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pubs.acs.org/IECR

Multiobjective Stochastic Optimization Approach Applied to a Hybrid Process Production−Separation in the Production of Biobutanol

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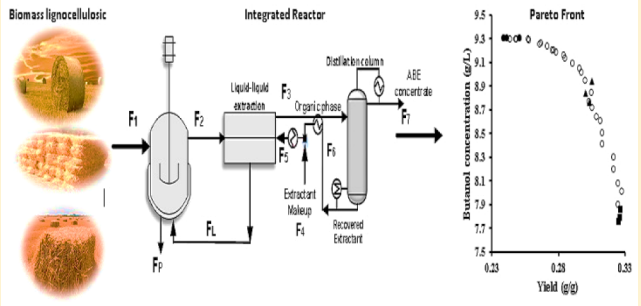
Supporting Information

ABSTRACT: Acetone, butanol, and ethanol are produced in an acetobutylic fermentation, butanol being the main interest product because of its superior properties making it a feasible substitute for fuels coming from fossil sources. In this work we have simulated and optimized under a rigorous scheme an integrated process to produce acetone, butanol, and ethanol from lignocellulosic biomass. Since ABE fermentation presents several hurdles such as low concentration broths or inhibitory effects during fermentation, here is proposed a hybrid simultaneous system of saccharification−fermentation−separation in which inhibition products during both fermentation and enzymatic hydrolysis are limited. A liquid−liquid extraction step is selected as the recovery technique. The reactor was modeled and simulated using Matlab software coupled with Aspen Plus which simulated the separation step. The entire optimization was developed taking into consideration several objective targets such as the total annual cost and some bioindexes involved in fermentation such as productivity, yield, and butanol concentration. Our results allowed us to find a feasible operative zone where all our objective targets were not compromised when the goal was the improvement of the process to produce biobutanol.



1. INTRODUCTION

During the acetobutylic fermentation process acetone, butanol, and ethanol (ABE) are produced, butanol being the main interest product. In the early twentieth century began the development of the platform for the ABE fermentation in response to a high demand in the production of acetone. This led, in 1916, to the use of the Weizmann process (by means of the microorganism *Clostridium acetobutylicum*) in the first industrial-scale ABE fermentations. A quick progress in petrochemical production during the second half of the twentieth century meant a decline in the use of ABE fermentation for obtaining butanol. However, the problems currently afflicting the energy sector (i.e., depletion of natural resources, climate change, environmental pollution, etc.) have led to a reappraisal of ABE fermentation for sustainable production of butanol, considered as a possible biofuel and increasing its demand. One of the main factors impacting its performance and total cost of production is the selection of the substrate to ferment. Since the strains of Clostridia are able to use a wide range of carbon sources this flexibility makes them excellent options for integration into biofuels production according to the cost-benefit of substrates which are the most suitable locally).[1] Traditionally several species of the Clostridium genus are involved in this fermentation process such as *Clostridium acetobutylicum*, *C. beijerinckii*, *C. saccharobutylicum*, *C. saccharoperbutylicum*, and *C saccharoperbutylacetonicum*.[2,3] These are strict anaerobic Gram-negative bacteria whose metabolic pathways carry out the ABE fermentation on two distinctly divided phases: acidogenesis (sugars are converted to acetic and butyric acids accompanied by a decrease in culture pH), and solventogenesis (sugars and some of the acids are metabolized into acetone, butanol, and ethanol, accompanied by an increase in culture pH).[3−6] Presently, the use of strains of *C. saccharoperbutylacetonicum* are preferred over other species due mainly for two characteristics: first, a higher yield and better butanol/acetone ratio (>4:1) in the final solvents mix;[8] and second, as mentioned above, its ability to ferment a great variety of substrates that could be enriched in glucose,

Received: October 31, 2016
Revised: January 16, 2017
Accepted: January 26, 2017
Published: January 26, 2017

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

saccharose, lactose, xylose, starch, glycerol, and many other sugars.[7]

A boost to the production of biobutanol would consist of two converging strategies: (1) A biological approach, engineering Clostridias' metabolic pathways for butanol hyper-production[8] and (2) the theoretical optimization and modeling of more efficient hybrid production-separation processes, such as that described in the present study.

This separation stage allows the resolution of two problems associated with the ABE fermentation. The first one is to withdraw the interest components in a continuous process which represents a great benefit such as to maintain the concentration of acetone, butanol, and ethanol in such levels to avoid any damage to microorganism. The second one is to avoid high water concentration which consequently prevents azeotropic formation. The ABE metabolic pathway in the Clostridia suffers substrate inhibition by glucose and xylose concentrations, and product inhibition by butanol concentration,[7] both of which represent big obstacles in strain growing, so that several restrictions must be faced including low yields during fermentation. Moreover, the correct selection of raw materials are also an important challenge. Considering a first generation raw material with high sugar concentration such as corn as a substrate would represent in practice 78% of the total production cost.[2] That is why lignocellulosic biomass seems to be a wise selection as raw material for fermentation considering its economic and environmental advantages in comparison with first generation raw materials.[3] Moreover, lignocellulosic biomass is currently considered a widely promising substrate during fermentation ABE by several authors.[9−14] Lignocellulosic biomass is composed mainly of cellulose, hemicellulose, and lignin. Before lignocellulosic biomass can be used, a biocatalytic pretreatment is necessary to reduce hemicellulose to xylose and decrease the crystallinity in cellulose.[15] After pretreatment, the biomass must be either chemically or enzymatically hydrolyzed.[16]

Enzymatic hydrolysis may offer several advantages over both physical and chemical mechanisms such as low byproducts, less energy requirements, and easier operative conditions. However, enzymatic hydrolysis represents also a huge inhibition by glucose and xylose concentrations.[15] One alternative which decreases inhibition is an integrated fermentation−saccharification (SSF) reactor; this option is more suitable since monosaccharides are simultaneously consumed during fermentation.[15]

During ABE fermentation using lignocellulosic biomass as raw material, these two integrated processes (SSF) may show additional advantages reducing the inhibitory effect of the final products in both the hydrolysis and fermentation processes. The SSF process shows an improvement generating better yields and minimizing energy requirements. Moreover, the main advantage of SSF is that both the bacteria and enzymatic complex involved in those processes reduce the presence of sugar inside the reactor. Consequently a better performance is observed and the saccharification rate is improved.

The inhibition caused by high butanol concentration in the fermentation process is also a big hurdle in this process; that is, when a concentration of butanol near 15 g L^{-1} is reached the fermentation process is completely inhibited. In this scenario, the low yields, the performance in reactors, and the high energy requirements during the entire process represent an obstacle that must be overcome. To improve the performance, several options have been currently proposed, one of them is the integration of both reaction and recovery processes. Using external units stimulates the purification because a wide range of temperatures can be used in the selective removal of components from the fermentation broth. However, when temperature is increased a higher number of equipment is required since either a cellular immobilizer or biomass recycler must be used. Considering the separation unit, diverse options have been proposed in order to remove all fermentation products. Yang et al.[17] proposed adsorption as a recovery technique, showing promissory results at the laboratory scale. Qureshi and Maddox[18] proposed liquid−liquid extraction as a good alternative to purify the ABE mixture. Moreover, pervaporation[19] and gas stripping[20] are also proposed as alternatives in order to remove and purify mainly the butanol produced in ABE fermentation. Despite all those approaches there is not a definitive separation technique: each of them have their advantages and disadvantages,[21] however liquid−liquid extraction has been reported as the recovery technique which exhibits the most potential to be used in butanol purification.[22,23]

On the other hand, since optimization techniques represent a very useful tool which helps improve several processes, its application in the fermentation process is mandatory. Sharma et al.[24] analyzed, under a multiobjective optimization approach, an integrated reactor with gas stripping and pervaporation to produce biobutanol having as objective targets the productivity, performance, yields, and sugars conversion. After their analysis they obtained an improvement using integrated reactors during fermentation, emphasizing an increase of the productivity and conversion of the integrated reactor. Further, Mariano et al.[25] optimized an ABE fermentation integrated with a flash unit and recycling biomass using genetic algorithms having as the objective function to maximize butanol production for an expected substrate conversion. Rohani et al.[26] performed a multiobjective optimization of a bioreactor integrated with pervaporation and gas stripping, highlighting its productivity and sugar conversion. However, note that a rigorous optimization applied to a hybrid process of saccharification−fermentation−separation (SFS) has been little studied. Furthermore, there is a similar situation in the study of the role that all variables included in this kind of process have.

Under this scenario, the aim of this study was to model, simulate, and optimize a continuous fermentation process. This process consists of two distinct sections: reaction and separation. For the reaction section we considered an integrated process in which 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. In this manner, this work is proposed as an intensified process since both saccharification and fermentation are performed in the same process unit. This intensification represents economic advantages and diminishment in inhibitory effects. Note this work is only focused in the reaction step which is the initial stage for all ABE production processes. However, this approach is quite complicated to solve and optimize since we are considering several variables involved in the optimization process, furthermore the fermentor model (showed as Supporting Information) is relatively complex and considers all compounds involved in ABE fermentation and its operative conditions. As results we obtain an effluent with the main ABE compounds coming from the fermenter under certain operative conditions obtained by means of a rigorous optimization process. This effluent may be further separated

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

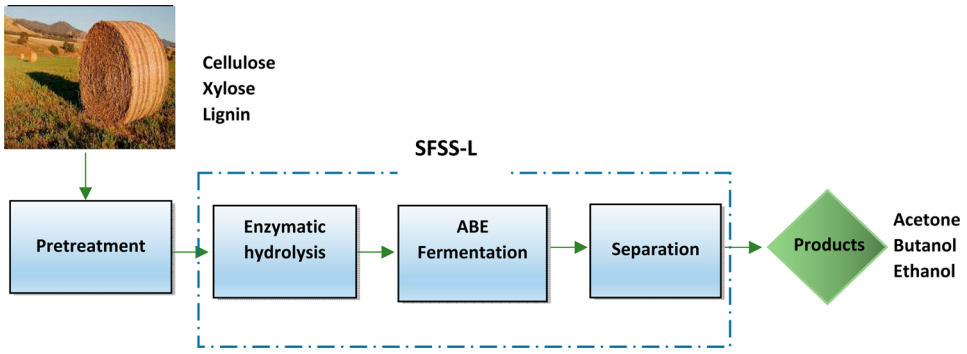


Figure 1. Simplified process flowsheet of biobutanol plant.

considering several alternatives already reported by several authors.[27,28]

The modeling of fermentation, saccharification, and extraction was developed in Matlab, the solvent recovery unit is modeled using Aspen Plus; and the optimization process is carried out using a stochastic optimization algorithm written in visual basic, both programs linked to each other.

The Differential Evolution with Tabu List has shown to be capable of solving complex nonlinear problems and potentially nonconvex. Further, through a reasonable computational time it is totally feasible to find solutions quite near the optimal solution.[29] By means of this optimization algorithm it was possible to obtain Pareto fronts of the integrated reactor through two proposed methods: first a biobjective optimization was performed to find the feasible operation zone, and finally a multiobjective optimization was performed to verify the influence and improvement by including several objective functions at the same time.

2. PROCESS DESCRIPTION

Currently, biobutanol is produced by fermentation using clostridium species. A simplified flowsheet is observed in Figure 1. We took as process parameters a continuous feed with constant sugar concentration. A volume of 1000 m^3 is considered. To control the fermenter volume, a purge is included in our model, having as a target to remove the nonreactant compounds and also avoiding inhibition concentrations inside the reactor. Also proposed is a feed flow with cellulose/hemicellulose/lignin which is varied according to the raw material until an optimal feed flow is found.

The presence of a mixed cell population (acidogenic cells, solventogenic cells, and spores) characterized by mutual interferences and the butanol production by means of one element of the cell population makes the design of a continuous reactor a complex task.

The fermentation−saccharification process has been modeled in Matlab taking into consideration a complex system which includes a rigorous mathematical model which describes adequately all metabolic reactions of the ABE pathway for *C. saccharoperbutylacetonicum*. Further, considering pH changes and the distinctive temperature profiles of this strain, a wide description of the model was described previously by Shinto et al.[30] (see Supporting Information). Starting from their model allowed us to predict a dynamic profile taking in 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.[30] described the effect of butanol at low−medium butanol concentrations considering those current 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.[31] The model was developed for two different substrates, either glucose or xylose, at the beginning of the metabolic route. The kinetic model involved in the saccharification process is taken from the study of Kadam et al.[32] (see Supporting Information). This previous work allowed us to account for the effect of both substrate and product inhibition. Also a competitive inhibition by xylose and enzyme adsorption is considered.

To calculate the volume of the reactor, all raw materials and reactions are included. This work considers the volume occupied by solids which produce areas without reaction. However, those solid materials must be eventually purged. The necessary purged flow (F_P) is obtained by calculating the difference between the initial volume and final increased volume due to solids, multiplied by a proportionality constant according to the operative ranges[32] which monitors the total volume (V_T). The overall balance of the integrated reactor is described as follows:

$$\frac{dCi}{dt} = R_i V_F + F_1 x_{1i} - F_p x_{Pi} + F_L x_{Li} \quad (1)$$

where Ci is the concentration of each component: butanol, ethanol, acetone, butyric acid, acetic acid, glucose, and xylose.

The simulation of a simultaneous saccharification−fermentation−separation (SFSS-L) is shown in Figure 2. This process is carried out in a pseudostable state (the reactor in transitory state and the liquid−liquid extraction unit in steady state). Also, 2-ethyl-1-hexanol was selected as the extractant agent because of its high partition coefficient, high selectivity, low cost, and appropriate medium boiling point.[34,28]

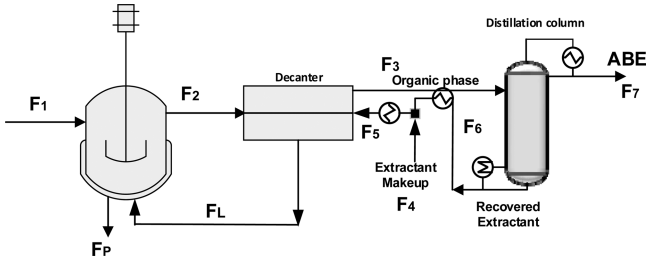


Figure 2. Schematic diagram of a continuous fermentation process coupled with a liquid−liquid separation unit and a column to recover extractant.

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

The compositions in liquid−liquid equilibrium inside the decanter are calculated as follow:

$$x_{\mathrm{I}i}\alpha_{\mathrm{I}i} = x_{\mathrm{II}i}\alpha_{\mathrm{II}i} \tag{2}$$

On the other hand, the flow reactor F_L (see Figure 2) is the calculated aqueous phase in the decanter; this flow in aqueous phase F_2 comes from reactor and might be calculated fixing a recycle rate on fermenter r_F of 0.95 according to

$$r_F = F_2/F\mathrm{p} \tag{3}$$

As an initial operative variable a cellulose feed of 46 g L^{-1}, avoiding substrate inhibition, is used. The reactor starts as a batch process and after 20 h the feed flow rate and purge flow starts; also the extractant agent is fed in the liquid−liquid extraction column.

The total fermentation time is simulated as 500 h; however, this time could be longer trying to avoid the loss of all material before steady state is reached.

3. OPTIMIZATION PROBLEM FORMULATION

The modeling and optimization processes offer several advantages when some economic index is evaluated since they allow us to identify many operative conditions for which economical improvements are reached. An optimization process can be used to find optimal operative conditions during a fermentation process integrated with a separation section. However, being that the ABE fermentation involves a complex set of equations highly nonlinear with degrees of freedom, using optimization algorithms may help to identify the optimal condition in this process.

First an optimization process considering only two objective function was performed. This biobjective optimization was performed to know the range of all operation variables and also know the impact of each target when it is evaluated against the total annual cost (TAC), which we considered as the most important target. Furthermore, this biobjective optimization will let us know certain zones where it is possible to operate the reactor without compromising any target.

Once both range variable and operation zone were known, a multiobjective optimization was performed facing all objective functions. This kind of optimization gave us a wider point of view since all bioindexes such as productivity, butanol concentration, and butanol yield are in conflict with the total annual cost. Also, this optimization process lets us know the best operative condition at fermenter without compromise of any objective function. All objective function are described below.

To optimize the TAC, the optimization problem might be written as follows:

$$\begin{aligned} &\min(\mathrm{TAC}) = f_1(D, E_N, E_{xt}, C_c, C_x, C_l) \\ &\text{s.t.} \quad \vec{y}_k \geq \vec{x}_k \end{aligned} \tag{4}$$

where D is the dilution rate (h^{-1}), E_N is the amount of enzyme added ($/kg biomass), and E_{xt} is the amount of extractant in feed stream.

The TAC has been calculated taking as base the methodology presented by Guthrie[35,36] as follows:

$$\mathrm{TAC} = \frac{\text{operating cos t}\left(\frac{\$}{\text{year}}\right) + \frac{\text{total investment }(\$)}{r\ (\text{year})}}{\text{annual ABE production}\left(\frac{\text{Kg}}{\text{year}}\right)} \tag{5}$$

Where r is the time of return of the investment. We considered 3 years.[33]

The total investment of process is given by

$$\text{total investment} = C_R + C_T + C_{IN} + C_{IE} \tag{6}$$

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

The annualized operative cost is calculated as follows:

$$\text{operating cos t} = C_E + C_V + C_{AE} + C_S + C_{ENZ} + C_{Ex} \tag{7}$$

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.

As has been told, we considered a stirred reactor of 1000 m^3. Only 0.7 of total volume is full in order to prevent high volume changes during a hypothetical control of the process. Despite the TAC being the main economic index, we used other targets simultaneously during the optimization process. The second objective function is written as follow:

$$\begin{aligned} &\max(\text{productivity}) = f_2(D, E_N, E_{xt}, C_c, C_x, C_l) \\ &\text{s.t.} \quad \vec{y}_k \geq \vec{x}_k \end{aligned} \tag{8}$$

The main reason for maximizing the productivity is to reduce the size of the reactor and consequently the production cost.[37] The productivity is defined as follows:

$$\begin{aligned} &\text{productivity } (P_B) = \frac{1}{V}(C_{B,3}MW_B F_3 + C_{B,p}MW_B(F_p)) \\ &\text{s.t.} \quad \vec{y}_k \geq \vec{x}_k \end{aligned} \tag{9}$$

Moreover, the yield evaluation let us know the amount of substrate converted in the interest product. Consequently it is possible to know the substrate cost during fermentation. Maximizing the yield is equivalent to minimizing biobutanol production. Further, maximizing the yield produces a minimization of biomass accumulated in the fermenter, which is totally desirable since the elimination of waste material is a serious problem.[36]

To maximize yield inside the fermenter, the third objective function is described as follow:

$$\begin{aligned} &\max(\text{yield}) = f_3(D, E_N, E_{xt}, C_c, C_x, C_l) \\ &\text{s.t.} \quad \vec{y}_k \geq \vec{x}_k \end{aligned} \tag{10}$$

where yield is defined in next equation:

$$\begin{aligned} &Y_B = \frac{C_{B,3}MW_B F_3 + C_{B,p}MW_B(F_p)}{C_{S,1}F_1MW_S - C_{S,p}(F_p)MW_B} \\ &\text{s.t.} \quad \vec{y}_k \geq \vec{x}_k \end{aligned} \tag{11}$$

Currently the main hurdle in the fermentation process is the low concentration in products. The main production cost is highly influenced by product concentration. Further, since the separation technique is also not efficient, maximizing biobutanol concentration is equivalent to minimize operative costs (reboiler heat duty and cooling water) in purification units such as liquid−liquid extraction column or distillation columns. In this manner our fourth and last objective function is described as follows:

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

$$\max(\text{butan ol concentration}) = f_4(D, E_N, E_{xt}, C_c, C_x, C_l)$$
$$\text{s.t.} \quad \vec{y}_k \geq \vec{x}_k \tag{12}$$

where butanol concentration is defined in next equation:

$$C_B = \frac{C_{B,3} MW_B F_3 + C_{B,p} MW_B (F_p)}{F_1}$$
$$\text{s.t.} \quad \vec{y}_k \geq \vec{x}_k \tag{13}$$

With all those objective functions a complex scenario could be observed since almost all our objective functions are in conflict to each other; under this behavior a multiobjective function would let us know several steady states in the fermentation process trying to reach high productivities, yields, and concentrations with as small as possible total annual costs. All objective functions are subject to several decision variables observed in Table 6.

4. MULTIOBJECTIVE OPTIMIZATION STRATEGY

To optimize the bioreactor to produce butanol, we used a stochastic optimization method, the Differential Evolution with Tabu List (DETL).[29] Stochastic optimization algorithms have been proven in several works to be able to solve highly nonlinear problems and potentially nonconvex problems, similar to variables involved in this work (shown[38,28] in Table 1). Those methods even have been tested in MINLP problems involved in other works.[39−41]

Table 1. Decision Variables and Their Ranges Used in the Multiobjective Optimization of a Bioreactor

decision variable	range used in optimization	variable category
dilution rate (D) h^{-1}	$0.001 \leq D \geq 0.1$	continuous
enzymes E_z (g-enzyme/kg-butanol)	$40 \leq E_z \geq 180$	continuous
solvent (E_x) kg-extractant/kg-butanol	$40 \leq E_x \geq 80$	continuous
concentration cellulose C_C g L^{-1}	$80 \leq C_c \geq 140$	continuous
concentration xylose C_X g L^{-1}	$50 \leq C_X \geq 100$	continuous
concentration lignin C_L g L^{-1}	$35 \leq C_L \geq 90$	continuous

DETL has its basis in natural selection theory, similar to genetic algorithms. In the DETL method it is possible to find some parameter such as initial population, size of Tabu List, crossover, and mutation. Srinivas and Rangaiah[42] showed that the use of some concepts of the metaheuristic tabu could improve the performance of the DE algorithm. In particular, the Tabu List (TL) can be used to avoid the revisit of search space by keeping record of recently visited points, which can avoid unnecessary function evaluations.

The implementation of this optimization algorithm is performed using a hybrid platform considering Microsoft Excel where the algorithm is programmed, Matlab where the bioreactor is modeled, and Aspen Plus where the separation unit is simulated. The vector of decision variables (i.e., the design variables) are sent from Microsoft Excel to Matlab using DDE (Dynamic Data Exchange) in which the bioreactor is simulated and gives the inlet streams to the separation unit. In Microsoft Excel, these values are attributed to the process variables that Matlab needs. After the simulation, Matlab and Aspen Plus return to Microsoft Excel the resulting vector. Finally, Microsoft Excel analyzes the values of the objective function and proposes new values of decision variables according to the stochastic optimization method used. To optimize our cases of study, we have used the following parameters for the DETL method: 120 individuals, 500 generations, a tabu list of 50% of total individuals, a tabu radius of 1×10^{-8}, and 0.85 and 0.5 for crossover and mutation fractions, respectively. These parameters were obtained through a tuning process via preliminary calculations. All the objective functions are subject to a range of values and restrictions of the decision variable described in Table 1. Those degrees of freedom were selected because of their importance in the ABE fermentation. Note that the variation in dilution rate directly affects several indexes such as productivity and product concentration; besides, the amount of enzyme determines the available sugars in fermentation and directly impacts the process cost, in the same manner that the amount of extract directly impacts the process cost because further recovery is necessary. Also the sugar and lignin concentrations fed to the system must be correct.

5. RESULTS AND DISCUSSION

5.1. Preliminary Biobjective Optimization Results. As mentioned in section 3, a biobjective optimization was initially performed to determine both range variable values and zones where it is feasible to operate the reactor without compromising any target. The results from this biobjective optimization process are presented in the Pareto fronts in Figure 3a. Note that Figure 3a shows both objective functions TAC and butanol concentration. When these two objective function are evaluated it appears they are in conflict, in other words, while butanol concentration grows the TAC increases too. The lowest butanol concentrations are obtained by using the lowest sugar concentrations and vice versa. However, note that an increase in sugar concentration implies an increase in the amount of enzyme, and consequently, the amount of extractant agent increases as well as the TAC. Approximately after 9.297 g L^{-1} the TAC value rises drastically. On the other hand, with low concentration values such as 7.6 g L^{-1}, the TAC values obtained are near 0.268 $/kg-ABE.

A deeper analysis can be carried out observing the values in Table 2. Basically, three areas in the Pareto front of Figure 3a can be noted. In the zone where higher TAC values are located a higher amount of butanol is produced if the dilution factor is increased; however, if this happens the amount of enzyme decreases, both behaviors producing a higher TAC. A contrary behavior is obtained in the zone where the smallest TAC values are.

On the other hand, in the middle zone of the Pareto front both objective functions converge. This zone is considered more feasible since the lowest values for both objective functions are obtained. The average amount of butanol produced is 9.3 g L^{-1} approximately with a TAC value of 0.282 $/kg-ABE.

Another relevant index in the fermentation process is the productivity, which must be optimized for increasing the performance of the process. After this biobjective optimization process it was possible to obtain the Pareto front in Figure 3b; in this Pareto front the productivity was evaluated bearing in mind the total annual cost. It is possible to observe a similar behavior than in Figure 3a, in this case when productivity increases the TAC value increases as well. This behavior is resumed in the convergence zones showed in Table 4.

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

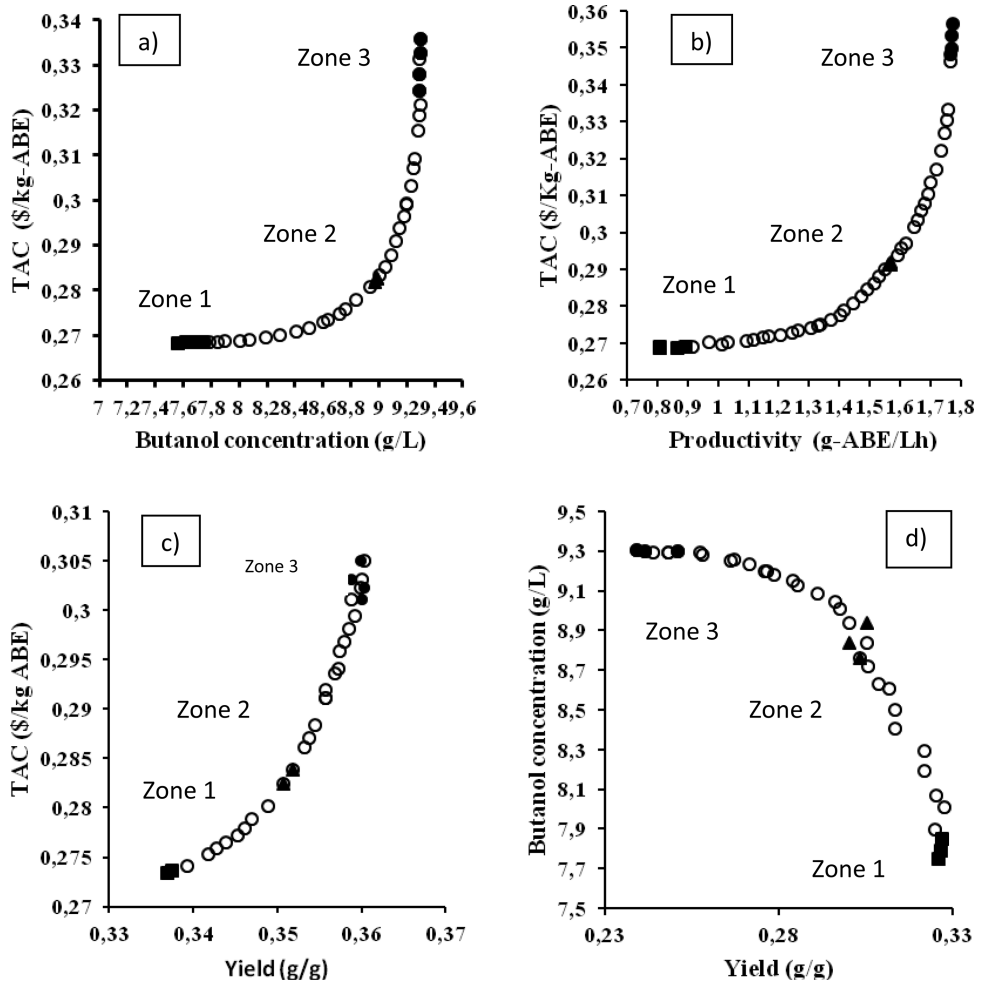


Figure 3. Pareto-optimal fronts obtained of biobjective optimization of TAC vs bioindicators.

Table 2. Results of the Biobjective Optimization Evaluation of TAC vs Concentration of Butanol at Representative Points of the Zones

	f_1	f_4	D	E_z	E_x	C_c	C_x	C_l
zone 1	0.26844	7.736	0.013015	195.592	42.603	90.22	89.96	45.69
	0.26830	7.565	0.012578	197.938	41.025	90.35	89.80	73.19
zone 2	0.28262	8.988	0.017524	193.249	40.370	90.56	89.97	46.11
	0.28244	8.983	0.017482	198.704	40.281	90.85	89.96	46.68
zone 3	0.33271	9.298	0.020445	184.685	40.256	121.71	88.73	45.73
	0.33583	9.303	0.020623	178.941	40.204	122.27	88.63	45.19

Table 3. Results of the Biobjective Optimization Evaluating TAC vs Conversion at Representative Points of the Zones

	f_1	f_3	D	E_z	E_x	C_c	C_x	C_l
zone 1	0.2686	0.3375	0.012205	195.836	41.30	90.39	89.79	75.32
	0.2684	0.3369	0.012913	191.788	43.27	90.81	89.99	70.33
zone 2	0.2821	0.3507	0.010010	149.568	55.77	128.38	89.88	74.03
	0.2819	0.3501	0.010011	160.037	56.34	129.54	89.75	77.80
zone 3	0.3168	0.3603	0.010047	80.231	78.49	119.64	78.02	79.75
	0.3204	0.360	0.010025	80.234	78.12	119.84	74.27	56.81

Table 3 shows several values obtained through the biobjective optimization process. In brief, if the sugar feed stream increases, the sugar concentration in the reactor increases, but the sugar conversion decreases. On the other hand if the rate conversion increases, the productivity increases as well; however, those two measurements are not able to reach high values because of substrate inhibition. In this way a feasible zone exists, where the best values of those two measurements are located. This zone can be found through a multiobjective optimization process.

Figure 3c shows the Pareto front obtained when sugar conversion is evaluated with the total annual cost. In this Pareto

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

Table 4. Results of Optimization Biobjective of TAC vs Productivity at Representative Points of the Zones

	f_1	f_2	D	E_z	E_x	C_c	C_x	C_l
zone 1	0.26860	0.865	0.01457	198.436	50.66	90.85	89.98	76.09
	0.26876	0.808	0.01369	190.450	46.43	90.77	89.60	72.29
zone 2	0.29194	1.570	0.03055	191.285	79.81	101.14	89.88	78.91
	0.29142	1.567	0.03064	188.726	79.91	98.95	89.81	78.27
zone 3	0.35640	1.773	0.03853	139.749	79.97	129.89	89.24	66.35
	0.34982	1.770	0.03781	139.707	79.90	128.56	89.24	79.84

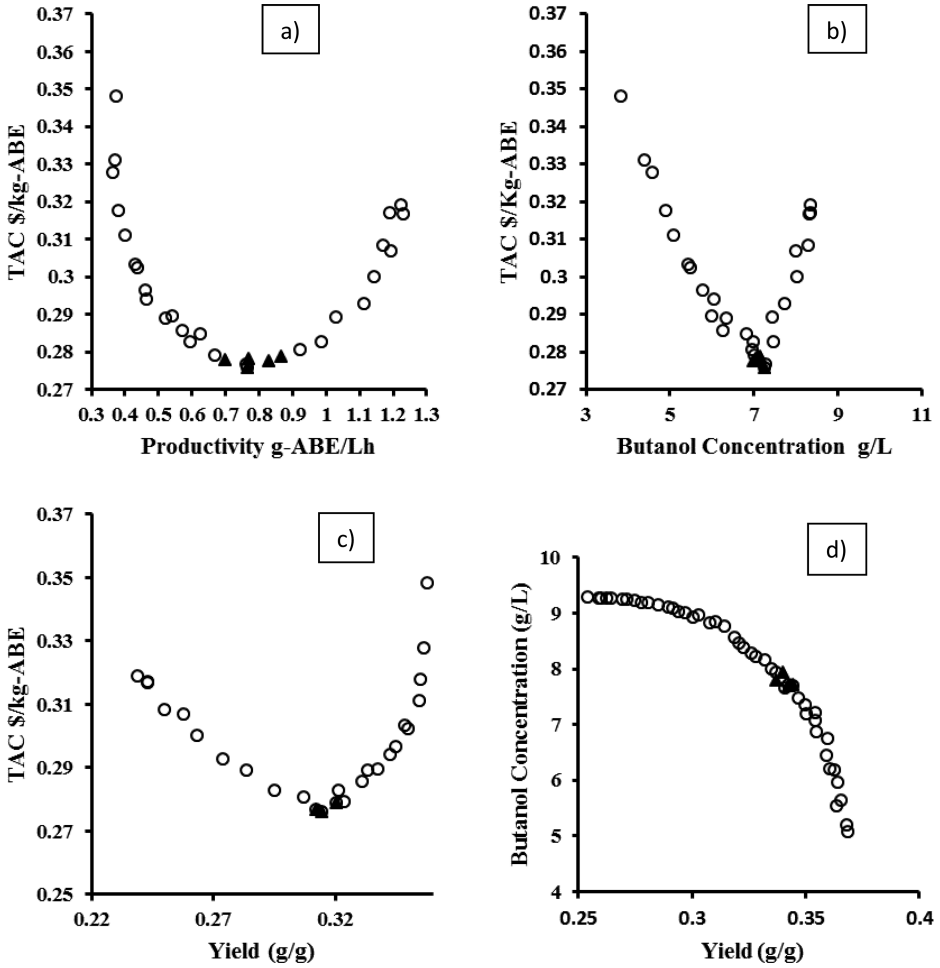


Figure 4. Pareto-optimal front obtained at 500 generations for the simultaneous minimization of TAC, maximization of butanol concentration, and productivity.

front, the decision variable which produces a great impact in conversion is the dilution rate. Note that is possible to obtain butanol with low prices; however, the conversion decreases notably. Also, it is observed that work with high dilution rates implies a higher amount of enzyme which implies more butanol produced; however, if there is more butanol the amount of extractant needed increases as well, increasing energy requirements in the separation unit.

On the other hand, when the dilution rate is set to increase, the butanol conversion implies that solvent requirements would increase in the separation unit, which obviously requires energy to separate the ABE mixture. In other words, work under the low dilution rate values produces higher residence time, which implies the addition of a lower amount of enzyme because the sugar takes more time to be fermented, subsequently more extractant and energy are required in the separation unit.

Finally, Figure 3d shows the behavior when yield and butanol concentration are evaluated. In this test it was possible to observe how difficult it is to obtain high butanol concentrations with high yield as well. Therefore, the operative zone must be selected according to the operative necessity, just as in all the cases already studied.

5.2. Multiobjective Optimization Results. In all results presented so far, it is possible to notice the role of each target against others during this optimization process. It was feasible to minimize the TAC when it is evaluated with several targets such as productivity, butanol concentration, and sugar conversion. However, since only two objective functions are involved in the optimization process, it is not possible to know the behavior of the other targets, which probably would generate a huge impact and several alternative scenarios. In this manner, a multiobjective optimization is mandatory since this

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

Table 5. Results of Multiobjective Optimization

objective functions				decision variables					
f_1	f_2	f_3	f_4	D	E_z	E_x	C_c	C_x	C_l
0.2760	0.766	0.3171	7.24	0.01527	199.03	45.15	80.58	79.92	70.75
0.2775	0.687	0.3169	7.46	0.01348	195.54	38.85	82.69	79.11	63.17
0.2772	0.770	0.3083	7.38	0.01527	199.03	45.15	83.03	79.74	54.03
0.2788	0.866	0.3191	7.13	0.01771	168.63	52.91	80.67	79.49	65.59
0.2782	0.792	0.3070	7.60	0.01598	176.71	43.86	82.85	79.96	62.34
0.2776	0.710	0.3191	6.84	0.01359	191.90	45.43	82.43	79.77	72.10
0.2782	0.818	0.3169	7.67	0.01673	199.03	45.15	83.03	79.74	55.06

process would let us know a more complete and more promissory scenario, where any targets would be compromised.

Further, it is clear that under the light of a multiobjective optimization process it is possible to find a zone of several states where it is totally feasible to operate the bioreactor without compromise to economic or productivity indexes.

Figure 4 shows the Pareto fronts after optimization. In those Pareto fronts all aforementioned objective functions are evaluated. Besides, note in Figure 4 some highlighted points that represent process designs with better values in all objective functions. The values of those states are in Table 5. It is clear that under a multiobjective optimization we know an operative zone where all those conflicting objective functions might reach a maximum or minimum without affecting other targets (see Figure 4). For example, probably a good operative point of the process could be near 0.2786 $/kg-ABE, with a productivity of 0.81 g-ABE L^{-1} h^{-1} and a concentration of 7.41g L^{-1}. Those values of this highlighted point are shown in Table 8.

Table 6. Parameters Used in Economic Evaluation

parameter	value	unit
low pressure steam	0.017	$/MJ
medium pressure steam	0.022	$/MJ
2-ethyl-1-hexanol	4.3	$/kg-extractant
cooling water	0.06	$/ton
electricity	0.12	$/Kwh
enzyme	1.22	$/kg-enzyme
operation time	8000	h
time of return investment (r)	3	year

Table 7. Operative Conditions at the Integrated Reactor with Liquid−Liquid Extraction

operation conditions	
temperature of the fermentation	30 °C
final fermentation time	500 h
initial glucose concentration	60 g L^{-1}
initial biomass concentration	0.1 g L^{-1}
maximum permissible biomass concentration	250 g L^{-1}
volume reactor	1000 m^3
reactor constraints	
maximum biomass concentration in the reactor	30 g L^{-1}
maximum butanol concentration	16 g L^{-1}

The results reported in this work represent a significant improvement in comparison with those presented by Mariano et al.[43] who reported an ABE concentration at reactor of 5.6−10 g/L and yields between 0.29 and 0.43 g/g. Rohani et al.[26] reported ABE concentrations at fermentor between 7.9 and 13.2 g/L. Diaz et al.[44] used a fermenter with vacuum evaporation, producing ABE productivities of 1.8 g/L/h, yield of 0.33 g/g, and a TAC of 0.57 US$/kg-ABE.

Moreover, note that at the end of this proposed fermentation, the obtained effluent could be separated and purified with several alternatives already reported in the literature.[27,28] However, electing any of all those scenarios depends totally on the necessity of production. In any case, the use of a multiobjective approach allowed us to know in a wider view several scenarios, considering interesting economic or productivity indexes.

As a brief summary of the interaction of our objective functions, note that high butanol concentration involves high performance and productivity. However, this scenario also requires an increase in the amount of enzyme, sugar, and extractant agent, producing a concurrent increase in the TAC (see Figure 5 and Table 5).

With respect to the optimal feed conditions, a ratio of 1.389/1.129/1 (cellulose/hemicellulose/lignin) must be fed to the integrated reactor to obtain the best objective function values. Nowadays this amount of sugars and lignin can be supplied combining some lignocellulosic raw materials already characterized such as corn fiber,[45,46] corn stover,[47] corn stalk,[46] rice bran,[48] rice straw,[49] barley straw,[45] wheat straw,[50−52] wheat bran,[53] switchgrass,[47] and cassava bagasse.[54] Furthermore, the extractant agent must be equal to 45 kg-solvent/kg-butanol. The optimal dilution rate is 0.01527 h^{-1} producing an optimal yield of 0.3144 g-ABE/g-substrate.

Moreover, Figure 5 shows the entire behavior of some important species involved in the bioreactor. This behavior belongs to the best point found in the multiobjective optimization where TAC is minimized, and productivity, butanol concentration, and performance are maximized. It is possible to observe that all species reach a state where their concentration remains almost constant. Further, the necessary time to reach this state might be neglected taking into consideration the total time involved in the operation. Also, the glucose concentration is kept at low values, avoiding substrate inhibition. Note we set 500 h as operation time. According to Figure 5 the equilibrium is reached before this time; however, this operation time helps us notice that indeed we did not obtain improved values after several hours. In Table 7 the fermenter operative conditions are shown for the simulation of reactor integrated with liquid−liquid extraction.

After performing this multiobjective optimization process and comparing the results with those obtained in the biobjective optimization, it is possible to note that when only two objectives are involved the scenario might not be so feasible in comparison when all targets are involved at the same time. For example, results from the biobjective optimization showed a scenario where it was possible to reach 9.3 g L^{-1} of butanol concentration and 1.75 g-ABE L^{-1} h^{-1} of productivity,

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

Table 8. Streams Results for the Optimized Solution

		wt %			
stream	ton/h	acetone	butanol	ethanol	extractant agent
F_1	102.3	0	0	0	0
F_2	63.1	4.30×10^{-04}	5.40×10^{-03}	8.60×10^{-04}	0
F_3	34.727	0.429	0.146	0.089	0.697
F_4	0.024	0	0	0	1
F_5	24.197	0		0	1
F_6	24.173	0	0	0	1
F_7	10.530	0.4292	0.4815	0.0893	0
F_P	91.770	4.30×10^{-04}	5.40×10^{-04}	8.60×10^{-04}	0
F_L	52.570	0	0		0

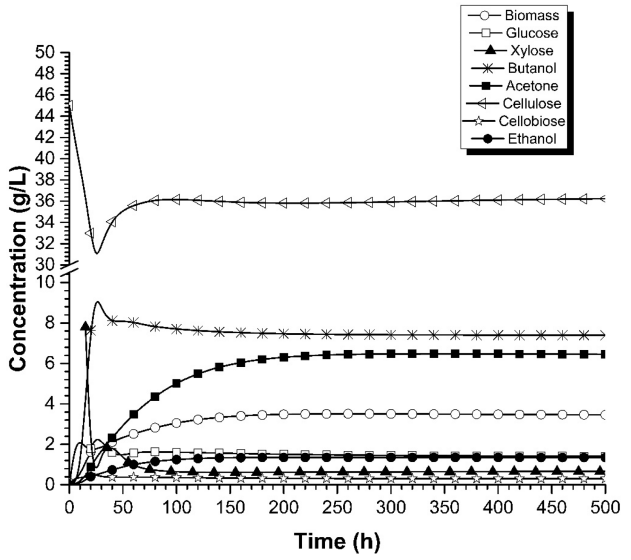


Figure 5. Concentration profiles of a reactor with simultaneous fermentation, saccharification, and separation.

respectively. However, when all objective functions are evaluated at the same time, those values were not observed in the Pareto front, probably because one or more objective functions could be compromised.

CONCLUSIONS

The reactor optimization integrating saccharification, fermentation, and liquid−liquid extraction to produce biobutanol in a semicontinuous process was possible using a hybrid stochastic optimization algorithm with several targets at the same time. Considering the results facing TAC against concentration we conclude that high concentrations are obtained only with high TAC values. The same tendency is observed evaluating productivity and performance against TAC. However, a multiobjective optimization evaluating all indexes showed a clear convergence tendency; that is, it is possible to find a feasible operative zone without compromising one target for another. In other words, the operative zone and operative variables in the reactor obtained after the optimization process consider the balance among all our objective functions in order to improve the performance of the ABE fermentation process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b04230.

Kinetic model; differential equations to describe the rate of all involved components during fermentation; list of fermentation model constants; metabolic pathway for xylose and glucose consumption (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors wish to acknowledge financial support from CONACyT for the development of this project and Universidad de Guanajuato for all the support.

NOMENCLATURE

D = Dilution rate (h^{-1})
X = biomass concentration (g L^{-1})
P_B = butanol productivity (g-ABE L^{-1} h^{-1})
V = fermenter volume (m^3)
MWi = molecular weight of species i (g/mmol)
C_B = butanol concentration (g L^{-1})
C_i = concentration of species i (mmol/L)
F_n = stream volumetric flow rate (m^3/h)
Y_{ABE} = yield (g-ABE/g-substrate)
R_i = reaction rate g L^{-1} s^{-1}
x_i = molar composition in the reactor
r_F = recycle rate in fermenter
E_n = amount of enzyme added($/kg biomass)
E_{xt} = extractant in feed stream
C_c = concentration of cellulose
C_x = concentration of xylose
C_l = concentration of lignin
C_R = reactor cost
C_T = column cost
C_{IN} = condenser cost
C_{IE} = initial investment
C_E = electricity cost
C_V = steam cost
C_{AE} = cooling water cost
C_S = substrate cost
C_{ENZ} = enzyme cost
C_{EX} = cost due to extractant lost
$\vec{y}_k$ = vectors of restrictions
$\vec{x}_k$ = vectors of restrictions

DOI: 10.1021/acs.iecr.6b04230
Ind. Eng. Chem. Res. 2017, 56, 1823−1833

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