (η).

$$\varepsilon = \frac{\text{Mass of product (kg)}}{\text{Theoretical mass of product (kg)}} \tag{4}$$

Note that eq 4 refers to the theoretical mass production obtained. In this sense, the theoretical maximum production is based on the experimental work developed by Heydenrych et al.,[44] which subsequently led to eqs 9−24 that chemically describe the production of various cuts, highlighting for this work the biojet fuel.

The entire mass of raw materials utilized to create a given mass of product is known as mass intensity. When no waste is created and all materials are used to create the product, this should equal unity.

$$\mathrm{MI} = \frac{\text{Total Mass Input (kg)}}{\text{Mass of product (kg)}} \tag{5}$$

Resource energy efficiency (η_E) is the ratio of the energy of the products (quantity of the raw materials converted to the desired product) to the total resource used in the same units.[45] The materials considered in this study are all inputs, specific energies of ethylene and hydrogen, and specific energies of products, light, jet fuel, and diesel. For this indicator, services are not accounted for, only the specific energies of the reactants and products of the process.

$$\eta_E = \frac{\text{Energy content of the product (kJ)}}{\text{Total material} - \text{input energy (kJ)}} \tag{6}$$

The calculation of efficiency can take two relatively different approaches. If the energy efficiency of a process or process unit is being measured in terms of the amount of energy used to produce a specific product or service, then, it is appropriate to exclude the services and utilities used in the process. This is because services and utilities, such as electricity, steam, and water, are used to supply energy and not to produce a specific product or service. Including these services/utilities in the energy efficiency calculation would distort the measurement of actual process efficiency. However, if the objective of the energy efficiency calculation is to measure the overall process efficiency, including the energy efficiency of the services/utilities used to supply energy, then, they should be included in the energy efficiency calculation. In this case, the services/utilities are considered part of the overall process and their energy efficiency is important in determining the overall energy efficiency of the process.[46,47]

In this case study, the impact of services/utilities was not considered for the efficiency calculation since we wanted to consider the first approach mentioned. This co-consideration was taken into account since this indicator is accompanied with other indicators where the impact of utilities is directly considered, for example, the total annual cost. Also, for this case study, the specific energies considered for hydrogen, ethene, biojet, bioethanol, heavy cut, and light cut were 119.8, 4751, 45,000, 26,000, 996.94, and 2303.62 kJ/kg, respectively. Please note that these light cut, and heavy cut values were considered according to the data reported in the literature for light gases and green diesel.[48,49]

Considering the energy density of the biojet as 45,000 kJ/kg,[50] and specific energy of reactants and products, energy is a crucial factor in this era of economic competition. Specific energy consumption is used for measuring the energy consumption per unit of product

$$R_{\mathrm{SEI}} = \frac{\text{Net energy used as primary fuel equivalent (kJ)}}{\text{Mass of product (kg)}} \tag{7}$$

Exergy is a thermodynamic potential; it is a general measure of work, "difference", or contrast. The ability of an energy carrier to do work expresses the general ability to be converted into other kinds of energy, and therefore, exergy can be used to investigate technological processes. The exergy efficiency is the ratio of the total outgoing exergy flow to the total incoming exergy flow during the total recycling process:

According to Seader and Henley's work,[51] thermodynamic efficiencies can be calculated using the standard equation when continuous-flow and steady-state-flow systems are subject to the principles of thermodynamics.

$$\eta = \frac{W_{\min}(\mathrm{kJ})}{\mathrm{LW} + W_{\min}(\mathrm{kJ})} \tag{8}$$

where $W_{\min}$ is the minimum work for separation and LW = $T_0 \Delta S_{\mathrm{irr}}$ is the waste of work in the system and η the thermodynamic efficiency.

4. METHODOLOGY

A feed stream of 44,865 kg/h of ethylene was defined. This flow has been defined based on the work done by Rivas-Interian et al.[52] for the production of jet fuel through a conventional process from biomass. The modeling was done in the Aspen Plus simulator. The non-random two-liquid (NRTL) thermody-

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Table 1. Estimated Kinetic Parameters of the Power-Law Model in eqs 1−16

oligomerization−hydrogenation production					
reaction number	k	E (kJ/kmol)	reaction number	k	E (kJ/kmol)
9	38728.5907	4.623	17	6146.3487	5.1584
10	74825.7294	14.934	18	7150.2255	2.4686
11	48935.42	164.8806	19	6409.9637	5.5759
12	110614.018	16.2112	20	2465.1438	2.8607
13	83400.8644	17.5098	21	6052.2691	7.6072
14	116517.955	21.4748	22	4027.1747	7.9935
15	27140.8737	19.7567	23	1723.794	6.935
16	3349.1216	158.5374	24	746.1161	6.0205

namic method correlates the activity coefficients of one compound with its mole fractions, and the reference methods are NRTL-HOC.[53] The NRTL-RK model is appropriate because the majority of compounds are non-electrolyte polar and the operating pressure is less than 10 bar.[54−56]

In an experimental investigation, Heydenrych et al.[44] performed oligomerization processes on a nickel(III)-based catalyst and silica-alumina substrate. Their study group did the oligomerization experiment in a 700 mL volume reactor fed with ethene at operating settings of 180 °C, 3.4 MPa, and a mass hourly Space velocity between 1 and 12. The products generated from the oligomerization procedure were evaluated using spectrophotometric techniques. Gas chromatographic measurements were done as mass fractions for all products (alkenes starting from C2). The complexity of the system is reflected in the following chemical equations.

$$2(C_2H_4) \rightarrow C_4H_8 \tag{9}$$

$$C_2H_4 + C_4H_8 \rightarrow C_6H_{12} \tag{10}$$

$$C_2H_4 + C_6H_{12} \rightarrow C_8H_{16} \tag{11}$$

$$C_2H_4 + C_8H_{16} \rightarrow C_{10}H_{20} \tag{12}$$

$$C_2H_4 + C_{10}H_{20} \rightarrow C_{12}H_{24} \tag{13}$$

$$C_2H_4 + C_{12}H_{24} \rightarrow C_{14}H_{28} \tag{14}$$

$$C_2H_4 + C_{14}H_{28} \rightarrow C_{16}H_{32} \tag{15}$$

$$2(C_4H_8) \rightarrow C_8H_{16} \tag{16}$$

$$C_4H_8 + H_2 \rightarrow C_4H_{10} \tag{17}$$

$$C_6H_{12} + H_2 \rightarrow C_6H_{14} \tag{18}$$

$$C_8H_{16} + H_2 \rightarrow C_8H_{18} \tag{19}$$

$$C_{10}H_{20} + H_2 \rightarrow C_{10}H_{22} \tag{20}$$

$$C_{12}H_{24} + H_2 \rightarrow C_{12}H_{26} \tag{21}$$

$$C_{14}H_{28} + H_2 \rightarrow C_{14}H_{30} \tag{22}$$

$$C_{16}H_{32} + H_2 \rightarrow C_{16}H_{34} \tag{23}$$

$$C_8H_{16} + H_2 \rightarrow C_8H_{18} \tag{24}$$

As noted, the RD column took into account eqs 9−24. The following is how the power-law response was reduced to represent the kinetic reaction

$$k = k_0 \times \exp(-E/RT) \tag{25}$$

where k_0 and E stand for frequency or pre-exponential factor and activation energy according to the Arrhenius equation. The estimated kinectic parameters of power law are shown in Table 1[57]

As stated by Huang et al.,[58] there is no standard and systematic methodology for the optimal construction of RD columns. Therefore, in this work, the heuristics given by Subawalla and Fair[59] were considered. This heuristic is summarized in an algorithm that may be used to estimate parameters such as column pressure, the position of the reactive zone, theoretical stages of the column, reflux ratio, column diameter, etc. These variables were changed to boost the yield and generation of jet fuel. The magnitude of the holdup was not established arbitrarily; to obtain a suitable value, the recommendations offered by Barbosa and Doherty[60] were followed. The methodology initially consisted of stating the compositions of the products and the value of the reflux ratio (obtained with the strategy of Subawalla and Fair); in this way, the volume of the plates could be found such that the chemical reaction was carried out. The implementation of the algorithm proposed by Subawalla and Fair[59] is straightforward but does not guarantee the optimal design. Once the technique was done, it was feasible to obtain a design to create jet fuel; further, a similar parametric procedure was undertaken to maximize the production of jet fuel with the lowest possible energy consumption.

Additionally, the requirements presented by Shah et al. were considered,[61] and they were deemed essential to establishing the viability of any RD technique before beginning any synthesis or design work. The accomplishment of those requirements in this case study must be highlighted by their guidelines:

(1) The presence of several products. (2) The temperatures needed for reaction and separation are compatible. (3) Neither the operating pressure nor the temperature is in the critical range for any of the components.

Figueredo et al.[62] suggest a sensitivity analysis where the influence of each variable on a shared target is examined. In this study, the minimization/maximization of several objectives was also developed, having as a restriction the standard composition of the biojet mixture, and the right distribution of components in the column to be able to purify the effluent.

Finally, all conventional distillation columns were originally designed through short procedures using the DSTWU module in Aspen Plus (Winn-Underwood-Gilliland method). Based on the results of the short techniques, they were rigorously simulated in compliance with the MESH equations using the Radfrac module of Aspen Plus.

Figure 3 shows a general flowsheet methodology to develop the sensitivity analysis. Several variables (reflux ratio, number of stages, reactive zone, feed stage, etc.) were considered to obtain

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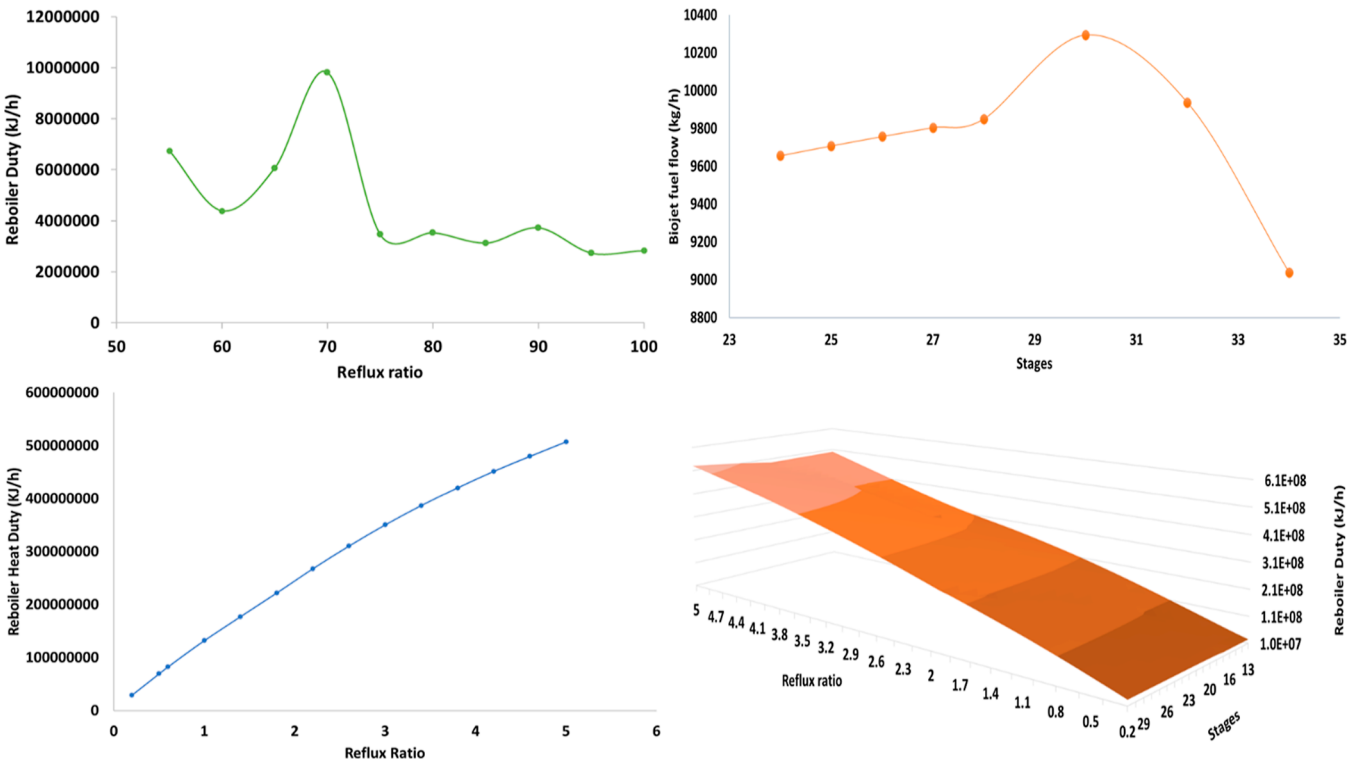

Figure 4. Sensitivity analysis between the design parameters reflux ratio, reboiler heat duty, biojet flow, and the number of stages. (a) Oligomerization reactive column. (b) Hydrogenation reactive column. (c) Hydrogenation reactive column. (d) 3D analysis for the double-reactive column.

the best performance in terms of energy consumption in biojet production.

5. RESULTS

This section will discuss the results obtained by evaluating the different scenarios addressed in this work, as shown in Figure 2.

As mentioned in the Methodology section, the initial task was to perform a sensitivity analysis to minimize various indicators of each process scheme. Special attention was paid to reboiler duty and equipment size due to the impact of these parameters on the selected target functions, e.g., total annual cost, greenhouse gas production, thermodynamic efficiency, etc. Thus, it was possible to obtain the highest jet fuel production with the lowest possible energy consumption for each case.

The parametric optimization task yielded designs that were subsequently analyzed in light of the various performance indicators listed in Section 3.

In the sensitivity analyses performed, behavior similar to those observed in Figure 4 was obtained. In particular, Figure 4 shows some behavior observed for the three cases of study during sensitivity analysis.

Due to the impact that energy consumption has on the various performance indexes to be evaluated, following the strategy shown in Figure 3, it is possible to generate the designs of the 4 schemes (highlighted in Figure 3) with the lowest energy consumption. For example, according to eq 17, the cost of utilities plays an important role in the calculation of the TAC. Likewise, higher energy consumption is linked to higher amounts of greenhouse gas emissions represented in eq 19, etc.

Once the parametric optimization was carried out through a sensitivity analysis, it was possible to obtain the designs with less energy consumption, which is presented in Table 2. Note that RD, which involves combining reactions and distillation in a single unit, depends on the cooperation between these two processes. According to kiss et al.[63] since they occur simultaneously in the same unit, the operational parameters required for both must be compatible. This compatibility is often restricted by factors such as the properties of the components being used (such as their boiling points) as well as the design of the equipment and the catalytic activity and selectivity. Therefore, the feasibility of RD is typically limited to a specific range of pressure and temperature as it involves a trade-off between these factors.

Although an adequate presentation of the performance indicators evaluated in the various alternatives has not been made at this point, it is possible to have a fairly good preliminary picture of the possible performance of the schemes. According to Table 2, it is possible to observe trends in the energy consumption of the processes. Initially, the design parameters of the conventional scheme allow for establishing an immediate reference parameter. In this sense, scheme (b), where the hydrogenation reactor is replaced by a reactive column, does not show energy savings. Similarly, scheme (c), which includes an oligomerization RD column, does not present energy saving. On the other hand, scheme (d), which considers only one distillation column with two reactive zones, presents huge energy savings.

It must also be considered that not all schemes were able to produce the same amount of jet fuel. If only the amount of product obtained is considered, scheme (b) would ultimately be the best biojet production scheme. However, the energy consumption of this scheme is higher than for scheme (d), which makes the scheme considering a column with two reactive zones the most balanced.

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Table 2. Design Parameters of the Scheme (a) (Conventional) and (b) (Including a Hydrogenation Reactive Column)

	scheme (a)			scheme (b)			scheme (c)			scheme (d)
	oligomerization reactor	hydrogenation reactor	separation column	oligomerization reactive column	hydrogenation reactor	separation column	oligomerization reactor	hydrogenation reactive column	separation column	oligomerization-hydrogenation reactive column
number of stages			46	40		46		30	46	33
reflux ratio			27.16	75		27.16		0.884	27.16	69
feed stage			45	25		45		2 and 29	45	24 and 30
side stream stage			3 and 43	40		3 and 43			3 and 43	33
reactive stages				13−19				feb-29		12−20, 21−29
hold up (*l*)				0.35				35		3.5, 48
distillate flowrate (kg h^{-1})			6662.65	2130.01		6662.65		15512.67	6662.65	5422.44
condenser duty (kcal h^{-1})			2.37933 × 107	2.48788×10^{7}		2.37933×10^{7}		10146113.28	2.37933×10^{7}	9.56216 × 10 6
reboiler duty (kcal h^{-1})	1.84906×10^{7}	2.91078×10^{6}	2.28705×10^{7}	2.0817×10^{6}	2.91078×10^{6}	2.28705×10^{7}	1.84906×10^{7}	8.3714×10^{6}	2.28705×10^{7}	854,153
operative temperature (°C)	408.21	237.298			237.298		408.21			
operative pressure (atm)	5.28	8.89	1.68	25.66	8.89	1.68	5.28	21.21	1.68	21.71
jet fuel production (kg/h)	13621.21	25919.62	12543.26	19935.821						

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Table 3. Summary of Performance Indicators Evaluated in All Schemes

	GWP	ε	MI	η_E	RSEI [kJ/kg]	ROI (%)	TAC [$USD/kg]
base case scheme (a)	7.68799×10^{-6}	0.477	6.209	0.3001	1952.722	21.886	9.981
scheme (b)	2.30435×10^{-6}	0.908	3.262	0.5712	1113.752	42.936	0.782
scheme (c)	4.02203×10^{-6}	0.439	6.742	0.2764	940.738	86.464	1.124
scheme (d)	2.37047×10^{-7}	0.698	4.242	0.4393	88.121	58.194	0.457

Table 4. Summary of Feeds and Products in Oligomerization and Hydrogenation Reactive Columns

	hydrogenation Feed				
mass Flow (kg/h)	oligomer	hydrogen	products	feed	oligomerization Products
ethylene	1.10×10^{-17}	0	0.00	44865	22.86274
butene	1353.202	0	22.69	0	7471.192
hexene	7200.518	0	6901.90	0	13560.483
octene	2832.349	0	1758.68	0	1812.94926
decene	5857.454	0	83.16	0	3904.09597
dodecene	8220.565	0	3893.86	0	6065.01823
tetradecene	8460.981	0	6410.22	0	6554.67842
hexadecene	3474.714	0	3067.31	0	3343.71803
ethane	0	0	0.05		
butane	0	0	1378.32		
hexane	0	0	305.77		
octane	0	0	1092.95		
decane	0	0	5857.28		
dodecane	0	0	4378.53		
tetradecane	0	0	2071.81		
hexadecane	0	0	411.07		
hydrogen	0	440.1	0.00		

Of course, the performance indicators should be analyzed as a whole, but this preliminary analysis gives us an overview of what could be observed in the other performance indicators.

Thus, once all the indicators were evaluated in the jet fuel production schemes with the lowest energy consumption, the data presented in Table 3 were obtained.

Once the different performance indicators have been evaluated, it is directly observed that the application of a process intensification strategy does not always generate a more efficient process. Namely, when the conventional production scheme replaces the oligomerization reactor with an RD column that oligomerizes, a direct improvement is not observed. On the contrary, there is a detriment in several indicators. Table 2 shows how the reboiler duty rises when considering the oligomerization column, i.e., the overall process consumes a greater amount of energy when including this reactive column. This behavior has been observed in some other case studies (Torres-Ortega et al., 2018).[64] In this sense, many of the indicators that depend on reboiler duty suffer a detriment. For example, the fact that a large amount of energy is required in the reboiler without any improvement in performance or product yield is indicative of a detriment to thermodynamic efficiency.

Similarly, the indicator associated with cost suffers an important impact. According to eq 1, the TAC has a direct dependence on the cost of capital and the cost of utilities. In this sense, the increase in energy requirements has a direct impact on the cost-related indicators. However, it is important to mention that the presence of a reactive oligomerization column increases energy requirements and also improves the indicators related to product quantity. That is, if the oligomerization presents an important improvement in the production of hydrocarbons greater than C10, the final quantity of jet fuel will be greater. In this sense, it is possible to observe that there is an improvement in the performance of the reactive oligomerization column or the energy efficiency of the product. Thus, by directing the production of the reactive column more toward jet fuel, it was possible to increase the quantity of product obtained and the indicators related to it. Thus, scheme (b), despite consuming a greater amount of energy, was also able to generate a greater amount of jet fuel, which was reflected in a 70% improvement in the GWP value, close to 50% in efficiency, mass intensity, and ROI, and a significant improvement in the TAC/kg of jet fuel. Only an improvement in resource energy efficiency (RSEI) of about 35% was observed due to the amount of energy that must be input to scheme (b) for jet fuel production.

On the other hand, when the hydrogenation reactor (scheme c) is replaced by a reactive column performing the same task, a similar situation is observed. Again, the reboiler duty considered in the reactive hydrogenation column exceeds the thermal load required in the hydrogenation reactor. Thus, the CO_2 emission-oriented indicator is relatively similar. According to what was mentioned in the previous paragraph, the global productivity of jet fuel is highly influenced by the oligomerization stage; in this case, since we are limited by the production produced by the reactor and we cannot increase the production of the jet fuel anymore, we cannot obtain a direct improvement in the indicators that consider the amount of product obtained.

In the case of scheme (c), since there was no significant improvement in the amount of jet fuel produced, and having similar energy requirements, it was not possible to observe an improvement in the performance indicators. For example, efficiency, mass intensity, and thermodynamic efficiency show very similar values. An increment of close to 50% was observed for RSEI and ROI. The TAC was an improvement in annual costs observed due to the decrease in the cost of capital.

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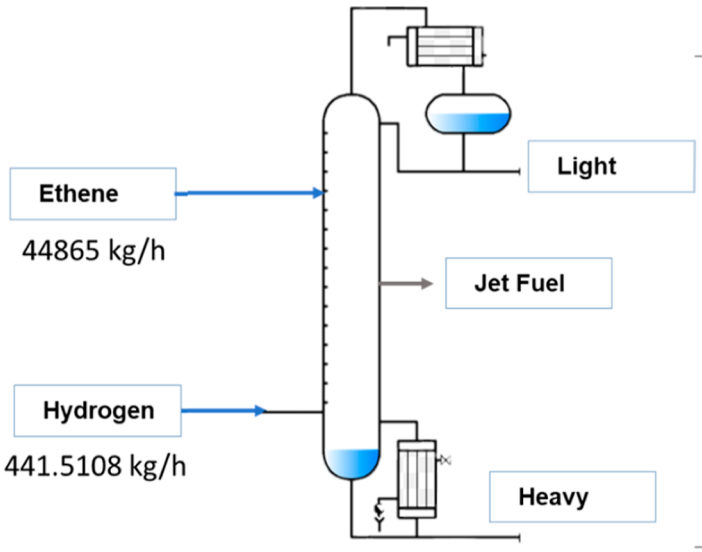

Mass Flow (kg/hr)	Ethylene	Hydrogen	Light	Jetfuel	Heavy
Ethylene	44865	0	10.204	4.21E-09	1.24E-21
Butene	0	0	2297.314	1.90E-09	9.85E-15
Hexene	0	0	3.78E-06	1.434	0.00089
Octene	0	0	2.88E-17	2.507	0.0054
Decene	0	0	4.02E-26	93.564	0.387
Dodecene	0	0	0	1671.989	21.339
Tetradecene	0	0	4.05E-27	7834.997	345.169
Hexadecene	0	0	2.29E-30	5933.34	371.886
Ethane	0	0	3112.742	0.114	5.37E-11
Butane	0	0	2.181546	0.0701	4.21E-06
Hexane	0	0	5.47E-07	14.652	0.023
Octane	0	0	1.62E-18	11.506	0.0503
Decane	0	0	0	375.125	4.228
Dodecane	0	0	0	3396.329	115.723
Tetradecane	0	0	5.18E-38	7068.589	855.461
Hexadecane	0	0	0	9095.778	2669.792
Hydrogen	0	441.51	9.79E-05	1.71E-15	0.0029

Figure 5. Process streams for scheme (d).

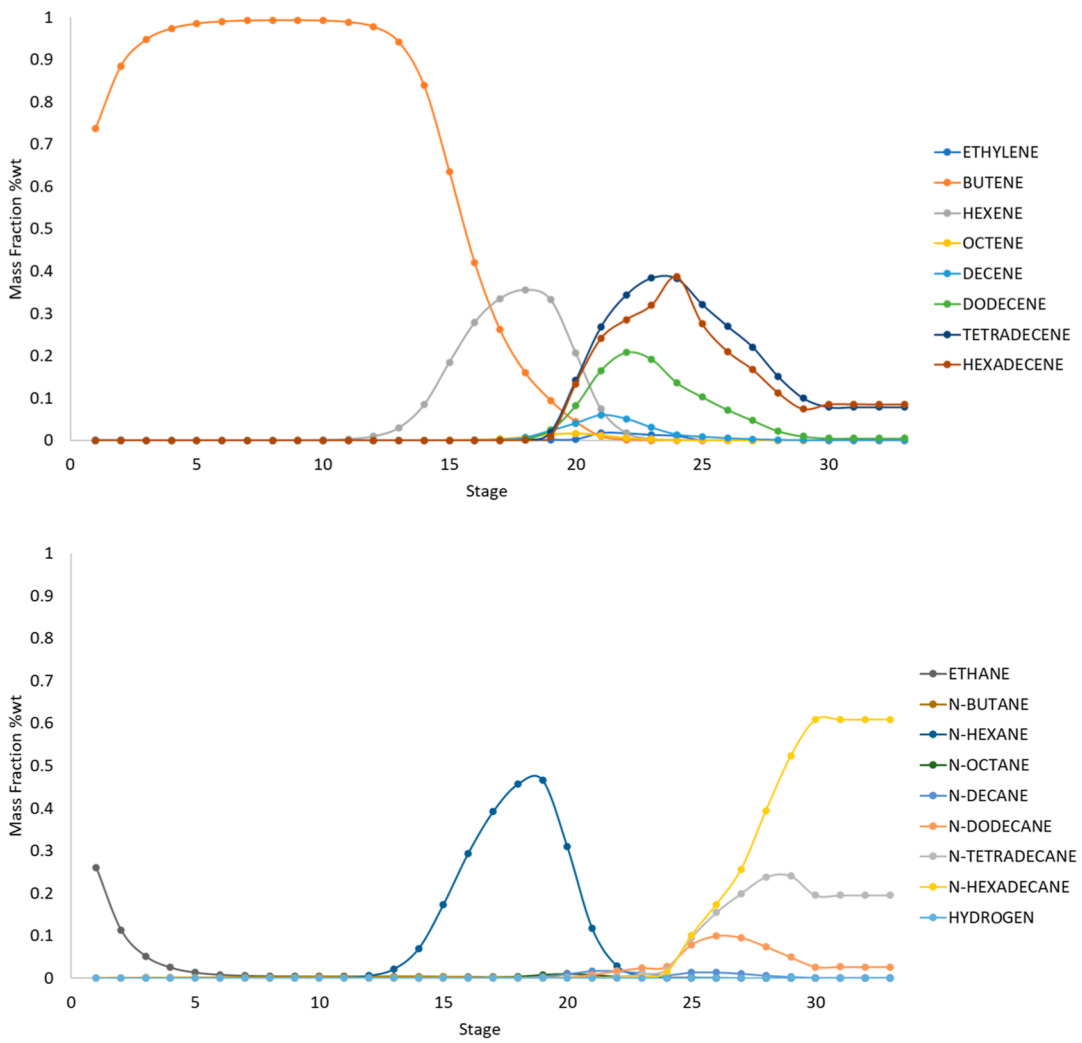

Figure 6. Composition profiles (mass fraction) of the double-reactive column of scheme (d).

Finally, the synergistic effect generated by joining the oligomerization and hydrogenation processes in a column with two reactive zones is quite good. During the parametric optimization process, it was possible to obtain design conditions that allowed one to obtain a significant amount of product with better operating conditions than the other schemes. In other words, observing Table 2, it can be seen that the reflux ratio of the double-reactive column is lower than that of the other

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columns, which had a direct impact on the energy consumed. This energy improvement was reflected in the environmental indicator referring to CO_2 emissions. Additionally, by being able to orient the operating conditions to a higher jet fuel productivity with a lower energy cost, all the performance indicators had a considerable improvement.

Considering Table 3, when considering two reactive zones in jet fuel production, a significant improvement in several indicators was observed. The ROI shows an improvement of close to 50%, not to mention that the TAC decreased by close to 90%. In the same sense, by reducing energy requirements and increasing jet fuel production compared to scheme (a), the GWP value improved by 70%. In the same way, an improvement of close to 30% was observed in efficiency, mass intensity, and thermodynamic efficiency.

Thus, the proposal of a double-reactive column generated a beneficial effect on jet fuel productivity and the energy requirements to carry out this activity. Table 4 shows the feed and products obtained in both oligomerization and hydrogenation columns. Additionally, Figure 5 shows the process, the matter streams associated with the process, and the composition profiles of the column.

Note that the double-reactive column is energetically favored when compared to columns where only an oligomerization or reaction chemical reaction is carried out. These savings depend on the operating conditions of the intensified systems that guarantee that the process occurs as well as the composition of the feed flows, volatilities, etc.

Also, energy savings can be affected when the system is semi-intensified or fully intensified as well as the position of the intensified process relative to the conventional system (intensified-conventional or conventional-intensified system). This behavior can be observed not only in reactive intensified systems but also in intensified systems involving only a separation process.[65]

In Figures 5−6, it can be seen that the distribution is carried out suitably so that the light elements are obtained in the dome of the column. The compounds corresponding to the jet fuel cut-off are obtained as a side stream, and finally, the heavy compounds are obtained at the bottom of the double-reactive column.

6. CONCLUSIONS

In this work, an intensified proposal for jet fuel production based on a distillation column with two reactive zones (oligomerization and hydrogenation) was presented. A scheme consisting mainly of reactors and a purification column was considered as a reference case. Process intensification strategies were implemented to design a scheme with a single reactive column (oligomerization or hydrogenation) that did not show a substantial improvement in performance indicators oriented to measure the sustainability of the processes. However, the synergy generated by designing a distillation column with two reactive zones allowed a substantial improvement in all the performance and sustainability indicators evaluated. In general, an improvement in the ROI value of close to 50% and a decrease in the TAC of close to 90% were observed. The GWP value improved by 70%. Likewise, an improvement of close to 30% was observed in the efficiency, mass intensity, and thermodynamic efficiency. Although the double RD column was not the scheme that generated the highest jet fuel production, it was the most balanced in terms of energy requirements, sustainability indexes, and jet fuel production.

In general, the possibility of designing more sustainable intensified schemes for jet fuel production from renewable sources has been observed, and the possibility of generating higher value-added products from ethanol has been observed. Although it was clear that not all intensified schemes are better than conventional ones, the synergy observed when designing a scheme with a higher degree of intensification made it possible to generate a section of the ATJ process with higher performance and sustainability.

Areas of opportunity were also observed to generate intensified schemes in other sections of the ATJ process, for example, the ethylene production reaction from ethanol. These processes are beyond the focus of this work but are interesting alternatives for future efforts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.3c00234.

Performance evaluation indices (PDF)

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Notes

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