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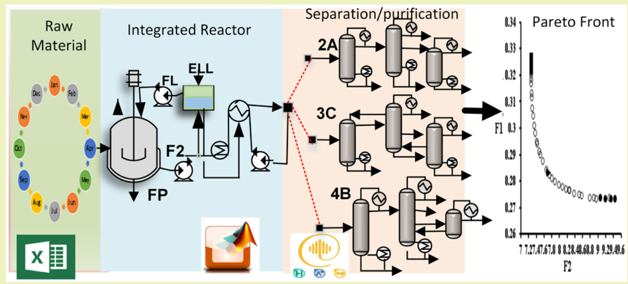
Optimal Planning of Feedstock for Butanol Production Considering Economic and Environmental Aspects

Juan José Quiroz-Ramírez,[†] Eduardo Sánchez-Ramírez,[*,†] Salvador Hernández-Castro,[†] Juan Gabriel Segovia-Hernández,[†] and José María Ponce-Ortega[‡]

[†]Chemical Engineering Department, Universidad de Guanajuato, Noria Alta s/n, Guanajuato, Gto. 36050, México

[‡]Chemical Engineering Department, Universidad Michoacana de San Nicolás de Hidalgo, Gral. Francisco J. Mugica S/N, Ciudad Universitaria, 58030 Morelia, Michoacan, México

ABSTRACT: This paper presents a multiobjective optimization to obtain the optimal planning of butanol production, considering the optimal selection of feedstock and the correct ratio of fermentable sugars. This multiobjective methodology was applied during both the fermentation and purification process of butanol. The multiobjective optimization problem considers minimizing the total annual cost and environmental impact as objective function. The economic objective function takes into account the availability of bioresources, the cost of feedstocks, the fermentation conditions, and the separation units. On the other hand, the environmental assessment includes the overall impact measured through the eco-indicator 99 which is based on a life cycle analysis methodology. Both objective functions were applied to a case study for the optimal planning to produce biobutanol in Mexico. After the optimization process, we generated a set of solutions represented by a Pareto curve that identifies a group of optimal solutions for both objectives. Considering the best compromise of both targets, the best solution involves initially a raw material with a moderate content of sugars followed by a separation unit designed as a hybrid separation process. This hybrid process considers the inclusion of a liquid−liquid extraction column followed by three thermally coupled distillation columns.



KEYWORDS: *Butanol production, Fermentable sugars, Butanol fermentation, Butanol feedstock planning*

■ INTRODUCTION

The increasing world energy demand has motivated the search for alternative energy sources as a possible substitute in the medium- and long-term for fuels from fossil sources. Those alternatives must also take into consideration the damage to the environment. Reducing dependence on fossil fuel is a key element of the energy policy adapted by many nations.[1] Recently attention has centered on renewable alternatives that could be produced from lignocellulosic raw material to meet the above-mentioned demands. Due to the physicochemical properties that butanol presents, mainly the energy content, there has been increased interest in its development by means of the fermentative route with the intention of implementing it as a fuel.

Current commercial biobutanol processes are based on fermentation of starch or sugar-based feedstocks such as corn[2] and molasses.[3] Most existing biobutanol plants use corn, which competes with food and animal feed. The relatively high cost of corn leads to higher butanol production cost. For this reason, there has been a growing research interest in developing technologies for producing biofuels such as butanol from nonfood cellulosic biomass including whey permeate,[4] dried distillers' grains and solubles,[5] corn fiber,[6,7] corn stover,[8] corn stalk,[7] rice bran,[9] rice straw,[10] barley straw,[6] wheat straw,[11−13] wheat bran,[14] switchgrass,[8] and cassava bagasse.[15] The production of butanol from these materials has a yield and concentration of product similar to those of the fermentations with corn; however, a detailed economic and technical evaluation is necessary to determine the feasibility of these processes.[16]

Commonly, butanol is a chemical with increasing demand and is also considered as a possible biofuel.[17] Nowadays, butanol is almost exclusively produced via chemical routes from fossil fuels through the oxo synthesis also known as hydro formylation. On the other hand, butanol can also be obtained by means of anaerobic fermentation typically using some of the Clostridial bacterium strains, such as *Clostridium acetobutylicum*, *Clostridium beijerinckii*, *Clostridium saccharobutylicum*, and *Clostridium saccharoperbutylicum*.[17,18] This kind of fermentation is called ABE fermentation, since acetone, butanol, and ethanol are obtained as the main products in a typical ratio of 3:6:1.

In contrast with bioethanol, the microorganisms involved in the ABE fermentation have the ability to consume a great variety of substrates which could be enriched in glucose, saccharose, lactose, xylose, starch, and glycerol.[19,20] Recently, some works have shown that Clostridium family strains can also

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ferment other cheaper forms of biomass, such as lignocellulosic materials, due to their saccharolytic ability.[1] However, acidic or enzymatic hydrolysis of lignocellulosic materials is essential to convert them into monosaccharides before using them as substrates in ABE fermentation.

Lignocellulosic biomass is globally the most abundant renewable resource for biofuel production.[21] The composition of the lignocellulosic material is principally constituted by cellulose, hemicellulose, and lignin. Research efforts are required to optimize the fermentation processes, including hydrolysis of substrate and removal of inhibitors, especially to use lignocellulosic raw materials in synthesizing biobutanol.

Before the fermentation process, the lignocellulosic raw material needs a pretreatment, which has as its main objectives reducing the hemicellulose to xylose and diminishing the crystallinity of cellulose.[22] After pretreatment, the lignocellulose must be hydrolyzed, by either chemical hydrolysis or enzymatic hydrolysis. It is remarkable that the hydrolysis of lignocellulosic materials is essential to convert all sugars from raw materials into monosaccharides before using them as substrates in ABE fermentation.

The use of various lignocellulosic hydrolysates for ABE fermentation has been reported in the literature. There are few reports on the use of these in continuous reactors. Qureshi et al.[8,23] reported use of various agricultural residues, such as barley straw, corn stover, and switchgrass hydrolysates, to produce biobutanol. The effect of both glucose and xylose concentrations was studied by Chen et al.[24] in an immobilized continuous column reactor using *Clostridium acetobutylicum* CGMCC 5234. Furthermore, enzymatic hydrolysis offers different advantages over other physical or chemical conversion mechanisms because it produces a low level of byproducts, is highly specific, requires low energy, provides higher yields, requires ambient operating conditions, does not lead to corrosion, and has lower environmental impact. Although the enzymatic hydrolysis has a strong inhibition by glucose and xylose, using integrated reactors with fermentation and saccharification decreases the inhibition because the monosaccharides are consumed simultaneously in the fermentation.[25]

Biobutanol production has several challenges: the cost of the feedstock is a key factor and major economic constraint (60% the total cost of biobutanol production) for the process of ABE fermentation followed by the cost of butanol separation from the dilute broth.[26] The culture liquid after the process of culturing contains a mixture of butanol and other products. To obtain pure butanol, it is necessary to separate this mixture. One of the possible ways to extract butanol is integrating the butanol extraction stage within the process of continuous fermentation or the so-called extractive fermentation. The use of such technology has allowed researchers to minimize the inhibitory effect of butanol and reduce the energy consumption to concentrate the target product.

The selection of the optimal method for product recovery should balance all issues, such as efficiency, energy requirements, costs, and process simplicity.[27]

In recent years, new advances in butanol recovery techniques, including liquid–liquid extraction, adsorption, pervaporation, and gas stripping, have allowed them to be integrated jointly with fermentation in an effort to develop a commercial process for biobutanol production.[28−33]

Different types of integrated reactors with recovery techniques have been proposed in the literature to reduce the energy requirements of the process.[34−37] Promising techniques such as liquid–liquid extraction and adsorption have been proposed because they have a higher selectivity for butanol.[38] For example, several kinds of reactors have already been reported; Diaz and Tost[39] reported an integrated reactor considering pervaporation as the separation technique. They claimed a diminishment in the total annual cost using an optimization methodology. Quiroz Ramírez et al.[40] reported an integrated reactor jointly with liquid–liquid extraction showing as a result an increase in productivity. Sharif Rohani et al.[41] implemented different kinds of integrated reactors, highlighting an improvement in performance by means of optimization techniques. Recently Eom et al.[42] proposed an integrated fermentation process with ex-situ recovery and continuous production of butanol. In these systems butanol is selectively separated after fermentation, which limits its toxicity to the microorganism and decreases the inhibition byproduct. In this manner an integrated reactor allows an increase in productivity and in the concentration of the product;[43] additionally, a relatively more concentrated substrate may be used in comparison with traditional reactors. Finally, fermentation broth is sent to the separation/purification stage where acetone, butanol, and ethanol are obtained.

According to the previous reports, it is pointed out that the production of butanol by ABE fermentation cannot compete economically with the petrochemical synthesis of the butanol. To achieve a competitive biological production, it is necessary to address five disadvantages or limitations: (1) High cost of substrates and substrate inhibition. (2) Low final concentration of butanol (less than 20 g/L) due to inhibition by butanol.[21] (3) Low productivity of butanol (less than 0.5 g/L h) due to the low cell density caused by butanol inhibition. (4) Low yield of butanol due to heterofermentation. (5) High recovery cost of butanol due to low yield and low concentration in broths.[43−46]

In order to efficiently carry out butanol production, the best type of raw material, optimum conditions of fermentation, and optimized purification process must be considered. Taking into account these considerations, there are involved a lot of variables and probably a lot of degrees of freedom; so, a robust optimization technique is required to guarantee the best performance of the process. Recently, many researchers have used multiobjective (MOO) techniques for analysis processes to produce clean fuel or energy with improved economic indexes and lower environmental impact.

Regarding the environmental impact, Azapagic and Clift introduced the life cycle assessment methodology in optimization problems; they showed the advantage of life cycle evaluation in multiobjective problems where the economic and environmental aspects are a main concern.[47]

Hugo and Pistikopoulos[48] presented a multiobjective mathematical programming-based methodology for the explicit inclusion of life cycle assessment criteria as part of the strategic decisions related to the planning and supply chain networks. Also, Guillen-Gosalbez et al.[49] proposed a new structure for optimal design of chemical processes, incorporating environmental constraints through life cycle assessment.

Under this scenario, in this work we developed a complete framework to produce biobutanol focused on the correct planning of raw materials, the fermentation, and finally the purification stage. In other words, we consider that all feedstocks we are working with are not always available throughout the year; in this manner, every raw material should be correctly chosen in concordance with its availability to work

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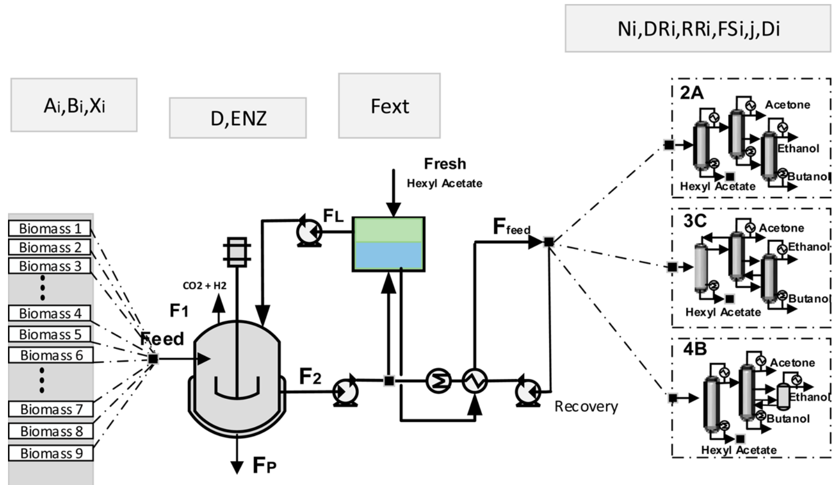

Figure 1. Representation of the different sections of the addressed problem.

Table 1. Eco-Indicator 99 for Processed Feedstock Amount for Biofuel Production[52,78]

	Raw Material	Cellulose %(w/w)	Hemicellulose %(w/w)	Lignin %(w/w)	Cost (USD/ton)	Eco-indicator 99 (points/ton)
1	wood chips	40	24	18	27	39.31
2	wheat straw	30	50	15	38.29	11.84
3	sugar cane	43	24	20	30.49	1.84
4	wheat	30	39	18	50.68	13.1
5	corn grain	41	23	12	55.86	17.16
6	sorghum grain	20	42	18	53.2	5.85
7	cassava root	30	22	22	88.2	42.05
8	sugar beet	35	29	22	27.5	2.75
9	sweet sorghum	22	48	18	16.1	5.85

in each month. This complete picture considers a real scenario as concerns the availability of different raw materials and their sugar content. To simulate and obtain the best parameters for fermentation/saccharification, it was jointly modeled both for operation to predict the behavior and guarantee the best operative conditions based on the previous raw material planning. Further, the flow stream generated by the integrated reactor was considered as the feed stream to the downstream process to find the best separation schemes, which, as in the fermentation step, let us minimize the economic aspect as well as the environmental index. This wider point of view, involving the optimization of both biomass planning and separation/purification in the downstream process, is totally helpful to determine the optimal composition of biomass as feed stream to the fermentation process, taking into account the necessary contract terms, feedstock costs, fermentation cost, environmental impacts, production capacity constraints, and the entire configuration of the downstream process (See Figure 1).

■ PROBLEM STATEMENT AND GEOGRAPHIC SITUATION

As has been described, the main issue to be solved in the ABE fermentation can be summarized in three sections: the correct selection of raw materials, improvements in the fermentation process, and the energy-efficient downstream process. Then, a brief description is presented for those three hurdles.

First, the biomass used as feedstock must be identified and characterized for its use. This problem becomes transcendental, since every single lignocellulosic raw material has its own amount of sugar which needs to be further fermented. In other words, the final butanol concentration depends of the sugar concentration in the fermentation reactor. So, here it is necessary to find either a single feedstock or a combination of raw materials to reach a higher butanol concentration after fermentation.

The second stage is to identify, based on the rigorous kinetics at the integrated reactor, the best conditions (temperature, sugar concentration, dilution factor, biomass concentration, etc.) to obtain relatively high bioindicators in the fermentation process. It should be highlighted that this is a sequential step, so it takes into account the interaction generated in the raw material planning.

Finally the third step consists in selecting the best configuration to separate/purify the mixture coming from the integrated reactor. Those three hurdles contain a lot of degrees of freedom, so the entire problem can be optimized.

Raw materials scenario and feedstock selection. Since the global availability of raw material is extremely wide, this work is focused on the lignocellulosic material available in México. Table 1 shows the costs and composition for different available raw materials, as well as the individual eco-indicator 99 of each of them. Data of the annual feedstock availability were taken from governmental reports which consider the temporary and regional availability in México (see Table 2). Those reports summarize data from institutions such as the Ministry of Agriculture (SAGARPA), Ministry of Energy (SENER), Ministry of Economy (SE), and Ministry of Environment (SEMARNAT), and also considers reports from the United States of the Department of Energy (DOE) and the Department of Agriculture (USDA). For the case study presented in this paper, the data were taken from the

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Table 2. Availability of Feedstocks Used for Biofuels Production in Mexico[52]

	Raw Material	Availability (ton/year)
1	wood chips	190600
2	wheat straw	52559
3	sugar cane	51090720
4	wheat	1902794
5	corn grain	1573914
6	sorghum grain	6593050
7	cassava root	13639
8	sugar beet	167
9	sweet sorghum	5032396

SAGARPA-SIAP,[50] SEMARNAT,[51] and Santibañez-Aguilar et al.[52]

The environmental impact factor of each raw material was obtained by applying the life cycle analysis methodology considering the products, processes, and associated activities (transportation, waste production, etc.) from cradle to grave. It was quantified by the eco-indicator 99.

Trying to simplify the complex scenario of raw materials, we considered only nine types of lignocellulosic mass coming from Mexican territory. Furthermore, we set as a constraint that only a mixture of two kinds of lignocellulosic biomass was fed to the reactor. However, this mixture can be blended anyway with both raw materials. Despite the fact that we are considering this simplification, the right feedstock selection is quite a complex problem, since the possibilities to form the feed stream are pretty high. So, the optimization algorithm must be able to obtain the correct feedstock combination to optimize any index.

Furthermore, we also consider the maximum available raw materials reported in Tables 1 and 2 which mathematically are represented by a set of mass balances and inequality constraints to avoid using more than the existing amount of feedstock. In other words, the maximum available feedstock can be stated as the sum of the feedstock used in the manufacture of each product through each processing route, and it must be lower than the total amount of available feedstock. These constraints are stated as follows:

$$\sum_m F_m \leq F_m^{\max} \tag{1}$$

where $F_m^{\max}$ is the maximum available amount of bioresource m; commonly, it is a well-known parameter before optimization.

Design of the simultaneous fermentation−saccharification unit. Process integration plays a major role in making a more efficient process. When several operations can be performed in the same single unit, the possibilities to improve the performance of the process are higher. An integrated reactor applied to butanol fermentation is an example of intensification, since different biological transformations take place during butanol production.[53] The integrated process consists of two distinct sections: reaction and separation. For the reaction section, we considered an integrated process where both fermentation and saccharification are carried out together; in the separation section, we selected liquid−liquid extraction as the recovery technique to purify the fermentation products.

The modeling and simulation of simultaneous fermentation−saccharification, and also the recovery unit, were performed in Matlab, considering the nonlinearity of kinetics in the hydrolysis and fermentation reactions. Likewise, the reactor simulation was considered as a continuous operation according to the work presented by Quiroz Ramírez et al.[40] With regard to the modeling of the fermenter, we considered the kinetic model of the metabolic pathways of glucose and xylose consumption by *Clostridium saccharoperbutylacetonicum* N1−4 previously proposed by Shinto et al.[54,55] Their model allowed us to predict a dynamic profile, taking into account all intermediary products in the fermentation as well as both substrate and product inhibitory effects for Clostridium strains. The inhibitory effect modeled by Shinto et al.[54,55] describes the effect of butanol at low−medium butanol concentrations considering currently Clostridium strains, just like those obtained in this work. So, by means of this model, a conventional ABE fermentation might be represented with relatively good accurracy.[56]

The kinetic studied by saccharification was developed by Kadam et al.[57] The parameter of enzymatic reactivity was adapted to continuous operation by the following equation:[39]

$$R_S = \frac{S(t)\cdot V(t) + \int_0^{t_f} x_{BS}\cdot F_B\cdot dt}{x_{1s}\cdot F_1\cdot (t_f - t_a) + S(0)\cdot V(0)} \tag{2}$$

where S, V, x_{BS}, x_{1S}, t_a, and t_f are the concentration of cellulose in the reactor (mmol/L), the volume (L), the mole fraction of cellulose in the reactor or bleeding, the mole fraction of cellulose in the feed stream, the initial time, and the final time of fermentation, respectively.

The mass balances in the reactor are stated in this work as follows:

$$\frac{dM_i}{dt} = R_i\cdot V + F_a\cdot x_{ai} - F_p\cdot x_{pi} \tag{3}$$

where M, R, V, F, x, and y are the amount of mass in the reactor, the reaction rate, the reactor volume, the flow, and the composition respectively, and the subscripts a, ai, and p represent the feed of compound i and purge, respectively.

The feed flow of the aqueous phase (F_2) in the decanter ifs given by

$$r_F = F_2/Fp \tag{4}$$

where F_2 is a fixed recycle ratio of fermentation (r_F). An integrated reactor with 99.95% efficiency of liquid−liquid extraction can be obtained if r_F is assumed to be 0.9999. In this work, F_2 was calculated assuming a recycle of 0.95. As extractant agent we select *n*-hexyl-acetate according to Barton and Daugulis,[58] and Groot et al.[34] *N*-Hexyl acetate is indeed a good extractant agent because of its high coefficient of partition, high selectivity, low cost, medium boiling temperature, and nontoxicity. Its liquid−liquid equilibrium was calculated as follows:

$$x_{Ii}\alpha_{Ii} = x_{IIi}\alpha_{IIi} \tag{5}$$

Moreover, it is assumed the volume of the reaction is 0.7 of the maximum reactor volume, previously set as 1000 m^3.

Downstream section. After obtaining the optimal feedstock selection and reactor conditions, the correct purification unit must be selected, which needs to be able to accomplish all recovery and purity constraints: 99.5 wt % for biobutanol, 99.5 wt % for acetone, and 95.0 wt % for ethanol. The downstream process was totally modeled in Aspen Plus, and it stands out that the entire process was robustly modeled, since we consider NRTL-HOC as a thermodynamic model.[59]

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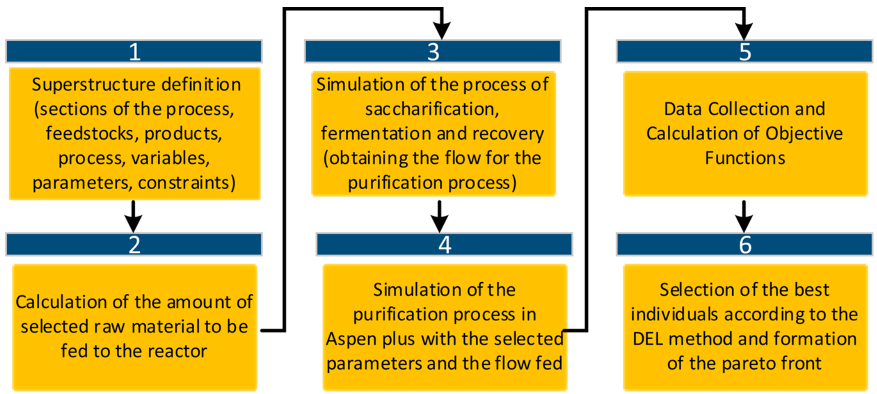

Figure 2. General representation of the proposed solution strategy for the addressed problem.

Since we have many possibilities to separate and purify the stream coming from ABE fermentation, we decided to focus this task on alternatives previously reported. Recently, Errico et al.[60] presented a set of alternatives that purify a flow stream coming from ABE fermentation: those alternatives evaluated under a robust optimization scheme minimizing the total annual cost and eco-indicator 99 as economic and environmental indexes, respectively. Their results highlighted three alternatives, those designs showed promising results when both objective function were evaluated. So we decided to employ these same alternatives to perform the same purification task. As a brief description, those alternatives involve three different schemes: a reference case which involves only conventional distillation columns with a side stream named in further paragraphs as scheme 2A, a thermally coupled design named scheme 3C, and a thermodynamic equivalent design named in this work as scheme 4B. It must be highlighted that in the results sections we continuously reference those names; however, since we are considering the production of butanol from a biorefinery point of view, as long as we reference schemes 2A, 3C, and 4B it means this entire process includes the planning of feedstock, the integrated reactor, and the downstream process. As in the feedstock selection and fermentation–saccharification process, the purification was also evaluated under the same robust optimization framework considering the same objective function as in the two last processes (See Figure 2).

BRIEF DESCRIPTION OF EVALUATION INDEXES AND OBJECTIVE FUNCTION

The addressed problem in this paper can be stated as follows: Given a set of feedstock with different sugar contents, there is a desire to produce a given product (with specified characteristics). The problem consists then in identifying the best selection and planning of feedstock, to operate with the best condition at the fermenter and to select a good alternative in the downstream process to convert the bioresources into purified products. The addressed problem is challenging because there are many variables that must be selected according to economic and environmental indexes (see Figure 1). To evaluate the entire process, we decided to use the total annual cost (TAC) and eco-indicator 99 as economic and environmental indexes, respectively. Both indexes are described in the following paragraphs.

Economic objective function. In order to calculate the total annual cost (TAC), we used the method published by Guthrie,[61] which was modified by Ulrich.[62] This method performs cost estimation of an industrial plant separated in units. The equations were published by Turton et al.[63]

The objective function for the total annual cost was used to carry out a cost approximation of the process using the following equation:

$$\text{TAC }(US\$/\text{kg-Butanol}) = \frac{\frac{\sum_{i=1}^{n} C_{TM,i}}{t_{ri}} + \sum_{j=1}^{n} C_{ut,j}}{F_{\text{Butanol}} \cdot t_o} \quad (6)$$

where TAC is the total annual cost, C_{TM} is the capital cost of the plant, F_{Butanol} is the production flow (kg-butanol/h), t_{ri}, is the payback period (3 years), and it was assumed that the plant is running 8000 h per year (t_o), respectively.

The total investment of the process is given by

$$\mathit{Total\ investment} = C_R + C_T + C_{IN} + C_{IE} \quad (7)$$

where C_R, C_T, C_{IN}, and C_{IE} are the reactor cost, column cost, condenser cost, and initial investment, respectively. All costs were calculated as a function of the installation cost.

The cost of the feedstock was calculated as the sum of all feedstock purchased from each supplier i (F_i) according to eq 8.

$$\mathit{Feedstock\ Cost} = \sum_i C_i^{Biomass1} F_1 + \sum_k C_k^{Biomass2} F_2 \quad (8)$$

where C_i is the raw material cost and F_1 and F_2 are the biomass flux considered as feed stream to the reactor.

The cost of the biochemical reactor and the cost of the heat exchangers (reboiler, condenser, and heater) are given by eq 9:[63]

$$C_{reactor/HEX} = (\text{M\&S}/280) \cdot (474.7 \cdot A^{0.65}) \cdot (2.29 + F_m(F_d + F_p)) \quad (9)$$

where M&S is the Marshall and Swift equipment cost index (M&S = 1536.5 in 2012), A is the area (m^2), $F_m = 1$ (carbon steel), $F_d = 0.8$ (fixed-tube), and $F_p = 0$ (less than 20 bar). To calculate the heat transferring area, a heat transfer coefficient U = 500 kcal m^{-2} h^{-1} K^{-1} was assumed. For the reboilers, the design factor was taken as $F_d = 1.35$.

The distillation columns diameter (D) was obtained by the tray sizing utility from Aspen Plus, while the height was evaluated as $H = 0.6(\text{NT} - 1) + 2(m)$. Afterward, the cost of the columns shell was calculated as follows:[63]

$$C_{Shell} = (\text{M\&S}/280) \cdot (957.9 \cdot D^{1.066} \cdot H^{0.82}) \cdot (2.18 + F_c) \quad (10)$$

where $F_c = F_m \cdot F_p$, $F_m = 1$ (carbon steel), and $F_p = 1 + 0.0074(P - 3.48) + 0.00023(P - 3.48)^2$. The cost of the trays was given by

$$C_{trays} = N_T \cdot (\mathrm{M\&S}/280) \cdot 97.2 \cdot D^{1.55} \cdot (F_t + F_m) \quad (11)$$

with $F_t = 0$ (sieve trays) and $F_m = 1$ (carbon steel).

Finally, the annualized operative cost can be expressed as

$$Operating\ Cost = C_E + C_V + C_{AE} + C_S + C_{ENZ} + C_{Ex} \quad (12)$$

where C_E, C_V, C_{AE}, C_S, C_{ENZ}, and C_{Ex} represent the electricity cost, steam cost, cooling water cost, substrate cost, enzyme cost, and cost due to extractant lost, respectively.

A payback period of 3 years was used,[64] and it was assumed that the plant is running 8000 h per year. In addition, the following heating and cooling costs were taken into account: high-pressure (HP) steam (42 bar, 254 °C, \$9.88 GJ^{-1}), medium-pressure (MP) steam (11 bar, 184 °C, \$8.22 GJ−1), low-pressure (LP) steam (6 bar, 160 °C, \$7.78 GJ−1), and cooling water (\$0.72 GJ−1).

Environmental objective. The environmental impact is evaluated and introduced into the model using eco-indicator 99, with the hierarchical weighting perspective being used to assess the relative importance of the damages.

Life cycle assessment (LCA) provides a very useful tool to evaluate the overall environmental loads associated with a process, product, or activity that identifies and quantifies the materials and energy used as well as the wastes released to the environment. The studies by Alexander et al.,[65] Guillén-Gosalbez et al.,[49] and Gebreslassie et al.[66] showed some applications of the LCA methodology for some chemical processes to improve their environmental performance. Contributions of several LCA experts have focused on the use of eco-indicator 99, where the main contributions came from several Swiss experts and the National Institute of Public Health and the Environment (RIVM).[67]

In the eco-indicator 99 methodology, 11 impact categories are considered:[68]

1. Carcinogenic effects on humans.
2. Respiratory effects on humans that are caused by organic substances.
3. Respiratory effects on humans caused by inorganic substances.
4. Damage to human health that is caused by climate change.
5. Human health effects that are caused by ionizing radiation.
6. Human health effects that are caused by ozone layer depletion.
7. Damage to ecosystem quality that is caused by ecosystem toxic emissions.
8. Damage to ecosystem quality that is caused by the combined effect of acidification and eutrophication.
9. Damage to ecosystem quality that is caused by land occupation and land conversion.
10. Damage to resources caused by the extraction of minerals.
11. Damage to resources caused by extraction of fossil fuels.

These 11 categories are aggregated into three major damage categories: (1) human health, (2) ecosystem quality, and (3) resources depletion. In this case study, for the eco-indicator 99 calculation we considered the impact of four factors we assumed as the most important in this process: the feedstock used for fermentation, steam used to produce heat duty, electricity for pumping, and steel to build major equipment and accessories. The values for those three factors are summarized in Table 3.

Table 3. Unit Eco-Indicator Used To Measure the Eco-Indicator 99 in Both Case Studies[67]

Impact category	Steel (points/kg) × 10^{-3}	Steam (points/kg)	Electricity (points/kWh)
Carcinogenics	6.320×10^{-3}	1.180×10^{-4}	$4.360 \times \mathrm{x}10^{-4}$
Climate change	1.310×10^{-2}	1.600×10^{-3}	$3.610 \times \mathrm{x}10^{-6}$
Ionizing radiation	4.510×10^{-4}	1130×10^{-3}	8.240×10^{-4}
Ozone depletion	4.550×10^{-6}	2.100×10^{-6}	1.210×10^{-4}
Respiratory effects	8.010×10^{-2}	7.870×10^{-7}	$1.350 \times \mathrm{x}10^{-6}$
Acidification	2.710×10^{-3}	1.210×10^{-2}	2.810×10^{-4}
Ecotoxicity	7.450×10^{-2}	2.800×10^{-3}	1.670×10^{-4}
Land Occupation	3.730×10^{-3}	8.580×10^{-5}	4.680×10^{-4}
Fossil fuels	5.930×10^{-2}	1.250×10^{-2}	1.200×10^{-3}
Mineral extraction	7.420×10^{-2}	$8.820 \times \mathrm{x}10^{-6}$	5.7×10^{-6}

It is important to highlight that the calculation of the environmental loads associated with the generation of energy and raw materials requires the expansion of the system boundaries, to include the upstream processes associated with the main process. However, the data associated with these upstream activities generally are taken from standard databases.[69]

In this environmental approach, the main contribution to eco-indicator 99 is associated with the use of external agents such as fossil fuels for heating as well as the use of solvents. For the weighting, we have followed the method of eco-indicator 99, separating the impact categories as damages to human health (expressed in disability adjusted life years "DALYs"), damage to the ecosystem quality (expressed as the loss of species over a certain area), and damage to resources (expressed as the surplus energy needed for future extractions of minerals and fossil fuels). Based on the work by Mettier,[70] the negative effects on human health and on the ecosystem quality are considered to be equally important, whereas the damage to the resources is considered to be about half as important. Furthermore, in the presented approach the hierarchical perspective was considered to balance the short- and the long-term effects. The normalization set is based on a damage calculation for all relevant emissions, extractions, and land-uses. The scale is chosen in such a way that the value of 1 Pt is representative for 1000th of the yearly environmental load of one average European inhabitant.[67]

Finally, eco-indicator 99 is calculated as stated in eq 13.

$$Eco\ indicator\ 99\ (EI99) = \frac{\sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} 7}{F_{\mathrm{Butanol}} \cdot t_0} \quad (13)$$

where β_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused in category k per unit of chemical b released to the environment, ω_d is a weighting factor for damage in category d, and δ_d is the normalization factor for damage of category d,

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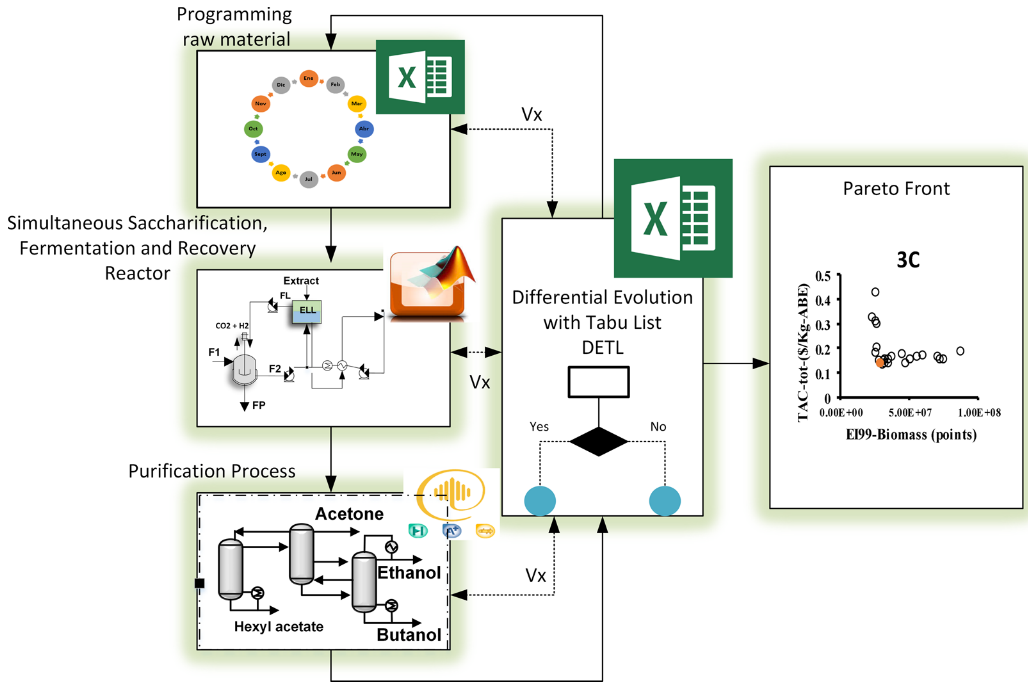

Figure 3. Connection of Excel-Mathworks Matlab and AspenTech Aspen Plus.

respectively. In the Eco 99 analysis, the acetone, ethanol, and biobutanol were considered for potential release; however, their impacts were not relevant. It is clear that the impact of steam will be very influenced by the 11th category in eco-indicator 99, which corresponds to the use of fossil fuels. So, it is relevant to know the importance of this category in comparison with the others.

Furthermore, since we are considering a biorefinery scenario, the eco-indicator 99 calculation must be calculated in two zones: the fermentation and purification processes. So, in this manner the eco-indicator 99 of feedstock selection stage is calculated according to eq 14:

$$EI99_{mat}(\text{points/year-kg ABE}) = \frac{\sum F_1 ecoindicator_m^{Biomass1} + \sum F_2 ecoindicador_n^{Biomass2}}{F_{\text{Butanol}} \cdot t_o} \tag{14}$$

Finally, the entire eco-indicator 99 calculation is calculated as the sum of the fermentation environmental impact and the downstream environmental impact, according to eq 15.

$$EI99_{tot} = \frac{EI99_{mat} + EI99_{pur}}{F_{\text{Butanol}} \cdot t_o} \tag{15}$$

Optimization objective function. The process described in previous sections was designed using a multiobjective optimization approach where both economic and environment aspects were measured through the total annual cost (TAC) and the eco-indicator 99, respectively, both previously explained.

The minimization of these objectives is subject to the required recoveries and purities in each product stream, where the multiobjective problem is stated as

$$\begin{aligned} &\text{Min}(TAC_{tot}, EI99_{tot}) \\ &\quad = f(A_i, X_i, D, \text{ENZ}, F_{ext}, N_{tni}, N_{fni}, R_{rni}, F_{rni}, D_{cni}) \\ &\qquad \text{Subject to } \vec{y}_m \geq \vec{x}_m \end{aligned} \tag{16}$$

where A_i is the type of raw material, X_i, is the fraction of raw material to be used over the months, D is the rate of dilution of the fermenter, ENZ is the number of enzymes to be added, F_{ext} is the amount of extractant, N_{tn} are total column stages, N_{fn} are the feed stages in the column, R_{rn} is the reflux ratio, F_{rn} is the distillate fluxes, D_{cn} is the column diameter, and y_m and x_m are vectors of obtained and required purities for the m components, respectively (see Figure 1).

MULTIOBJECTIVE OPTIMIZATION METHODOLOGY USED IN THE BIOBUTANOL PRODUCTION PROCESS

Description of the multiobjective optimization method. We have used a multiobjective an optimization method for the process of biobutanol production. This multiobjective optimization strategy is an evolutionary method based on the combination of differential evolution (DE) and tabu meta-heuristics. Particularly, Sharma and Rangaiah[71] used the concept of taboo list (TL) with DE to avoid the revisit of search space and developed a powerful hybrid stochastic optimization method (DETL). The advantage of including a taboo list in a differential evolution algorithm is to avoid the evaluation of the same point in the search space.[72] This characteristic improves the performance and decreases the computational time for global optimization. This algorithm has been extended by Sharma and Rangaiah[22−25] for handling multiobjective optimization problems with promising results.

Results reported by Sharma and Rangaiah[71−74] showed that MODE-TL is reliable for solving multimodal optimization problems due to the synergic performance caused by the integration of multiobjective DE with TL.

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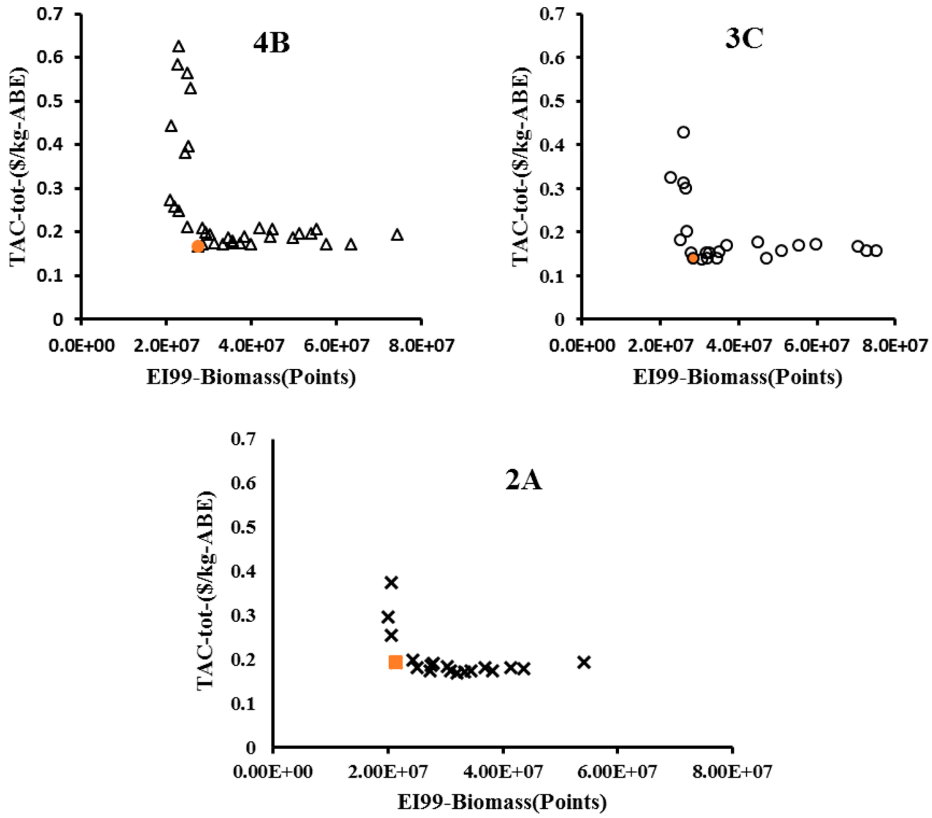

Figure 4. Pareto front of different scheme analyses.

The implementation of the multiobjective optimization approach was performed using a hybrid platform which considers Matlab, where the integrated reactor is modeled, Microsoft Excel, where the stochastic hybrid algorithm is programed, and Aspen Plus (Figure 3). This particular methodology has been described and tested by several authors.[60,75−77] For the multiobjective optimization of process routes analyzed in this study, we have used the following parameters for the MODE-TL method: 200 individuals, 500 generations, a taboo list of 50% of total individuals, a taboo radius of 2.5×10^{-06}, and 0.80 and 0.6 for the crossover and mutation fractions, respectively. We have to remark that these values were chosen based on a tuning process via preliminary calculations.

As a brief description of this methodology, the optimization process starts selecting the amount and type of raw material; both decision are totally programmed in a visual basic framework. Once the selection is made, it is possible to calculate the amounts and concentration of cellulose, hemicellulose, and lignin to be used throughout one year. These input variables are sent to Matlab, where the fermentation−saccharification−recovery process is rigorously simulated; in this process a dilution rate and amount of extractant are selected. As product of this step a stream containing acetone, butanol, ethanol, and the extractant agent is obtained. This flow stream is further sent to Aspen Plus, where the downstream process is modeled and simulated. As product of the entire process, the necessary data to calculate the objective functions is obtained. This whole process is repeated several times until all constraints are accomplished and the objective function does not show any meaningful improvement (see Figure 2). It is remarkable that optimizing a chemical process is typically a nonlinear problem, is potentially nonconvex, and is likely to have multiple locally optimal solutions. Such problems are intrinsically very difficult to solve, and the solution time increases with the number of variables and constraints. A theoretical guarantee of convergence to the globally optimal solution is not possible for nonconvex problems.

RESULTS AND DISCUSSION

After the optimization process, most of the results can be summarized in Pareto fronts; see, for example, Figure 4. Please remember we are evaluating simultaneously the total annual cost and the eco-indicator 99, considering at the same time three main sections of the entire process: feedstock selection, the integrated reactor, and the downstream process. So all Pareto fronts represent the conflict between both objective functions. In other words, when the optimization algorithm converges in low values of TAC, high values of eco-indicator 99 are obtained in parallel. Under this scenario the optimization methods should find a feasible zone where we assumed, assisted by the Pareto front, that both objective functions reached minimum values. First, in Figure 4 it is possible to analyze this behavior; there, the total annual cost and the eco-indicator 99 are evaluated. This Pareto front shows several points representing a set of solutions which accomplish all recovery and purity constraints. Basically it is possible to find several scenarios; an example, is to find a point with low environmental impact but high cost. This behavior is due to the fact that we are working with expensive raw materials containing relatively high sugar concentrations, but it causes a low environmental impact; its sugar concentration will produce a more concentrated broth, which consequently will have less energy demand and also be cheaper as concerns the downstream

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process. On the other hand, some solutions offer to select cheaper raw materials but cause a higher environmental impact. In this scenario the cheaper raw material will produce more diluted broths, which eventually will increase the cost of the downstream process. So it is necessary to find a zone in which both objectives reach their minimum values, typically located in the curve of the Pareto front. In Figure 4 is highlighted a single point which we assume accomplishes both compromises. Comparing those three Pareto fronts in Figure 4, it is clear that the highest costs are produced by scheme 4B with a TAC of 0.1679 USD/kg-butanol and an eco-indicator of 27357939 points. On the other hand, the process which produced the lowest cost was scheme 3C with a TAC of 0.1407 USD/kg-butanol and an eco-indicator of 10843661 points. The obtained data as concerns the downstream process show that the thermally coupled design (3C) produced the best TAC values and minor environmental impact. This result confirms those obtained in the work published by Errico et al.[60]

Regarding the optimal selection of raw materials, Figure 5 shows the behavior of the TAC and the cost of biomass. So, it is

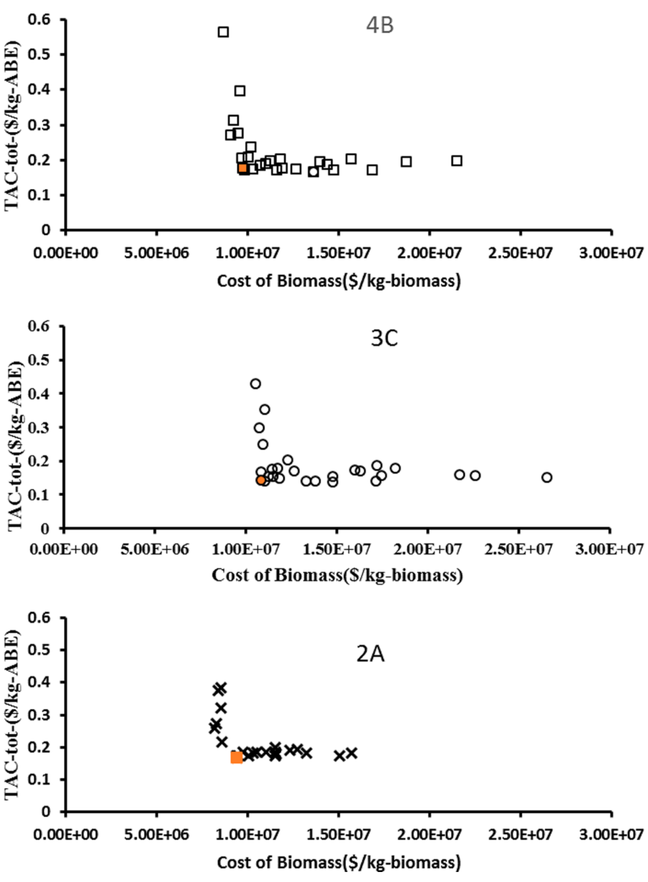

Figure 5. Pareto-optimal solution of different scenarios of TAC vs cost of biomass.

possible to observe the economic side of the process as regards the planning and biomass cost. Besides it should be highlighted that it is possible to obtain cheap schemes from a global point of view, since the raw material influences the TAC. In this manner, there is a great influence between the amount of raw material and the total annual cost. The amount of raw material should be selected considering the zone where both objectives find their better compromises; despite a wide variety of raw materials throughout the optimization process, it was possible to find that zone. In Figures 4 and 5 is highlighted a point at which all constraints and a trade-off between both objective functions is accomplished. It is remarkable that in this Pareto front scheme 3C showed again the lowest biomass cost and the lowest TAC.

An interesting point of view is shown in Figure 6a: we already know that the process which includes a thermally

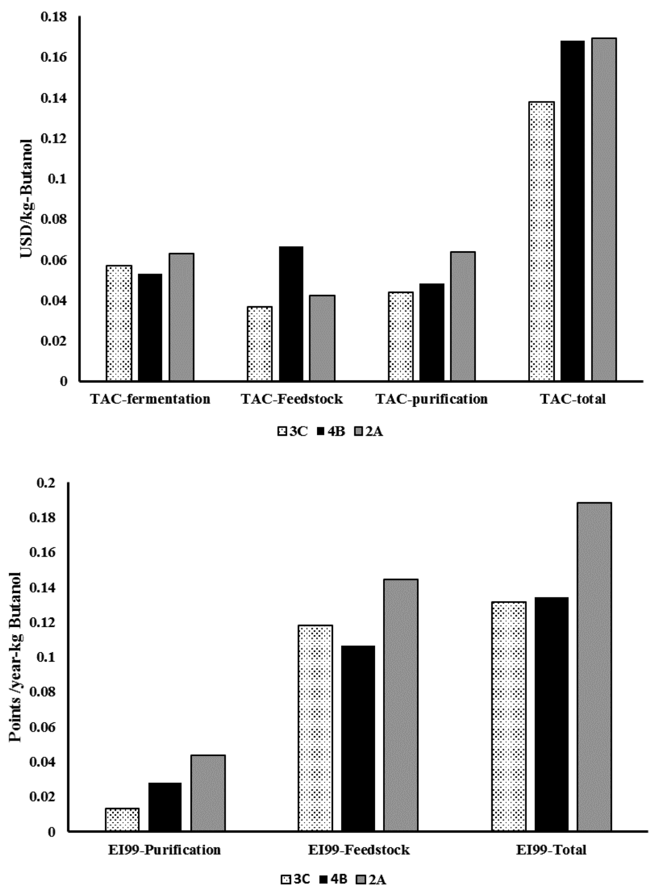

Figure 6. Contribution of each section of the problem to (a) the TAC and (b) the eco-indicator 99.

coupled design (3C) is the most promising scheme; however, it is interesting that, under this purification scenario, the lowest TAC values (except in the fermentation stage) were obtained . Also, this figure denotes that thermodynamically equivalent design 4B showed higher TAC values as concerns raw materials and purification/separation stages but lower TAC values in the fermentation−saccharification stage; in this manner, this entire configuration is not indeed a good alternative. So there is a close relation between the downstream process and the reaction zone; note, that when selecting a relatively expensive raw material, the TAC in this zone also increases. However, this impact can be softened if it is possible to reach a diminishment in the TAC of the fermenter and purification stages.

Moreover, a remarkable relation may be observed: a raw material with relatively high sugar content represents a higher cost; however, because of its higher sugar concentration, the cost related with the fermenter decreases, since its productivity and performance increase. This increase in performance impacts directly the purification process, since we are handling a higher amount of compounds. However, you can also observe contrary behavior.

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Table 4 shows the results regarding the reactor stage. Scheme 3C reaches the highest butanol concentration, 6.79 g/L. Also shown is the highest productivity, 0.7383 g/L h. On the other hand, scheme 4B shows the lowest cost; this value is totally related to its performance.

Table 4. Design Parameters for the Configuration Schemes 2A, 3C, and 4B

Parameter [unit]	2A	3C	4B
Concentration of Butanol [g L^{-1}]	6.3	6.79	6.77
Productivity [g $L^{-1}h^{-1}$]	0.7088	0.7383	0.7386
yield [g g^{-1}]	0.3213	0.3086	0.3103
Dilution [h^{-1}]	0.01934	0.01978	0.01967
Enzyme [kg-enzyme/kg-butanol]	0.083	0.073	0.090

Further, the downstream process is totally influenced by those previous stages; if we fed a more concentrated stream, it is possible to obtain cheaper processes. In this manner analyzing only the purification stage, scheme 3C showed the lowest cost, followed by schemes 4B and 2A. Table 5 shows the main parameters of all purification stages.

Table 5. Design Parameters for Configuration Schemes 2A, 3C, and 4B

	Scheme 2A		
Parameter [unit]	C-1	C-2	C-3
Number of trays	34	47	28
Feed tray number	6	24	23
Diameter/[m]	1.06	0.98	0.57
Reboiler duty/[cal s^{-1}]	22783.40	3483.73	1441.11
Condenser duty/[cal s^{-1}]	9934.42	3201.71	1596.16
Installed cost/[k$]		457.08	
Utilities/[k$ $year^{-1}$-1]		13757.88	
Eco-indicator 99 [kPoints $year^{-1}$]		7129.35	
	Scheme 3C		
Number of trays	78	72	30
Feed tray number	22	29	15
Diameter/[m]	0.77	0.89	0.65
Reboiler duty/[cal s^{-1}]	15070.96		3513.66
Condenser duty/[cal s^{-1}]		3348.21	3055.36
Installed cost/[k$]		333.43	
Utilities/[k$ $year^{-1}$]		9174.39	
Eco-indicator 99 [kPoints $year^{-1}$]		3429.54	
	Scheme 4B		
Number of trays	24	85	35
Feed tray number	12	42	26
Diameter/[m]	0.81	0.90	0.66
Reboiler duty/[cal s^{-1}]	21821.60	12365.94	
Condenser duty/[cal s^{-1}]	9655.23	11957.91	273.05
Installed cost/[k$]		589.38	
Utilities/[k$ $year^{-1}$]		16544.38	
Eco-indicator 99 [kPoints $year^{-1}$]		7129.35	

Under this scenario it is clear that a correct combination (not always the best) of stages will produce the best results. Moreover, Figure 6 shows the sum of all economic impacts, which is indeed the TAC of the highlighted point in Figures 4 and 5.

From a brief analysis about eco-indicator 99, it is clear that the main contribution lies on the feedstock selection; a relation observed is that high costs in feedstock are linked with low eco-indicator values. Figure 6b shows that scheme 4B produces the highest cost related to raw material, scheme 3C produces the lowest environmental impact, and scheme 2A the biggest environmental impact. Under this scenario, it is clear that a good selection considering the sugar content in the feedstock is necessary; a high sugar content is not always a guarantee of a good alternative, since fermentation and purification steps must also be considered.

Figure 6b shows the environmental impact of every single highlighted point in the Pareto front; observe all impact is also shown separately by sections. In this figure it is shown that, in general, terms for scheme 3C resulted in the lowest environmental impact. On the other hand, scheme 2A showed the highest total value. As was discussed, the feedstock represents the main impact in this measure.

Regarding the purification stage, the lowest environmental impact was obtained by scheme 3C and the biggest obtained by scheme 2A. This behavior is totally related with the energy consumption of each separation process. Thereby, scheme 3C is considered as the best option, since it is the most balanced, as concerns its economic and environmental indexes.

The amount of sugar, the cost of raw materials, and the environmental impact associated with this selection are major influencing factors in the planning of the feedstock to minimize those proposed objective functions. A deeper analysis allows us to know that raw materials with high cellulose and hemicellulose contents are the best option along a year; however, this lignocellulosic biomass also represents a higher cost. This economic behavior impacts directly the economic objective function, so in this manner the optimization method turns its attention to raw materials with low sugar content and also low economic impact (See Figure 7 4B and 7 2A).

Once the optimization process was carried out, it was possible to obtain the complete planning for each considered downstream process. This planning corresponds to the highlighted point in Figure 4 for each scheme. Figure 7 denotes that it is possible to reach a convenient combination of raw material for each month which guarantees the lowest economic and environmental impact.

As has been described, the entire process which involves the thermally coupled design (3C) to purify the stream coming from the fermenter was the most promising in comparison with the other alternatives with an annual production, accomplishing the minimization of both objective functions, near 25860 Ton/year of butane. However, it is interesting to analyze the main reason for this behavior. Figure 7 shows the best planning for scheme 3C, which considers a feedstock with high sugar cellulose and hemicellulose content. This selection impacts directly the economic objective function, since this raw material is relatively more expensive. Nevertheless, because of this selection, there is a meaningful diminishment in the fermenter cost; moreover, since the fermenter is fed with a higher sugar content, the produced flow stream is relatively more concentrated. Remember that a more concentrated fermentation broth generates a cheaper purification process.

Despite the fact that the most promising scheme for biobutanol production is already known, Figure 8 shows the amount of feedstock used for a year for each considered scheme. Note that the most used feedstocks are sugar cane and sugar beet. With regard to the thermally coupled options, after optimization they converge in approximately 33.6% of sugar cane and 22.8% of sugar beet. As a preliminary conclusion, a wider scenario which implies the correct feedstock selection,

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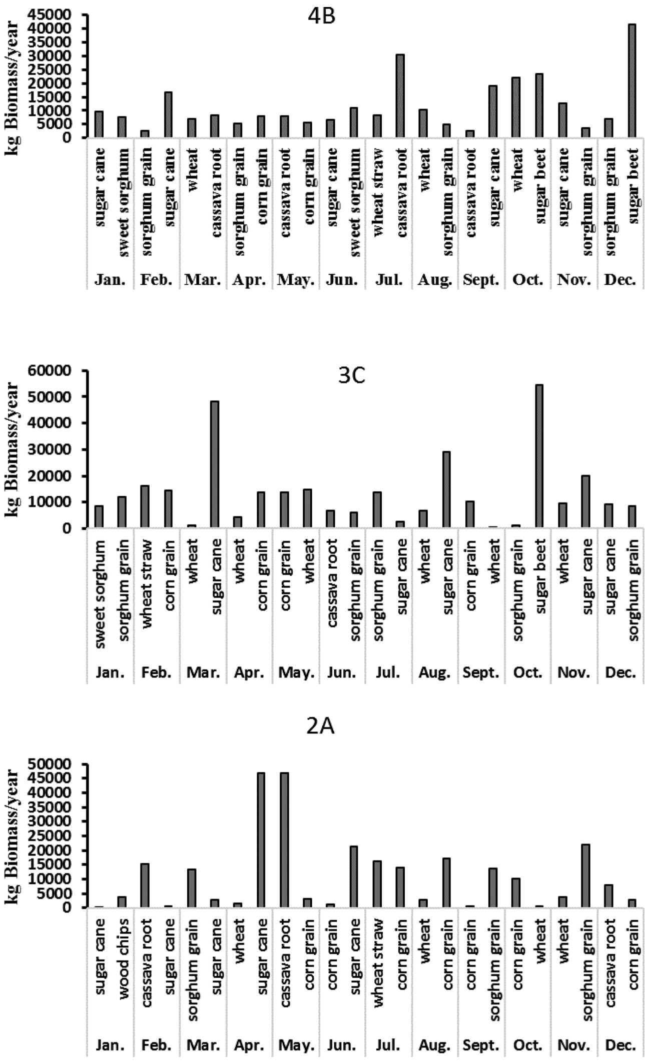

Figure 7. Planning of raw material throughout the months of a year.

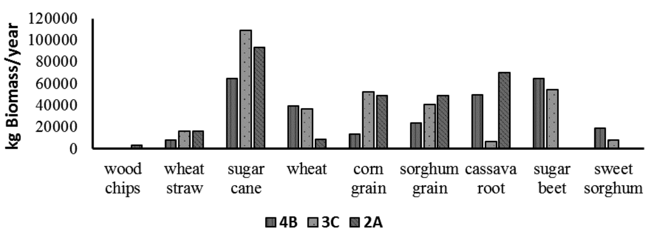

Figure 8. Total amount of raw material used in planning.

the best operative condition in the fermenter, and also the best downstream process will make more profitable the production of biobutanol.

■ CONCLUSIONS

In this study, three stages of the process to produce biobutanol were considered: feedstock planning, fermentation, and purification. These three stages were robustly optimized considering two objective functions: the total annual cost and the eco-indicator 99.

Through this study we realized that the sugar content, cost, and environmental impact of the raw material are key issues if a good performance is required for the entire process to produce butanol. From a variety of raw materials, a correct combination of feedstock with high sugar content combined with another without must be selected. This correct mixture produces the necessary sugar source to produce a biobutanol but with a relatively low economic impact in this area. In brief, a raw material with relatively high sugar content causes both a diminishment in fermenter cost and better performance, and vice versa. In this manner, the necessity of obtaining an optimal output from the fermenter to consequently obtain a more efficient downstream process is clear. Among all schemes analyzed in this study, the process which includes the thermally coupled design (3C) was shown to be the most promising option, with a cost of 0.1376 \$/kg of butanol and an environmental impact of 0.1315 point/year kg of butanol and an annual production of 25860 Ton/year of butanol.

One of the most important factors, not only for biobutanol production but also for the entire industry of biofuels, is the use of cheap substrates. The costs of biomass production, as well as its delivery and storage, will also be especially important. The use of cellulosic and lignocellulosic biomass has special importance for biofuel production. The process of butanol production may become competitive if it is based on a systemic approach involving every aspect of its production, such as fermentation, metabolic engineering of strains, selection of cheap alternatives as raw materials, and the downstream process.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sanchez.ramirez.eduardo@gmail.com.

ORCID

Eduardo Sánchez-Ramírez: 0000-0002-4326-4837

José María Ponce-Ortega: 0000-0002-3375-0284

Notes

The authors declare no competing financial interest.

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