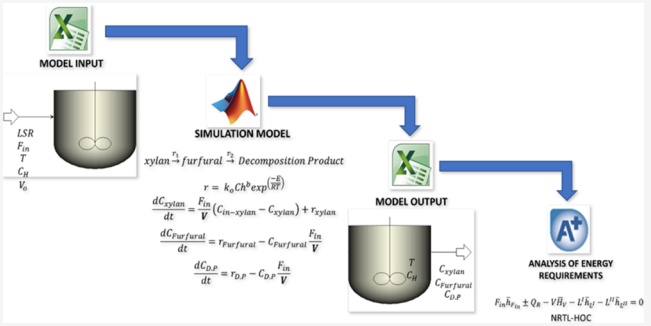
I&EC research
Industrial & Engineering Chemistry Research
pubs.acs.org/IECR
Article

Simultaneous Design and Controllability Optimization for the Reaction Zone for Furfural Bioproduction

Ana Gabriela Romero-García, Oscar Andrés Prado-Rúbio, Gabriel Contreras-Zarazúa, César Ramírez-Márquez, Jorge Humberto Ramírez-Prado, and Juan Gabriel Segovia-Hernández*

Cite This: *Ind. Eng. Chem. Res.* 2020, 59, 15990−16003

ABSTRACT: For sustainable production and consumption, emerging green technologies must be optimized in order to achieve a minimal environmental impact, a maximal economic impact, and dynamic behavior. The need for environmentally sustainable production and consumption is now one of the main developmental goals. To enable a more sustainable production in the chemical sector, new green chemical technologies from renewable feedstock such as furfural (a chemical compound produced from biomass used as a building block in the production of biofuels) are currently being developed. Furfural, a versatile chemical, is also employed as a solvent, an extractant base for fungicides, and a platform for other compounds. In this work, the simultaneous optimization of design parameters and control properties, which are highly relevant targets according to the principles of green chemistry, is performed within the reaction zone in the production process of furfural from biomass. The Differential Evolution with Taboo List algorithm (DETL) is used to carry out the multiobjective optimization. The total annual cost (TAC), eco-indicator 99 (EI99), and condition number, which represent the objective functions for a sustainable process, are combined as economic, environmental, and controllability criteria, respectively. Based on the results, the operating conditions found allow for an acceptable furfural production of 2014.4 kg/h, which reduce costs by 39% and its environmental impact by 42% in a system with satisfactory control properties compared to a case base.



1. INTRODUCTION

Over the past decades, the growing scarcity of fossil fuels and the expanding problems of greenhouse gases have raised concerns in the energy sector and in society as a whole. Therefore, research on the development of technology to exploit potential renewable fuel sources has become the focus. Biofuels are a promising initiative, especially in the transport area, which ensure a decrease in environmental problems while providing an opportunity to support the agricultural sector in certain regions.[1] As a result, the improvement of alternative renewable resources mainly biomass (the most abundant feedstock on Earth) has been fiercely promoted in recent years within the context of biorefineries.[2] One of the limitations of biomass conversion is that separation and purification technologies account for about 25 to 50%[3] of the total production costs of biorefineries. Consequently, there is still a need to improve the process design and operation of bioprocess technologies to decrease the total production cost while also aiming to reduce the environmental impact.

Biomass energy is produced from agricultural or forestry waste materials and energy crops harvested for this specific purpose. Biomass, composed of cellulose, lignin, and hemicellulose, represents more than 70% of Earth's biomass. It is for this reason that the utilization of this type of biomass is of special interest. Furfural is a key component derived from lignocellulosic biomass that provides a wide range of products with high added value such as fuels, polymers, lubricant oils, pesticides, insecticides, and composite materials, among others.[4]

The production of furfural is not new. Furfural, along with acetic acid and ethanol, is one of the oldest renewable chemicals produced from biomass; therefore, it does not have a petrochemical synthesis.[5,6] Furfural is produced from the dehydration of pentoses contained in the lignocellulosic biomass.[7] Industrially, there are two implemented technologies for furfural production. The first technology implements the depolymerization of pentosans and then the dehydration of the pentoses in furfural in two different steps that involve different process equipment. In the second technology, a single step

Received: May 4, 2020
Revised: August 4, 2020
Accepted: August 9, 2020
Published: August 9, 2020

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

carries out the depolymerization of pentosans in xylose, which is then dehydrated to furfural in a single vessel; this second option offers advantages in the economy of the process, avoiding an extra step in the biomass conversion with a lower furfural yield.[8]

Despite efforts made in the investigation of the furfural reaction mechanism, there is no well-established route toward maximum performance due to various side reactions that decrease furfural performance,[9] and few studies have researched efficient furfural production under different routes.[10,11] In the same line, the design of a furfural separation zone has been reported.[12] The importance of considering sustainability issues early in the design of intensified processes can help to differentiate between processes that are easy and processes that are difficult to operate. According to Jiménez-González et al.[13] and Thomassen et al.,[14] "green metrics" should be incorporated when designing a process toward the broader goal of environmental sustainability. Among these green metrics, the aspects of economic, environmental, and process control should be highlighted. Green chemistry principle #11 expresses a desire to have a real-time process analysis and monitoring in place. The aim of this principle is to prevent waste and safety issues (reflected in control properties) by identifying process excursions as they occur. By doing so, it allows process parameters to be modified in case the excursion might need to be reversed without any subsequent impact on safety and the final product's quality. Real-time analysis and process control are necessary to carry out this action. In this sense, there are no reports of the reactor optimization for furfural production under green chemistry concepts. In contrast, traditional chemical processes are designed by a sequential approach involving a sequence of decisions and evaluations. These processes are initially designed based on steady-state economic and sustainable calculations followed by the synthesis of a control structure that is generally based on heuristic controllability measures. Hence, the control system design only begins once the main features of the process have been established. This approach may sometimes lead to iterations between the process design and the control system design. It may also lead to poor dynamic operability in the face of disturbances and uncertainties. Although a closed-loop control system can be used to tackle the undesirable factors, including external disturbances and parameter or model uncertainties that affect the chemical process, studies in the literature[15] have shown that process design decisions may have a large impact on the process dynamics and the capability of the control systems. Improving the dynamic performance and functionalities of control systems is a key element in this case. Therefore, it is valuable and important to investigate the interactions between the process design and process control design and process operability to improve the dynamic performance of chemical processes at the early design stage. Optimization-based simultaneous design and control have two facets, the first one being research in basic principles, theories, and tools and the second one being research related to specific application domains. The strength of the optimization-based simultaneous design and control is the interplay between these two sides.[16] Therefore, in the case of the reactor for furfural production, the incorporation of these aspects addresses the reduction of excessive water use and high-energy consumption in the best dynamic behavior. In this work, the TAC as economic criteria, EI99 as environmental criteria, and condition number as controllability criteria were combined within a stochastic multiobjective optimization. Moreover, the model proposed shows the dynamic behavior of the system, yet there is no literature where the optimization of design parameters and simultaneous control for the furfural reactor are reported in an environment of sustainability. The assessment of the economic, environmental, and control potential is of major importance in the development of technology. In addition, it will only become more important as a transition is made to a more sustainable way of production and consumption. For this transition, information on the conductors of environmentally sustainable technologies is indispensable. The Differential Evolution with Taboo List (DETL) method is used to solve the mathematical problem in order to design the process including sustainability guidelines. By doing so, it aims to improve the reactor productivity in the reaction zone in the furfural production process from a more robust point of view. This aspect will help to reduce the use of excessive water and high-energy consumption during the subsequent processes related to furfural separation.

2. MODEL APPROACH

Furfural is obtained from biomass rich in pentoses. There are two steps in the reaction of furfural production. In the first step, xylan (from the hemicellulose as a raw material) is hydrolyzed to form xyloses. These xyloses are later hydrated to form furfural. Both reactions are catalyzed by an acid medium such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl).[17] The required acidity of the medium depends partially on the temperature, so both factors play an important role in the reaction kinetics for furfural production.

Different reaction models for furfural formation are reported in the literature, which vary from simplified to complex kinetics. The more complex model approach focuses on xylan fraction decomposition, which is divided into two parts: there is an easy and a hard way to hydrolyze xylose that then results in the formation of furfural, as a decomposition product.[18] On the other hand, Lu and Mosier[19] proposed two reaction models, the first one being a two-phase model similar to the one proposed by Mäki-Arvela et al.[18] and the second model is a Saeman-type reaction where hemicellulose hydrolysis is held. It is then followed by two successive first-order reactions.[20] In addition, Lavarack et al.[21] proposed three reaction models from a simplified Seaman-type reaction model to a complex reaction model like the one proposed by Mäki-Arvela et al.[18] Lavarack's model has the potential to provide similar results as it considers furfural in decomposition products. Recently, Bamufleh et al.[22] have proposed a simpler approach where furfural production can be represented as several first-order irreversible reactions under the assumption that the existing xylan in the raw material is susceptible to hydrolysate. Similar to the model proposed by Bamufleh et al.,[22] there are other works that show that the decomposition of xylan into xylose and other subproducts can be represented by a first-order irreversible reaction model.[23−25]

One of the difficulties of using kinetic models to describe a reaction evolution lies on the ability to identify the model parameters from the available experimental data. In this research, preliminary calculations showed the need to simplify the model using the available experimental data. The experimental data is taken from Bamufleh et al.[22] For the experiments, the date palm tree stem is used as a raw material with a composition of cellulose (glucan) 66.6 wt %, hemicellulose (xylan) 14.52 wt %, and lignin 13.72 wt %.

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

The model proposed in this contribution is analogous to the one proposed by Saeman[20] for the hydrolysis of cellulose catalyzed by dilute sulfuric acid. Here, furfural is obtained from xylan and furfural reacts to form the corresponding decomposition products such as methanol and acetic acid.[17] For simplicity, to increase identifiability parameters, decomposition products are condensed in a unique expression as shown in eq 1.

$$\text{xylan} \xrightarrow{r_1} \text{furfural} \xrightarrow{r_2} \text{decompostion product} \tag{1}$$

Equation 1 shows a simplified model for the formation reaction of furfural and decomposition products. There is a two-step reaction where in the first step, hydrolysis occurs to produce furfural followed by the degradation of furfural to decomposition products. In this model, the reaction rate r is given by eq 2, including temperature and acid concentration influence. Moreover, kinetic parameter values need to be defined.

$$r = k_o C h^b \exp^{(-E/RT)} \tag{2}$$

Due to the nature of the simplified model, a parameter estimation procedure is required. According to eq 2, there are six parameters to be estimated: two pre-exponential constants ($k_{o,1}$, $k_{o,2}$), two tunable parameters (b_1, b_2), and two activation energy parameters (E_1, E_2). For these six parameters, values from zero to infinite are considered as estimated limits. In order to perform the kinetic parameter tuning, batch experimental data obtained by Bamufleh et al.[22] were extracted and normalized to compensate differences in scales. The kinetic model parameters are estimated using the least weighted squares criteria using the trust-region-reflective method for constrained optimization.[26] This procedure requires the solution of the batch reactor model through the method for stiff differential equations. The model is implemented and solved in Matlab 2017b.

The model quality is assessed using reproducibility and identifiability analysis through the determination coefficient, correlation analysis, parameter sensitivity index, and collinearity index.[27] According to the reaction structure using a modified Arrhenius model, temperature T [K] and acid concentration C_H [wt %] play an important role in the reaction rate behavior. The operational constraints were 373−413 [K] for temperature and 5−15 [wt %] for acid concentration. Both constraints were taken from Bamufleh et al.[22]

To produce furfural, a continuous isothermal stirred tank reactor (CSTR) is employed as shown in Figure 1. At the

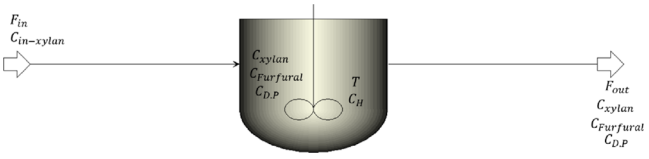


Figure 1. Representation of the CSTR reactor for furfural production.

entrance of the reactor, there is a feed flow F_{in} [kg/L] and the fraction of xylan at the entrance of the reactor $C_{in\text{-}xylan}$ [wt %], which depends on percentages of composition of lignocellulosic material contained in the raw material. Two other variables to consider are the temperature T [K] and the concentration of sulfuric acid C_H [wt %], and the manipulation of the acidity conditions and temperature play an important role in the reaction kinetics for furfural production.[17] Within the reactor, it is important to study the behavior that it will have during the reaction time: first, the degradation of raw material C_{xylan} [kg/L], as well as the formation of furfural $C_{Furfural}$ [kg/L] and decomposition products $C_{D.P}$ [kg/L].

The global mass balance is given by eq 3

$$\text{input} - \text{output} + \text{generation} = \text{accumulation} \tag{3}$$

Rewritten eq 3 in terms of process variables is expressed as indicated in eq 4. It should be noted that when dealing with a global mass balance, the generation term is equal to zero.

$$\rho F_{in} - \rho F_{out} = \frac{d\rho V}{dt} \tag{4}$$

For this case, the system presented is a diluted solution, so a constant density is expected; in doing so, the system is governed by the amount of water present. Thus, the overall mass balance is expressed as indicated by eq 5

$$F_{in} - F_{out} = \frac{dV}{dt} \tag{5}$$

For a continuous reactor, the input is equal to the output. This shows that there will be no volume variation with respect to time, so the volume will be consistent, making a mass balance by component. For xylan, eq 3 is taken as reference. The terms of variables corresponding to xylan are substituted, reaching the expression shown in eq 6.

$$F_{in}C_{in-xylan} - F_{out}C_{xylan} + r_{xylan}V = \frac{dVC_{xylan}}{dt} \tag{6}$$

where $F_{in}C_{in\,-\,xylan}$ represents the input, $F_{out}C_{xylan}$ represents the output term, $r_{xylan}V$ represents the generation where the term r_{xylan} is given by eq 2, and finally $\frac{dVC_{xylan}}{dt}$ represents the accumulation term. Having a constant volume in this case, it is taken out of the differential arriving at an expression, shown in eq 7.

$$F_{in}C_{in-xylan} - F_{out}C_{xylan} + r_{xylan}V = C_{xylan}\frac{dV}{dt} + V\frac{dC_{xylan}}{dt} \tag{7}$$

In eq 7, the term $\frac{dV}{dt}$ is replaced by eq 4, as is shown in eq 8.

$$F_{in}C_{in-xylan} - F_{out}C_{xylan} + r_{xylan}V = C_{xylan}(F_{in} - F_{out}) + V\frac{dC_{xylan}}{dt} \tag{8}$$

Performing the corresponding mathematical treatment, the mass balance for xylan is represented by eq 9.

$$\frac{dC_{xylan}}{dt} = \frac{F_{in}}{V}(C_{in-xylan} - C_{xylan}) + r_{xylan} \tag{9}$$

For the rest of the components, the mass balance was obtained following the steps shown from eqs 3 to 9 and by substituting the corresponding component terms.

The global energy balance was performed in Aspen Plus. To predict the energy required by the system, the NRTL-HOC model was used to predict the liquid−liquid−vapor phase formed.[27] The energy balance of the system can be represented according to eq 10.

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

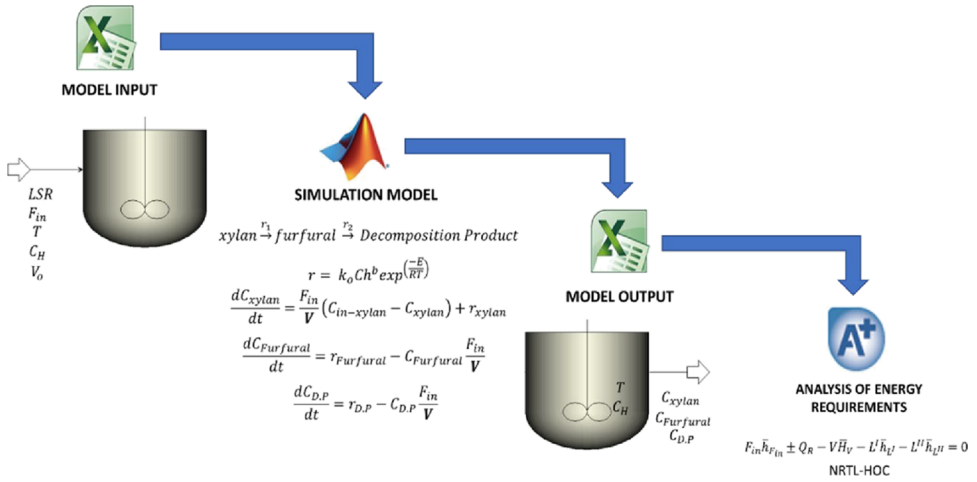


Figure 2. Software interaction used for reactor design.

$$F_{in}\bar{h}_{F_{in}} \pm Q_R - V\bar{H}_V - L^I\bar{h}_{L^I} - L^{II}\bar{h}_{L^{II}} = 0 \quad (10)$$

where $\bar{h}_{F_{in}}$ represents the enthalpy of the feed flow, V is the vapor flow phase formed, $\bar{H}_V$ is the enthalpy of the vapor phase, L^I and L^{II} are the two liquid phases formed, $\bar{h}_{L^I}$ and $\bar{h}_{L^{II}}$ are the two enthalpies corresponding to the two liquid phases, respectively, and Q_R is the heat duty. Here, Q_R was considered to be zero.

In order to model the reactor in the production of furfural, a software interaction between Microsoft Excel, Matlab, and Aspen Plus is used (Figure 2). First, initial values for the input variables are taken from Microsoft Excel and sent to Matlab where the mass balances are programmed. Once the mass balances are solved in Matlab, the values of the output variables are sent to Microsoft Excel to compile the output results with the input data. Afterward, the data collected is sent to Aspen Plus to calculate the energy balances. Once the energy requirements of the system have been obtained, this data is stored in Excel to start the reactor optimization (in the following section, a detailed explanation of the thermodynamics used in Aspen as well as the optimization methodology is given).

Usually, most of the optimization problems focus on finding design variables that minimize the total cost of the process and considering control properties independently. Flores-Tlacuahuac and Biegler[28] showed that the search for design conditions and control properties in a reaction system turns out to be a relevant optimization problem that needs to be resolved simultaneously. It is proven that design and control properties must be performed simultaneously since control properties affect the base design case.

According to Flores-Tlacuahuac and Biegler,[28] the reactor model is an appropriate case where control and design parameters are optimized simultaneously. Furthermore, the reactor system described as a case study presents continuous variables related to the design (i.e., feed flow, temperature, acid concentration, volume, and relation of solid and water). The model proposed features strong nonlinear behavior around optimal design regions as well as degrees of freedom.[28]

The model proposed in this work shows the dynamic behavior of the reaction system, yet there are no reported works in the literature where the design parameters and simultaneous controls are optimized for furfural reactors. In addition, simultaneous optimization of design and control parameters in furfural reaction processes is useful for possible industrial implementation.

3. OPTIMIZATION

As stated before, the proposed model is an appropriate case to be optimized since the reactor's design parameters and control properties are considered. It is also important to mention that the design of the studied reactor shows problems related to the immense consumption of water and energy to produce furfural. Moreover, because it is a bioproduct, the design of the equipment should be optimized under sustainable metrics and green chemistry standards. Likewise, the optimization of control properties will result in a sustainable and green process by increasing strict standards for furfural production and providing economic competitiveness by maximizing the efficiency of the process. Reliable indices are needed in an optimization of a process in the assessment of green chemistry. Although a number of reviews about green chemistry indices are available in the literature,[29,30] there are some works that report indices dealing with factors involved in evaluating the Process Greenness altogether. Moreover, there are few general agreements on methodologies and metrics to evaluate green chemistry. Therefore, a literature and standards analysis has been conducted in the search for green chemistry metrics, including advantages and limitations associated with their use.[31] It is expected that the analysis framework developed in this paper might contribute to the use of the indices to evaluate more than one aspect of green chemistry in order to integrate it into a based optimization on the Process Greenness.

The indices proposed in the development of green chemistry in this work are primarily related to the economy (TAC), the environmental impact measured (EI99), and the process controllability with the condition cumber (γ^*). These indices are taken into account since they represent the 12 principles of green chemistry.[31] On the other hand, Rafiei and Ricardez-Sandoval[32,33] have proven how to integrate different metrics as the indices can improve the sustainability due to inherent interconnection between different aspects of a process such as environmental impact, safety, profitability, energy-efficiency issues, etc. Thus, the contemplation of different metrics such as environmental impact, controllability, and economic issues provides an extensive outlook, which can help in the decision-making procedure. Multiple decision variables that affect operability of the process, lifetime of the project, and

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

economics of the process are simultaneously and commonly evaluated.[32] Finally, the indices considered in this work are described below:

3.1. Economy of the Process: Total Annual Cost (TAC). The TAC is an excellent indicator of the economy of a process since it relies on the product and on the characteristics of the process exclusively for informational and comparative purposes.[34] When the process is under development, it is necessary to have an estimate of the economic potential of the process. To achieve this, the TAC is used to quantify the economic performance of the process using eq 11.

$$\text{TAC} = \frac{\text{capital cost}}{\text{investment recovery time}} + \text{operation cost} \tag{11}$$

The Guthrie method was used to calculate the TAC.[35] The reactor cost and auxiliary equipment cost are included in the capital cost. Here, carbon steel is considered a construction material. All the parameters for the equipment and the utility costs were taken from Turton et al.[36] For the operating cost, the cost of steam and electricity were considered, assuming 8500 h/y operation. 10 years is employed for investment recovery time.

3.2. Environmental Impact Measured: Eco-Indicator 99 (EI99). EI99 is a methodology proposed by Geodkoop and Spriensma[37] as a quantitative life cycle analysis evaluated from beginning to end. This methodology accounts for the origin of the raw material in the process, processing, and degradation. It is based on the use of standard ecological indicators, which are numbers that express the total environmental burden of a product or a process. The higher the value of the indicator, the greater the environmental impact. This method is based on the evaluation of three categories:

The first category is human health; this set represents the span of an illness and years lost due to premature death because of environmental causes. The evaluated points in this category are carcinogenic effects, climate change, destruction of the ozone layer, radiation, and respiratory effects. The second category is the quality of the ecosystem, which shows the effects on different species. The effects it evaluates are ecotoxicity, acidification, and eutrophication due to land use. The third category is the depletion of resources, which refers to the surplus energy needed to extract mineral resources and fossil fuels. This part assesses fossil fuels and mineral extraction. Mathematically, EI99 can be expressed as shown in eq 12.

$$\text{EI99} = \sum_i \omega \cdot C_i \cdot \alpha \tag{12}$$

where ω represents the weight factor for the damage, C_i represents the impact value for category i, and α represents the amount of what is being evaluated. The unit used for EI99 is the eco-point, where 1 eco-point is representative of one thousandth of the annual environmental burden of an average European inhabitant.[38,39]

The EI99 index is a useful method to evaluate the general environmental impact related to chemical processes. It has been demonstrated in a study reported by Quiroz-Ramírez et al.,[40] where during the design phase, this methodology leads to significant improvements and waste reductions compared to the industrial installed processes. In the case of a reactor, the steam used to supply heat and the steel needed to build the equipment are the factors that have the biggest influence on EI99. Equation 12 is adjusted considering steam and steel supply as factors to be weighted. Equation 13 indicates the calculation of EI99 corresponding to the reaction system.

$$\text{EI99} = \sum_i \omega \cdot C_i \cdot \text{steam} + \sum_i \omega \cdot C_i \cdot \text{steel} \tag{13}$$

Table S1 shows the impact categories for EI99, as well as the values used in this study. These values were taken from the work reported by Geodkoop and Spriensma.[37] These values are associated and correspond to the use of steel for the construction of equipment and the use of heating steam.

3.3. Process Controllability: Condition Number (γ^*). The singular value decomposition (SVD) is a mathematical method used in the multivariable control theory as a measure of control properties of a dynamic system as a tool to quantify multivariable directionality as a function of frequency. The magnitude of singular values is associated with the system gains as the direction of the inputs is varied. This might relate to the "force" required by the inputs to move the system in a certain direction. On the one hand, the minimum singular value (σ_*) is associated with the direction where the system has more difficulties moving to. On the other hand, the magnitude of the maximum singular value (σ^*) indicates the easiest direction the system will move to.[41]

In order to maximize furfural concentration, it is necessary to have a higher consumption of raw material as well as to minimize the decomposition product concentration. Therefore, C_{xylan}, C_{Furfural}, and $C_{\text{D.P}}$ are selected as control variables. According to this model, xylan consumption equations, furfural equations, and decomposition product production equations are dependent on feed flow, temperature, and acid concentration. Therefore, F_{in}, T, and C_{H} are selected as manipulated variables.

The degree to which ill-conditioning prevents a matrix from being inverted accurately depends on the ratio of its largest to smallest singular value, a quantity known as the condition number (γ^*). The S matrix obtained from SVD is

$$S = \begin{bmatrix} \sigma_1 & & \\ & \ddots & \\ & & \sigma_n \end{bmatrix}$$

From both aforementioned values, γ^* can be obtained, and it is defined as the quotient between the maximum singular value and the minimum singular value as shown in eq 14.

$$\gamma^* = \frac{\sigma^*}{\sigma_*} \tag{14}$$

The condition number quantifies the sensitivity of the system to inaccuracies in process parameters and mode errors. Systems with small condition numbers present better control properties. Therefore, it is necessary to identify systems with high values of minimum singular value (σ_*) and low values of the condition number (γ^*). It is expected that these systems will have the best dynamic behavior. It is necessary to reiterate that the association of high condition number is due to ill-conditioning with poor control properties.

The obtained results are a function of frequency, which is why the cumulative value proposed is a helpful indication of what happens in the entire spectra. Shimizu and Matsubara[42] discussed the direction of combined disturbances in the frequency domain using the singular value decomposition. Skogestad and Morari[43] presented a similar analysis but also considered the direction of an individual disturbance. They

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

stressed that in multivariable systems, some disturbances may be difficult to reject if they are in the "bad" direction compared to the direction of the plant, and to quantify this, they introduced the disturbance condition number regarding input frequency, having better control properties at low frequency values.

For systems in a dynamic state, it is possible to evaluate the condition number (γ^*) as a function of the frequency. Cabrera-Ruiz et al.[44] proposed the methodology in which it is possible to evaluate the condition number in the entire domain of the frequency using the area under the curve, corresponding to a cumulative index.

Although the condition number is reported numerically, its interpretation is qualitative. It is not possible to know how good the control properties of a design are by the simple numerical value obtained. Its representation makes sense when compared with other designs. The design with the lowest value of condition number, compared to all comparative designs, is the one that presents the best control properties. Because of its qualitative representation, it is not possible to define a value from which a design has good control properties; therefore, in an optimization problem, the condition number should be considered as an index and not as a constraint.

3.4. Multiobjective Optimization Method. The method selected for optimizing the reactor is the Differential Evolution with Taboo List, also called DETL. The DETL is a stochastic global search technique where the search for the global optimum is carried out in all the feasible regions by an iterative procedure. The method was proposed by Srinivas and Rangaiah.[45] It has been proven to have several advantages over other optimization methods. For example, the DETL has a faster convergence of global optimum vicinity, smaller computational efforts, and less computational time to solve nonlinear and nonconvex problems than other methods such as genetic algorithms or simulated annealing. Other advantages of DETL are its abilities to memorize solutions and avoid the evaluations of solutions previously tested. These abilities reduce the computational time required to obtain the optimal solution.[45,46] The Differential Evolution with Taboo List has been applied successfully to a wide range of different problems in chemical engineering. For example, Bonilla-Petriciolet et al.[47] have evaluated the estimation of parameters of vapor−liquid equilibrium for different mixtures and have obtained outstanding results. Sharma and Rangaiah[48] applied the DETL optimization method for designing a biodiesel production process considering different objectives as profit and temperature of equipment. Ponsich and Coello[49] have used the DETL for the solution Job-Shop Scheduling Problem (JSSP) with exceptional results. Ramirez-Márquez et al.[50] applied the DETL method for tuning PI controllers in distillation columns obtaining distinctive results as well compared to traditional methods. Finally, Contreras-Zarazua et al.[51] and Vazquez-Castillo et al.[52] have implemented the DETL method successfully in the design of reactive distillations and conventional distillation columns, respectively, considering economic and controllability issues.

The DETL method consists of four basic steps based on the biological evolution theory. These steps are

(1) Initialization step: In this step, a random vector of possible solutions (x_i) is generated. The values of this random vector are constrained to the upper (max) and lower (min) bounds of each decision variable (i). These decision variables are arranged into two D-dimensional vectors, b_{max} and b_{min}. Finally, the vector of variables (x_i) is generated as follows

$$x_i^n = \text{rand}_i(0, 1)\cdot(b_{i,\max} - b_{i,\min}) + b_{i,\min} \tag{15}$$

where the rand (0,1) is a random generator constrained in the interval 0,1 and n is the number of generations considered to solve the optimization problem.

(2) Mutation step: This step consists of the generation of new vector sets, also known as donor vectors (v_i^{t+1}). The donor vectors (v^{n+1}) are created from three different vectors x_a, x_b, and x_c randomly chosen for each generation n. The mutation step can be summarized with the next eq 16

$$v_i^{n+1} = x_c^n + F(x_a^n - x_b^n) \tag{16}$$

where F is called differential weight, and it takes values in the continuous interval of 0−2. Differential weight provides stability and avoids the standstill of methods in similar solutions.[53]

(3) Crossover step: In the crossover step, the donor vectors (v^{n+1}) are combined with the vector of variables (x_i) generated during the initialization step. The objective of this step is to generate a trial vector (u_i^{n+1}). The crossover is carried out through a binomial scheme where the method randomly decides how each variable is exchanged with the donor vector. The mathematical formulation of the crossover step is as follows

$$u_{j,i}^{n+1} = \begin{cases} v_i & \text{if } (\text{rand}_{i,j}[0, 1]) \le Cr \\ x_i & \text{otherwise} \end{cases} \tag{17}$$

(4) Selection: Lastly, in the selection step, sets of vectors with the best fitness function values are chosen to be part of the next generation. This selection is executed as follows

$$x_{j,i,G+1} = \begin{cases} u_i^{t+1} & \text{if fit}(u_i^{t+1}) > \text{fit}(x_i^t) \\ x_i^t & \text{otherwise} \end{cases} \tag{18}$$

Additional DETL information is provided by authors such as Srinivas and Rangaiah.[45] The parameters used for DETL are given in Table S2; these parameters were taken from previous work of Rangaiah.[46] The parameters have been proven to work exceptionally well with nonlinear problems providing great results.[54]

3.5. Multiobjective Optimization Problem Statement. In this work, the TAC, EI99, and condition number are the objective functions to be minimized. Based on the previous information about the indices, a general mathematical expression for the objective function and its respective decision variables involved in the optimization procedure are shown in eq 19 as follows

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

$$\min[\mathrm{TAC}, \mathrm{EI99}, \gamma^*] = \begin{bmatrix} f(\mathrm{LSR}, F_{in}, T, C_H, V_0) = \dfrac{\text{capital cost}}{\text{payback period}} + \text{operating cost} \\ f(\mathrm{LSR}, F_{in}, T, C_H, V_0) = \sum_i \omega \cdot C_i \cdot \text{steam} + \sum_i \omega \cdot C_i \cdot \text{steel} \\ f(\mathrm{LSR}, F_{in}, T, C_H, V_0) = \dfrac{\sigma^*}{\sigma_*} \end{bmatrix}$$

$$\text{subject to:}$$

$$\vec{y_m} \geq \vec{x_m}$$

$$\mathrm{rank}(K) = n \tag{19}$$

where LSR is the liquid solid ratio, F_{in} represents the feed flow, T is the reaction temperature, C_H is the sulfuric acid concentration, and V_0 is the volume of the reactor. The optimization problem is constrained in order to produce 2000 kg/h of furfural, a typical production size for a furfural production plant.[17] So, in this work, $\vec{y_m}$ represents the production vector obtained from furfural, while $\vec{x_m}$ is the vector that represents the required furfural production of 2000 kg/h. Bigger plants are not recommended since they are required to transfer greater amounts of heat and utilize greater equipment.

The second constraint (rank $(K) = n$) shows that the optimization problem is limited to analyzing only designs that comply with Kalman controllability criteria. It can be known if a system has complete controllability from the construction of Kalman controllability matrix K, which is constructed as shown in eq 20.

$$K = [B \vdots AB \vdots A^2B \vdots \cdots \vdots A^{n-1}B] \tag{20}$$

where A and B represent the state-space and n represents the order of the system indicated by the number of state variables in the system. The system is completely controllable if the range of the controllability matrix is equal to n.[41] This constraint avoids the evaluation of a noncontrollable design, thus reducing the computational time.

Finally, the bounds of decision variables considered in this work are reported in Table 1. These bounds were determined based on physical restrictions reported by Turton et al.[36] and the experimental data conditions provided by Bamufleh et al.[22] This optimization problem was solved using the DETL method due to its availability to solve strong nonlinear equations with a low computational cost.

Table 1. Design Variables Considered for the Multiobjective Constrained Optimization

variable	type variable	symbol	range	unit
liquid solid ratio	continuous	LSR	1−15[22]	mL/g
feed flow	continuous	F_{in}	$(1 \times 10^3$ to $6 \times 10^6)$[22]	kg/h
temperature	continuous	T	(373−413)[22]	K
acid concentration	continuous	C_H	(5−15)[22]	wt %
volume	continuous	V_0	(300−520000)[36]	L

3.6. Multiobjective Optimization Implementation.

For the implementation of the DETL method, it is necessary to use a hybrid platform, which implies a link between Matlab, Microsoft Excel, and the Aspen Plus process simulator. The optimization algorithm is programmed in Excel through a Visual Basic macro as indicated in Figure 3.

Figure 3. Software interaction used for the hybrid optimization platform.

First, the design variables are specified in Microsoft Excel. Using the DETL algorithm programmed in Excel through a Visual Basic macro, the initial values that begin the optimization are randomly selected according to the methodology provided in the last section.[44]

(1) These initial values are sent to Matlab where they are evaluated, and the kinetic model is solved. The system controllability is used as a first checkpoint to determine if a design can pass onto the next stage of optimization.
(2) Controllability is defined by Kalman as the process ability to reach and maintain the desired equilibrium value, so a system is in a "fully controllable state" if it is possible to transfer the system from an arbitrary initial state to any other desired state in a finite time interval.[41] This can be determined if the rank of the Kalman controllability matrix is equal to the number of state variables, as explained above. When this is the case, the resulting state vector is returned to Microsoft Excel to collect the data. Otherwise, according to the definition of Skogestad and Postlethwaite,[41] if the rank of the Kalman controllability matrix is different from the number of state variables, the system is considered uncontrollable. A mode is called uncontrollable if none of the inputs can excite the mode. When this occurs, the program is reset to the first step.
(3) The resulting mass balances are then sent to Aspen Plus, where the analysis of energy requirements of the process is performed. In this step, Aspen Plus is used to predict the liquid−liquid−vapor equilibrium that exists in the mixture of components. The thermodynamic model used is the nonrandom two-liquid model with the Hayden−O'Connell state equation (NRTL-HOC), which considers the two liquid phases, the dimerization characteristics, and the interaction of mixtures with acids.[55]

The advantages of implementing Aspen Plus in this step of the optimization are that it reduces calculation times and provides the properties, which are useful in the prediction of balances.

(4) The resulting vector obtained in Aspen is returned to Microsoft Excel. Finally, taking all the resulting data, the values of the objective functions are analyzed, and new values are proposed for the decision variables according to the DETL algorithm.

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

3.7. Methodology Summary. In this section, a methodology summary is presented. Figure 4 explains the necessary

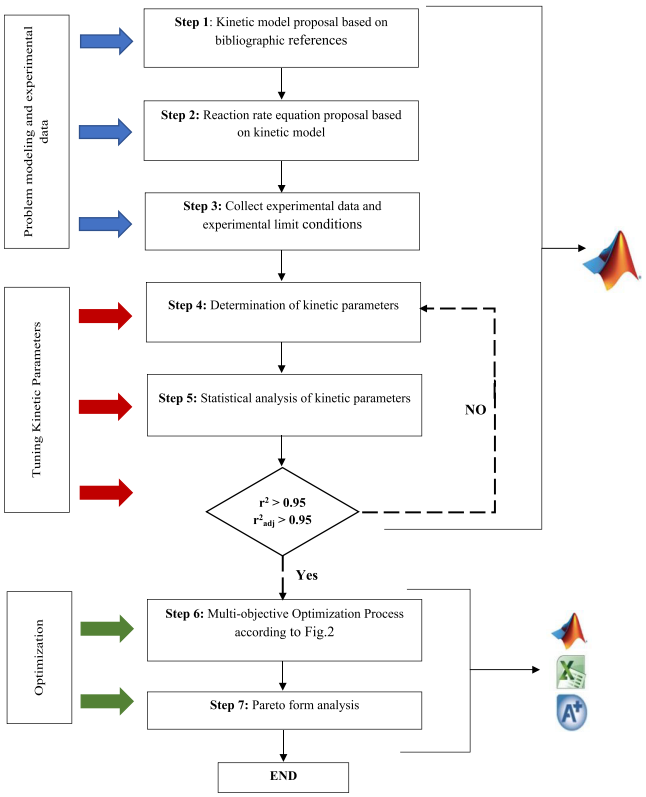


Figure 4. Methodology summary.

workflow needed to achieve multiobjective optimization for a furfural production reactor. It is presented systematically from the experimental data modeling the optimization process, both of which are explained in detail above.

4. RESULTS AND DISCUSSION

In the following section, the results obtained are presented. First, the analysis of the results obtained from the kinetic parameter adjustment is presented. A comparison of the proposed model to the experimental data reported is presented. Subsequently, the analysis of the designs obtained in the optimization is shown, being the minimization of costs, environmental impact and condition number as the control criterion its main objective functions. Finally, the comparison of the optimal design between two designs at the extremes of the Pareto fronts is presented.

4.1. Tuning Kinetic Parameters. The results of the practical parameter identification procedure are shown in Table S3. Taking the experimental data from the literature reported by Bamufleh et al.,[22] the kinetic parameters are estimated using mathematical and statistical tools according to the methodology proposed by Prado-Rubio.[56] The methodology used consists of a numerical method for large-scale optimization based on the interior reflective Newton method for nonlinear minimization subject to bounds. This method is available in Matlab using the function "lqscurvefit".[56] The developed kinetic model is employed to achieve the best furfural productivity, with lower cost, environmental impact, and best control properties.

From the statistical analysis, just 29.83% (Parameter Identifiability fraction) of the parameters reported by Bamufleh et al.[22] have an impact that represents the trend of the experimental model. Therefore, in the simplified model proposed in this work, the reduction of the number of parameters is considered so that each estimated parameter has a greater weight over the model, thus better representing the experimental data reported in order to avoid over fitting.

Figure S1 shows different experiments (1st to 7th) for furfural formation (black circles) compared to the trend the graph gives when using estimated kinetic parameters (indicated in the blue line). For the reported experiments, Bamufleh et al.[22] reported that different combinations of T, C_H, and LSR were made to represent the trend of the experimental data. The red dotted lines correspond to the nonsimultaneous functional confidence interval of the predictor. It can be seen that in the 1st, 4th, 5th, 6th, and 7th experiments, the model reproduction is acceptable achieving a global adjustment of the estimated parameters with respect to the experimental data of 96% (r^2_{adj}). In the 2nd and 3rd experiments, the reproduction of experimental data shows some problems. The experimental data is outside the predictor bound. Interestingly enough, the estimation results confirmed that the determination coefficient is a weak index to assess the nonlinear model capability to reproduce experimental data. Therefore, the following indicators are important.

By analyzing relative sensitivity of the model output toward each identified parameter (shown in Figure S2), it can be observed that the most representative parameters are the activation energies and the acidity power; thus, these are the parameters that can be estimated in a more reliable way from the experimental data. This is confirmed by the acceptable parameter confidence intervals. The collinearity index indicates in a quantitative way which parameters are to be estimated from the available experimental data and hence the degree of model overparameterization and/or information quality of the experimental data.[27] For the purposes of this work, although it was impossible to obtain the best parameters, these parameters that were estimated can be used in the design of a reactor to produce furfural and its decomposition products. To improve model parameters significance, interpretability and substantial experimental work must be performed.

4.2. Multiobjective Optimization. In this section, the main results obtained from the simultaneous optimization of the design and control parameters of a reactor to produce furfural are presented. The economic, environmental, and control criteria as objective functions are considered as well. The results obtained comply with the production restriction of furfural (2000 kg/h). The optimization process required 537 h in a Dell Power Edge T420 computer with an Intel Xeon E5-2420 processor with 2.2GHz and 16 GB RAM.

To represent the main results of the solution in the case of the reactor in furfural production from biomass, Pareto fronts are used to identify the best option to produce furfural with respect to the multiobjective function. The points studied on the Pareto fronts correspond to the 120 individuals of the 710 generation (last generation). After this generation, there does not seem to be an improvement in the objective functions, which means that the results obtained are in the region of the optimal solution.

Each point presented on the Pareto fronts shown in Figures 5−7 represents a different design with its own operating conditions. As a result, an analysis of the optimal design is

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

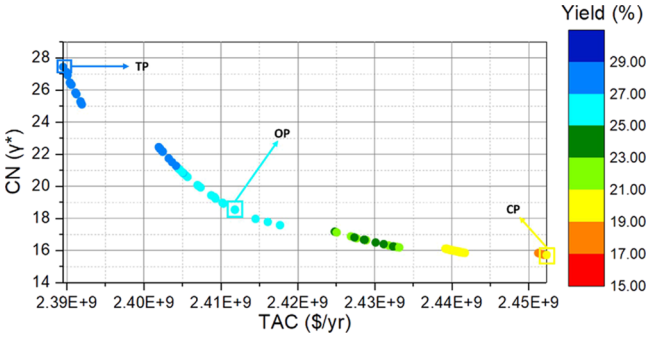


Figure 5. Pareto fronts between the condition number (CN), total annual cost (TAC), and furfural yield.

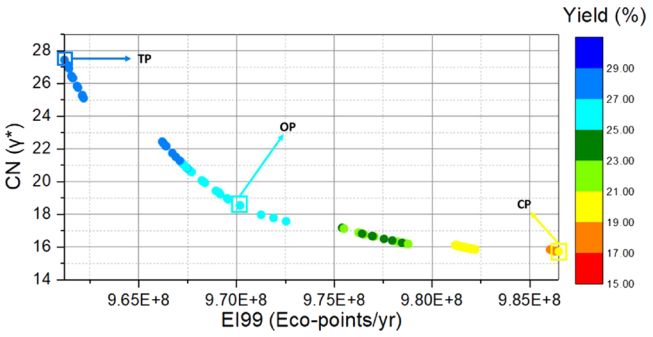


Figure 6. Pareto fronts between the condition number (CN), eco-indicator 99 (EI99), and furfural yield.

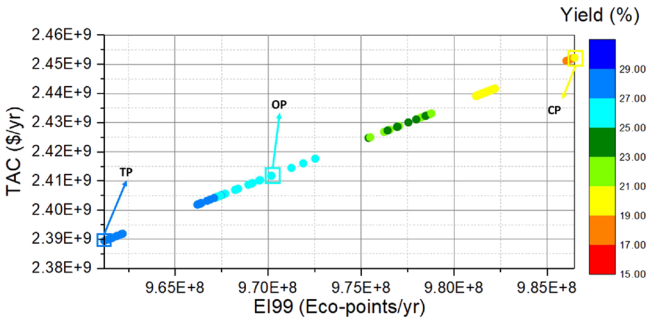


Figure 7. Pareto fronts between the total annual cost (TAC), eco-indicator 99 (EI99), and furfural yield.

shown with respect to other designs positioned at the extreme of the Pareto fronts. The two extreme points of the Pareto fronts are determined in a convex case, giving importance to only one of the objectives,[57] setting the two analyzed objectives in direct competition. For the designs located at the ends of the Pareto fronts, TP represents the design with the highest condition number and lowest TAC and EI99. The design CP represents the design whose conditions are opposite to those of TP with the lowest condition number and a higher TAC to EI99.

In selecting the best design, the concept of Pareto optimal and ″utopia point″ methodology were used. The Pareto optimal is defined by the relationship between the gradients of the objective functions, where the improving tendency of two objective function points is in an opposite direction to all of Pareto. The Pareto optimal point can be easily identified on the curve segment. Pareto points have no other point that improves at least one objective without damaging any other objective; that is, it is nondominated. A unique point is called the utopia point.[58] The utopia point is obtained by minimizing each objective function without regard for other objective functions. The utopia point corresponds to an ideal and a hypothetical solution, located on the edge of the Pareto fronts, where two objectives can no longer be improved, so both objectives are in equilibrium.[59] The design marked OP corresponds to the optimal design solution close to the point of utopia according to what was reported by Wang and Rangaiah.[59]

To simplify the analysis and have a better interpretation of the results, a comparison of the optimal design (OP) to the two other designs located at the extremes of the Pareto fronts (TP, CP) is shown in Table 2.

Table 2. Comparison of the Optimal Design Parameters for the Reactors to the Designs at the Ends of the Pareto

design variable	TP	OP (optimal design)	CP
design specifications			
reactor volume [L]	518201.39	518880.77	519838.69
diameter [m]	7.61	7.61	7.61
height [m]	11.40	11.41	11.42
operation specifications			
temperature [K]	402.94	411.26	412.89
acid concentration [wt %]	9.31	12.31	14.99
feed flow [kg/h]	705894.31	728422.31	764967.93
liquid solid ratio [mL/g]	11.48	10.497	7.86
total energy consumed [kW]	5557091.53	5608969.50	5703259.25
production			
furfural [kg/h]	2013.82	2014.4	2082.25
decomposition product [kg/h]	1010.94	1731.6	2191.96
furfural yield [%]	27.74	25.43	19.12
objective functions			
utilities cost [million$/yr]	2389.16	2411.46	2452.02
equipment cost [million$/yr]	0.331	0.322	0.294
TAC [million$/yr]	2389.491	2411.786	2452.297
EI99 [million eco-points/yr]	961.189	970.162	986.471
CN	27.45	18.55	15.72

To explain the data reported in Table 2, an analysis of the Pareto fronts is performed, while the mass yield percentage is shown in a color mapping. The corresponding diagrams are presented afterward: (a) condition number (γ^*) vs TAC, (b) TAC vs EI99, and (c) condition number (γ^*) vs EI99. It is important to state that the optimal design is marked as OP and that it corresponds to the same design point in the three Pareto fronts shown below.

The Pareto fronts presented have a discontinuous trend. This is because the designs obtained in these holes were discarded as they were considered "uncontrollable" according to the Kalman controllability matrix. A design is uncontrollable when the combinations of input variables have no effect on the outputs;[41] thus, these points are discarded according to the established restriction and do not enter the optimization.

4.2.1. Condition Number (γ^*) vs Total Annual Cost (TAC). Figure 5 shows the tradeoff between the condition number applied to a frequency range and the TAC. It is possible to observe that there is a direct influence of the design parameters

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

on control properties as well as on the TAC, which shows an antagonistic behavior. In order to have the best control properties, it is necessary to have an increase in the TAC.

To explain this trend, it is necessary to make a comparison between OP, TP, and CP designs. Design variables (reactor volume) and operation variables (temperature, acid concentration, and feed flow) are both related to the costs and control properties.

Relating the variables to the TAC, it is possible to see that when there is an increase in temperature, it also represents an increase in the energy duty needed to heat the reactor that implies an increase in operating costs and heating services. This produces a direct increase in the TAC. In the case of acid concentration and feed flow, when there is an increase in both conditions, it will also generate an increase in the utilities cost of the process, which also generates a direct increase in the TAC. From Table 2, it is possible to observe that the CP design presents an increase in temperature, acid concentration, and feed flow compared to the OP design. By having an increase in these variables, the total energy consumed increases and therefore so do the utilities costs. This has a direct impact on the TAC. In the case of the TP design, the opposite scenario is presented. By having a lower temperature, lower acid concentration, and feed flow required, the TAC will be lower.

The volume of the reactor has a direct influence on the TAC; bigger volumes require bigger equipment and, therefore, more construction materials. This results in a direct increase in the cost of equipment. From Table 2, the CP design has the highest TAC because it is the model with the biggest volume. Contrary to the TP design when the reactor has a lower volume, the TAC is also lower.

Relating the design and operation variables to control properties, it has been mentioned that the manipulative variables are temperature, acid concentration, and feed flow; therefore, any alteration directly affects control variables (furfural production), which also affect, in this case, control properties. This means that when increasing the temperature of acid concentration (within the established limits), the process will have higher furfural production and better control properties. If there is a decrease in temperature, the condition number will increase. This indicates that designs with low temperatures have poor control properties when compared to those that work at high temperatures. This can be corroborated with what was reported by Zeitsch,[6] indicating that under conditions of low temperature, it is difficult to control the reaction rate.

Concerning design variables to control properties, an increase in volume implies bigger equipment. If volume is bigger, the condition number will be lower because disturbances have lower influences on the system. From Table 2, it is possible to see these tendencies. TP has a smaller volume than CP, but CP presents a better condition number. It is important to emphasize that the condition number is a qualitative comparative measure between designs. That is, this only works when making a comparison between designs, as in this case. The design that will have better control properties is the one with the lowest value of condition number compared to other designs. In contrast to the TAC, the best design is the one with the biggest volume (CP).

4.2.2. Condition Number (γ^*) vs Eco-Indicator 99. Figure 6 shows the relation between the condition number and EI99. It is possible to observe that there is an antagonistic behavior between both objectives. This antagonistic tendency is strongly influenced by design and operation variables. First, it has been mentioned that bigger volume translates to bigger equipment, and therefore, disturbances have a less influence on the system, and in return, the system will have better control properties. Furthermore, bigger equipment represents the need for more construction materials. An increase in steel as a construction material increases the sum for the eco-points, thus making the design less eco-friendly. It seems that in order to create a design with better control properties, this objective comes into competition when compared to the ecological index.

This tendency can be seen in Table 2; the CP design, with a bigger volume, is the one with better control properties, but it is also the design with the biggest sum of eco-points. Contrary to the CP design, the TP design has the smallest volume, the smallest sum of ecopoints, and is also the one with worse control properties.

Relating operation variables by increasing the temperature, there is an increase in the energy requirements of the process. Likewise, by having an increase in the acid concentration and the feed flow, there is an increase in the utilities cost. As it was mentioned, a bigger volume reactor requires an increment in steel as a construction material. Although the CP design is the one with the biggest furfural production, it has the worst environmental impact as it favors the production of decomposition products, with a lower furfural performance. By having a bigger production of decomposition products, more raw materials are required. All the cases represent a direct increase in the sum of eco-points, directly affecting EI99. Therefore, it is observed that the objectives of the CP design are in competition with the objectives of the TP design. In order to have the best control properties, it is necessary to have a process that is not so excessively eco-friendly. To have an ecofriendly process, it is necessary to make the process less controllable.

4.2.3. Total Annual Cost (TAC) vs Eco-Indicator 99 (EI99). Figure 7 shows the relation between the TAC and EI99. It is evident that there is no competition in the objectives. In both cases, the variables of both design and operation give weight to the cost and environmental objectives. It is possible to observe that both objectives present the same ascending linear trend. This trend can be explained by an analysis of the contribution of the utilities and equipment costs in the TAC (see Figure S3) and with the individual contribution by category in the EI99 (see Figure S4). From Figure S3, utilities cost impacts directly the TAC. Utilities are significantly related to heat vapor: as more heat vapor is required for the process, the utilities cost will increase and therefore the TAC will increase as well. From Figure S4, "fossil fuels" is the category that has the highest contribution in the sum of eco-points. The heating vapor of the process is related to this category: in order to have vapor, it is necessary to burn fossil fuels. As more steam is required, the amount of burning fossil fuel increases and therefore the sum of eco-points in this category will also increase. In this sense, EI99 and the TAC are affected in the same way. This may explain how both objectives will always have the same trend. That is, if the cost increases, so will the cost of EI99; in the same manner, if one decreases, the other one will also decrease. Despite the counterintuitive appearance of the results where a cheap process is also the option with the lowest environmental impact, note that the TAC and EI99 are strongly influenced by the energy consumption. It is because of this that both objectives have the same tendency. In this manner, the

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

simplification on the kinetic models is not considered a relevant tendency on these objectives. The more complex kinetic models have been proven to give similar results in the evaluation of different parameters in previous work.[60]

The behavior presented can be explained because both the TAC and EI99 are strongly influenced by the design and operation variables of the process. By increasing the temperature, there is an increase in the energy requirements of the process. Likewise, by having an increase in the concentration of acid and the feed flow, there is an increase in the cost of utilities. Finally, having a bigger volume reactor requires bigger equipment. An increase in the material requirements for the construction of the equipment will cause a direct increase in the cost of the equipment, utilities and, therefore, in the TAC and EI99.

Data presented in Table 2 shows that both EI99 and the TAC are directly affected by the size of the equipment, energy supply, and raw material. From CP design, it is demonstrated that by increasing the energy requirements of the process, acid concentration, and feed flow, these requirements will have a strong influence on EI99 that considerably increases the sum of eco-points to the environmental indicator in comparison to the TP design. In addition, having a bigger volume requires more steel to be used in the equipment, thus increasing the eco-points for the construction material. This trend is reported by Sánchez-Ramírez et al.[61]

The evaluation of economic and environmental indices of a process is of major importance for the development of new technologies. According to the principles of green chemistry, it is necessary to have greener and more sustainable processes. Likewise, this new design will only be accepted if the economic indicator is profitable.

From Figures 5−7, it has been reported that furfural has a low yield; Zeitsch reported that theoretically a maximum yield of 50% can be obtained.[61] However, it is well known that when experimenting, the yield tends to be lower. Based on experimental data on furfural production, Bamufleh and colleagues reported that it is possible to achieve a furfural yield of 11−15% of raw material from date palm tree stem residues.[22]

Based on Figures 5−7, it is possible to appreciate that of all the existing designs, the optimum design yield percentage of furfural ranges from 15 to 30% for an industrial production. In Figure 5, it can be seen that the optimal yield is 25.43%. Based on these results, it can be said that in addition to obtaining an optimal design for furfural production, the yield percentage could be increased compared to the 11−15% reported by Bamufleh et al.[22] in a nonoptimized process. The optimal design parameters are shown in Table 2.

Comparing the optimization results and the experimental data reported by Bamufleh et al.[22] with an experimental temperature of 413 K and acid concentration of 15 wt %, it is possible to achieve a furfural yield of 15%. As a result, from the optimized conditions, the optimal design presents similar temperature to the experimentally used value of 411 K with a decrease in the percentage of acid of 12wt %. Due to this, it is possible to achieve an improvement in furfural yield up to 25.43%. If so, the optimization will have a better performance by improving the operating conditions. This means that the energy consumption, acid concentration, and the ecological footprint will all be reduced. Finally, the proposed models are useful to show the potential of the desired process and the approach used. However, to achieve a more accurate prediction, it is recommended to have better experiment designs that will allow the acquisition of more accurate data to predict a better model. The presented model is only a simplification of complex kinetics.

5. CONCLUSIONS

In this work, a simultaneous design and optimization of a furfural synthesis reactor have been proposed. Different aspects of the process such as controllability, environmental impact, and economic issues are considered. The evaluation of different metrics provides a wide overview of how different variables can affect the sustainability of the process. Therefore, we have taken into account different metrics that aid in the evaluation and selection of the most sustainable process.[32] In order to fulfill the aim of this work, it was necessary to propose a kinetic model for furfural production based on the reported experimental data.[22] It was also necessary to estimate the kinetic parameters corresponding to the proposed model, where from statistical analysis, kinetic parameters were obtained. When implemented in the model, they were able to reproduce the experimental data in 5 out of the 7 experiments presented, having an adjustment of 96% of the estimated parameters with respect to the experimental data reported.[22] Thus, from the proposed model, it was possible to perform the dynamic optimization of design and control to produce furfural from date palm tree waste.

From the simultaneous optimization of control and design parameters, it was possible to obtain multiple designs where the furfural mass yield percentage was maximized. The cost and the eco-points were also minimized in a system with satisfactory control properties. According to the analysis of the designs at the extremes of the Pareto fronts, it can be observed that the objectives are in competition. Having a design with lower cost and lower environmental impact implies sacrificing control properties. Conversely, having a design with favorable control properties represents having a more expensive and eco-friendly design. Therefore, the design where the objectives are not in competition under the utopia point methodology is chosen as the optimal design.

The optimal operating conditions of the system found to be a temperature of 411.26 K and concentration of sulfuric acid with a weight of 12.31% allow for an appropriate control of the reaction. Under these conditions, it is possible to maximize the yield of furfural to 25.43% with a production of 2014.4 kg/h. These conditions represent an improvement in the yield of furfural compared to the experimentally reported ranges of around 11 and 15%[22] for nonoptimized conditions of costs, environmental effects, and control properties. It can be concluded that it is possible to solve the dynamic optimization problem, considering the simultaneous optimization of control and design parameters of the reaction zone for furfural production. The objective was to minimize the TAC, EI99, and the condition number as economic, environmental, and control criteria, respectively. In order to have sustainable production, emerging green technologies need to be optimized toward a minimal environmental impact and a maximal economic impact. Moreover, these designs will only be able to replace conventional technologies if they can economically compete with them.

To conclude, this work creates the opportunity for future research in the field. In order to improve the modeling efforts, it is necessary to generate a more suitable experimental data for the kinetic model that is currently under study. Furthermore,

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

kinetic models depend on the use of biomass, so research can be applied for other and more promising biomasses, as well as the raw material for furfural production. A cogeneration research of by-products in the same reactor and an economy-of-scale research can also be performed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c02261.

Values of EI99 impact categories for reactors. Parameters for the DETL method, kinetic parameters obtained from the adjustment of parameters. Representation of experimental data indicating the reliability of the proposed model. Sensitivity to the parameters identified for the simplified model. Contribution of utilities and equipment costs to TAC. Contribution of impact categories to EI99 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Juan Gabriel Segovia-Hernández − *Chemical Engineering Department, University of Guanajuato, Guanajuato, Gto., México 36005;* orcid.org/0000-0003-4175-9809; Phone: +52 473 732 0006x8142; Email: gsegovia@ugto.mx; Fax: +52 473 732 0006x1403

Authors

Ana Gabriela Romero-García − *Chemical Engineering Department, University of Guanajuato, Guanajuato, Gto., México 36005*

Oscar Andrés Prado-Rúbio − *Departamento de Ingeniería Química, Universidad Nacional de Colombia, Manizales, Caldas 170001, Colombia*

Gabriel Contreras-Zarazúa − *Chemical Engineering Department, University of Guanajuato, Guanajuato, Gto., México 36005*

César Ramírez-Márquez − *Chemical Engineering Department, University of Guanajuato, Guanajuato, Gto., México 36005*

Jorge Humberto Ramírez-Prado − *Centro de Investigación Científica de Yucatán, A. C., Unidad de Biotecnología, 97200 Mérida, Yucatán, México*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.0c02261

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by CONACyT, Universidad de Guanajuato, and Universidad Nacional de Colombia, sede Manizales.

■ NOMENCLATURE

B	tunable parameter
σ_*	minimum singular value
σ^*	maximum singular value
C_i	impact value for category
k_o	pre-exponential constant
$r_{D.P}$	decomposition products reaction rate
$r_{Furfural}$	furfural reaction rate
r_{xylan}	xylan reaction rate
$C_{D.P}$	decomposition product concentration
$C_{Furfural}$	furfural concentration
C_H	sulfuric acid concentration
$C_{in\text{-}xylan}$	initial xylan fraction
CN	condition number
CSTR	continuous stirred-tank reactor
C_{xylan}	xylan concentration
DE	differential evolution
DETL	Differential Evolution with Taboo List
E	activation energy
EI99	eco-indicator 99
F_{in}	feed flow
F_{out}	outlet flow
H_2SO_4	sulfuric acid
HCl	hydrochloric acid
K	Kelvin degrees
LSR	liquid solid ratio
r	kinetic constant
R	universal gas constant
SVD	singular value decomposition
t	time
T	temperature
TAC	total annual cost
TS	Taboo search
V_0	volume
wt %	weight percent
γ^*	condition number
α	amount of what is being evaluated
ρ	density
ω	weight factor for indicator damage

■ REFERENCES

(1) Owusu, P. A.; Asumadu-Sarkodie, S. A review of renewable energy sources, sustainability issues and climate change mitigation. *Cogent Eng.* **2016**, *3*, 1167990.

(2) N.R.E.L. *NREL*; 2015, http://www.nrel.gov/biomass/biorefinery.html, (accessed 01.10.19).

(3) Kiss, A. A.; Lange, J.-P.; Schuur, B.; Brilman, D. W. F.; van der Ham, A. G. J.; Kersten, S. R. A. Separation technology−Making a difference in biorefineries. *Biomass Bioenergy* **2016**, *95*, 296−309.

(4) Zeitsch, K. J. *The chemistry and technology of furfural and its many by-products*; Elsevier: Amsterdam, Netherlands, 2000; 3−71.

(5) Peters, F. N., Jr. The Furans: Fifteen Years of Progress. *Ind. Eng. Chem. Res.* **1936**, *28*, 755−759.

(6) Zeitsch, K. J. Furfural production needs chemical innovation. *Chem. Innovation* **2000**, *30*, 29−32.

(7) Anthonia, E. E.; Philip, H. S. An overview of the applications of furfural and its derivatives. *IJAC* **2015**, *3*, 42−47.

(8) Yang, W.; Li, P.; Bo, D.; Chang, H. The optimization of formic acid hydrolysis of xylose in furfural production. *Carbohydr. Res.* **2012**, *357*, 53−61.

(9) Li, X.; Jia, P.; Wang, T. Furfural: A promising platform compound for sustainable production of C_4 and C_5 chemicals. *ACS Catal.* **2016**, *6*, 7621−7640.

(10) Liu, L.; Chang, H.-m.; Jameel, H.; Park, S. Furfural production from biomass pretreatment hydrolysate using vapor-releasing reactor system. *Bioresour. Technol.* **2018**, *252*, 165−171.

(11) Martín, M.; Grossmann, I. E. Optimal production of furfural and DMF from algae and switchgrass. *Ind. Eng. Chem. Res.* **2015**, *55*, 3192−3202.

(12) Contreras-Zarazúa, G.; Sánchez-Ramírez, E.; Vázquez-Castillo, J. A.; Ponce-Ortega, J. M.; Errico, M.; Kiss, A. A.; Segovia-Hernández, J. G. Inherently safer design and optimization of intensified separation processes for furfural production. *Ind. Eng. Chem. Res.* **2018**, *58*, 6105−6120.

(13) Jiménez-González, C.; Constable, D. J. C.; Ponder, C. S. Evaluating the "Greenness" of chemical processes and products in the pharmaceutical industry—a green metrics primer. *Chem. Soc. Rev.* **2012**, *41*, 1485−1498.
(14) Thomassen, G.; Van Dael, M.; Van Passel, S.; You, F. How to assess the potential of emerging green technologies? Toward a prospective environmental and techno-economic assessment framework. *Green Chem.* **2019**, *21*, 4868−4886.
(15) Yuan, Z.; Chen, B.; Sin, G.; Gani, R. State-of-the-art and progress in the optimization-based simultaneous design and control for chemical processes. *AIChE J.* **2012**, *58*, 1640−1659.
(16) Cabrera-Ruiz, J.; Santaella, M. A.; Alcántara-Ávila, J. R.; Segovia-Hernández, J. G.; Hernández, S. Open-loop based controllability criterion applied to stochastic global optimization for intensified distillation sequences. *Chem. Eng. Res. Des.* **2017**, *123*, 165−179.
(17) Marcotullio, G. *The chemistry and technology of furfural production in modern lignocellulose feedstock biorefineries*. TU Delft, Delft University of Technology: Delft Netherlands. 2011, 30−59.
(18) Mäki-Arvela, P.; Salmi, T.; Holmbom, B.; Willför, S.; Murzin, D. Y. Synthesis of sugars by hydrolysis of hemicelluloses- A review. *Chem. Rev.* **2011**, *111*, 5638−5666.
(19) Lu, Y.; Mosier, N. S. Kinetic modeling analysis of maleic acid-catalyzed hemicellulose hydrolysis in corn stover. *Biotechnol. Bioeng.* **2008**, *101*, 1170−1181.
(20) Saeman, J. F. Kinetics of wood saccharification-hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature. *Ind. Eng. Chem.* **1945**, *37*, 43−52.
(21) Lavarack, B. P.; Griffin, G. J.; Rodman, D. The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products. *Biomass Bioenergy* **2002**, *23*, 367−380.
(22) Bamufleh, H. S.; Alhamed, Y. A.; Daous, M. A. Furfural from midribs of date-palm trees by sulfuric acid hydrolysis. *Ind. Crops Prod.* **2013**, *42*, 421−428.
(23) Grant, G. A.; Han, Y. W.; Anderson, A. W.; Frey, K. L. Kinetics of straw hydrolysis. *Dev. Ind. Microbiol.* **1977**, *18*, 599−611.
(24) Téllez-Luis, S. J.; Ramírez, J. A.; Vázquez, M. Mathematical modelling of hemicellulosic sugar production from sorghum straw. *J. Food Eng.* **2002**, *52*, 285−291.
(25) Aguilar, R.; Ramírez, J. A.; Garrote, G.; Vázquez, M. Kinetic study of the acid hydrolysis of sugar cane bagasse. *J. Food Eng.* **2002**, *55*, 309−318.
(26) Nocedal, J.; Wright, S. *Numerical optimization*; Glynn, P., Robinson, S. M., Eds.; Springer: New York, USA, 1999; 2−26.
(27) Brun, R.; Reichert, P.; Künsch, H. R. Practical identifiability analysis of large environmental simulation models. *Water Resour. Res.* **2001**, *37*, 1015−1030.
(28) Flores-Tlacuahuac, A.; Biegler, L. T. Simultaneous mixed-integer dynamic optimization for integrated design and control. *Comput. Chem. Eng.* **2007**, *31*, 588−600.
(29) Tobiszewski, M.; Marć, M.; Gałuszka, A.; Namieśnik, J. Green chemistry metrics with special reference to green analytical chemistry. *Molecules* **2015**, *20*, 10928−10946.
(30) Dicks, A. P.; Hent, A. *Green chemistry metrics: a guide to determining and evaluating process greenness*; Springer: Toronto, Canada, 2015; 69−87.
(31) Jiménez-González, C.; Constable, D. J. *Green chemistry and engineering: a practical design approach*; John Wiley & Sons: New Jersey, USA, 2011; 17−34.
(32) Rafiei, M.; Ricardez-Sandoval, L. A. New frontiers, challenges, and opportunities in integration of design and control for enterprise-wide sustainability. *Comput. Chem. Eng.* **2020**, *132*, 106610.
(33) Rafiei, M.; Ricardez-Sandoval, L. A. A trust-region framework for integration of design and control. *AIChE J.* **2020**, *132*, No. e16922.
(34) López-Maldonado, L. A.; Ponce-Ortega, J. M.; Segovia-Hernández, J. G. Multiobjective synthesis of heat exchanger networks minimizing the total annual cost and the environmental impact. *Appl. Therm. Eng.* **2011**, *31*, 1099−1113.
(35) Guthrie, K. M. Capital cost estimation. *Chem. Eng.* **1969**, *24*, 114.
(36) Turton, R.; Bailie, R. C.; Whiting, W. B.; Shaeiwitz, J. A. *Analysis, synthesis and design of chemical processes*; Pearson Education: New Jersey, USA, 2009.
(37) Geodkoop, M.; Spriensma, R. The Eco-Indicator 99. A damage oriented for life cycle impact assessment. Methodology report and manual for designers. In *Technical Report;* PRe Consultants: Amersfoort, Netherlands, 2001; 7−98.
(38) Errico, M.; Sanchez-Ramirez, E.; Quiroz-Ramìrez, J. J.; Segovia-Hernandez, J. G.; Rong, B.-G. Synthesis and design of new hybrid configurations for biobutanol purification. *Comput. Chem. Eng.* **2016**, *84*, 482−492.
(39) Mettier, T. *Der Vergleich von Schutzgütern-Ausgewählte Resultate einer Panelbefragung. tze zum Vergleich von Umweltsch*; ETH: Zurich, Switzerland, 1999.
(40) Quiroz-Ramírez, J. J.; Sánchez-Ramírez, E.; Hernández-Castro, S.; Segovia-Hernández, J. G.; Ponce-Ortega, J. M. Optimal Planning of Feedstock for Butanol Production Considering Economic and Environmental Aspects. *ACS Sustainable Chem. Eng.* **2017**, *5*, 4018−4030.
(41) Skogestad, S.; Postlethwaite, I. *Multivariable feedback control. Analysis and Design*; John Wiley and Sons: NJ, 2007.
(42) Shimizu, K.; Matsubara, M. Directions of disturbances and modeling errors on the control quality in distillation systems. *Chem. Eng. Commun.* **1985**, *37*, 67−91.
(43) Skogestad, S.; Morari, M. Effect of disturbance directions on closed-loop performance. *Ind. Eng. Chem. Res.* **1987**, *26*, 2029−2035.
(44) Cabrera-Ruiz, J.; Gabriel Segovia-Hernández, J.; Rafael Alcántara-Ávila, J.; Hernández, S. Optimal dynamic controllability in compressor-aided distillation schemes using stochastic algorithms. *Comput.-Aided Chem. Eng.* **2012**, 552−556.
(45) Srinivas, M.; Rangaiah, G. P. Differential evolution with Tabu List for solving nonlinear and mixed-integer nonlinear programming problems. *Ind. Eng. Chem. Res.* **2007**, *46*, 7126−7135.
(46) Rangaiah, G. P. *Stochastic global optimization: techniques and applications in chemical engineering*; World Scientific: 2010.
(47) Bonilla-Petriciolet, A.; Rangaiah, G. P.; Segovia-Hernández, J. G. Evaluation of stochastic global optimization methods for modeling vapor−liquid equilibrium data. *Fluid Phase Equilib.* **2010**, *287*, 111−125.
(48) Sharma, S.; Rangaiah, G. P. Multi-objective optimization of a bio-diesel production process. *Fuel* **2013**, *103*, 269−277.
(49) Ponsich, A.; Coello, C. A. C. A hybrid differential evolution—tabu search algorithm for the solution of job-shop scheduling problems. *Appl. Soft Comput.* **2013**, *13*, 462−474.
(50) Ramirez-Marquez, C.; Miranda-Galido, E. Y.; Segovia-Hernández, J. G.; Hernández, S. Tuning of PI controllers by Differential Evolution with Tabu List method. *Comput.-Aided Chem. Eng.* **2017**, *40*, 1633−1638.
(51) Contreras-Zarazúa, G.; Vázquez-Castillo, J. A.; Ramírez-Márquez, C.; Segovia-Hernández, J. G.; Alcántara-Ávila, J. R. Multi-objective optimization involving cost and control properties in reactive distillation processes to produce diphenyl carbonate. *Comput. Chem. Eng.* **2017**, *105*, 185−196.
(52) Vázquez-Castillo, J. A.; Segovia-Hernández, J. G.; Ponce-Ortega, J. M. Multiobjective optimization approach for integrating design and control in multicomponent distillation sequences. *Ind. Eng. Chem. Res.* **2015**, *54*, 12320−12330.
(53) Yang, X. S. *Nature-inspired optimization algorithms*; Elsevier: London, 2014; 23−42.
(54) Sánchez-Ramírez, E.; Quiroz-Ramírez, J. J.; Segovia-Hernández, J. G.; Hernández, S.; Ponce-Ortega, J. M. Economic and environmental optimization of the biobutanol purification process. *Clean Technol. Environ. Policy* **2016**, *18*, 395−411.
(55) Nhien, L. C.; Van Duc Long, N.; Lee, M. Process design of hybrid extraction and distillation processes through a systematic solvent selection for furfural production. *Energy Procedia* **2017**, 1084−1089.

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003

(56) Prado-Rubio, O. A. Integration of Bioreactor and Membrane Separation Processes: A Model Based Approach: Reverse Electro-Enhanced Dialysis Process for Lactic Acid Fermentation; Technical University of Denmark (DTU): 2010, 101−124.
(57) Brisset, S.; Gillon, F. Approaches for multi-objective optimization in the ecodesign of electric systems. In *Eco-Friendly Innovation in Electricity Transmission and Distribution Networks*; Woodhead Publishing: 2015; 83−97, DOI: 10.1016/B978-1-78242-010-1.00004-5.
(58) Chang, K. H. Multiobjective Optimization and Advanced Topics. In *Design Theory and Methods Using CAD/CAE*; 2015; 325−406, DOI: 10.1016/B978-0-12-398512-5.00005-0.
(59) Wang, Z.; Rangaiah, G. P. Application and analysis of methods for selecting an optimal solution from the Pareto-optimal front obtained by multiobjective optimization. *Ind. Eng. Chem. Res.* **2017**, *56*, 560−574.
(60) Weingarten, R.; Cho, J.; Xing, R.; Conner, W. C., Jr.; Huber, G. W. Kinetics and reaction engineering of levulinic acid production from aqueous glucose solutions. *ChemSusChem* **2012**, *5*, 1280−1290.
(61) Sánchez-Ramírez, E.; Quiroz-Ramírez, J. J.; Hernández, S.; Segovia-Hernández, J. G.; Kiss, A. A. Optimal hybrid separations for intensified downstream processing of biobutanol. *Sep. Purif. Technol.* **2017**, *185*, 149−159.

https://dx.doi.org/10.1021/acs.iecr.0c02261
Ind. Eng. Chem. Res. 2020, 59, 15990−16003