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Optimal Design and Sensitivity Analysis of Reactive Distillation Units Using Collocation Models

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The optimal design of staged distillation units with chemical reactions is determined using a modeling approach that facilitates both rigorous optimization and sensitivity analysis with detailed models. The values of the design variables are determined so that an economic criterion is optimized while a set of safety, operating, and product quality constraints and specifications is satisfied. An equilibrium stage model with kinetically controlled chemical reactions describes the physical and chemical phenomena in the column. Orthogonal collocation on finite elements (OCFE) techniques that transform the integer-valued stage model into a continuous analogue are employed. OCFE models accurately reproduce the same optimal design as a full-order tray-by-tray model, while using a smaller set of equations and eliminating the use of integer variables associated with the column stages. Furthermore, the effects of multiple process parameter variations on the optimal operating point of the reactive distillation units are investigated on the basis of a sensitivity analysis of the optimal design. The parameter perturbations are performed along the dominant directions that result in the maximum change in the process variables. Sensitivity information regarding the optimal solution for different parameter values is utilized to modify the design variable values in order to improve the feasibility region and profitability of the final process design. The proposed modeling and design procedure is applied successfully in the production of high-purity ethyl acetate from ethanol and acetic acid carried out in a reactive distillation column followed by a recovery column. Design modifications to the process flowsheet allow for the achievement of better economic performance under multiple parameter variations.

Introduction

Separation processes with simultaneous chemical reactions are gaining increased attention for a large number of reactive systems of industrial interest. Reactions limited by chemical equilibrium constraints will be favored if the products can be continuously removed from the reaction environment, thus shifting the direction of the equilibrium reaction toward the products' side. Distillation processes with simultaneous chemical reaction would generally enhance the conversion of those equilibrium-controlled reactive systems that have significant differences between the volatilities of reactants and products. The reduction of total investment and operating costs when reactions can be carried out simultaneously with the separation can be substantial. This is usually achieved through the simplification of the process flowsheet (e.g., reduction of reactors and intermediate tanks, elimination of large recycle streams, and so forth) and the heat integration of the reactor and the separation units.

The design of such reactive distillation processes involves the determination of design parameters and operating conditions that are optimized with respect to economics and that meet the safety, environmental, and operating constraints. Because designs are based on a set of abstractions about the physical reality in which the process has to function, a good design method must take the expected variability in physical reality into account. The design procedure proposed and applied in this paper addresses three key elements in an integrated way: the design optimization problem, the design models, and a sensitivity analysis for variability. The sensitivity analysis builds on the design optimization, exploiting computationally efficient models.

The design of reactive distillation processes requires good knowledge of the physical and chemical phenomena that take place in the process. A number of design procedures for reactive distillation processes assume the presence of chemical equilibrium, use residue curve mapping based on composition coordinate transformation,[1–3] and examine the influence of azeotropic mixtures.[3,4] The task is further complicated when kinetically controlled reactions are involved. Slow kinetically controlled reactions are considered in material balances parametrized in terms of the Damköhler number, a measure of a characteristic liquid residence time to a characteristic reaction time for a given column section.[5–7] Attainable region approaches calculate the feasible composition space for reaction–separation systems with independent parameters such as the Damköhler number and the stage heating policy.[8]

The aforementioned design methods for reactive distillation, however, either require the reactions to have reached equilibrium or involve simplifying assumptions in the models (equimolar overflows, constant heats of vaporization, single reaction schemes, simplified energy balances, and so forth). In addition, the extension of the methods to the design of columns with multiple feed locations and the evaluation of the optimal

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feed-stream flow ratio when more than one feed stream is involved is not straightforward. Detailed tray-by-tray models have been employed for the static behavior using nonequilibrium cell models,[9] the identification of possible multiple steady states,[10] and the study of the dynamic behavior of stagewise reactive columns.[11,12] Ciric and Gu[13] presented an optimization-based approach with a tray-by-tray model for the process constraints and integer-valued variables that represent the existence or lack of each column stage. However, a large number of trays in the column or the simultaneous design of more than one distillation unit results in the introduction of an equally large number of integer variables, with a substantial increase in the computational effort for solution.

To avoid the handling of large numbers of integer decision variables associated with the column stages in a design optimization framework, a transformation to continuous decision variables by means of approximate modeling is a viable alternative. The issue of reducing the total number of integer decision variables becomes more important when the design of complex flowsheets is considered, which might require superstructure formulations. Orthogonal collocation on finite elements (OCFE) techniques for stagewise distillation units[14,15] transform the discrete number of stages in the column into a continuous variable. Composition and temperature are then treated as continuous functions of position in the column and approximated using piecewise polynomials. OCFE formulations are shown to successfully identify the optimal operating point of the tray-by-tray model with significant savings in computational time.[15] Furthermore, an OCFE formulation of the tray-by-tray model allows for the use of conventional nonlinear programming (NLP) methods for the calculation of the optimal number of stages as only continuous variables are involved.[16] The achieved model size reduction results in increased efficiency of the method, especially when the simultaneous design of more than one column is performed. An additional advantage of the OCFE formulation is that it can be easily extended for the simulation and design via optimization of reactive columns with sections filled with packing material (catalyst).

The optimal operating points of reactive distillation units determined in the design stage are subject to variations because of process-related disturbances that arise from interactions with upstream process units and recycle streams, changing conditions, and model mismatch. The process should be able to alleviate the effects of varying model parameters and disturbances and maintain a feasible operation. Moreover, a design that is sensitive to model parameter variations might cause the distance between the true and estimated values of the economic objective to vary significantly. Even though extensive research has been carried out regarding the effects of changing operating conditions on the performance of reactive distillation processes,[12,14] there has not been a systematic study of the influence of multiple model parameter variations and process disturbances on the design and operation of reactive distillation units. Furthermore, a set of design parameters is sought for reactive distillation that satisfies the product specifications and process constraints and maintains the economic benefits under extensive model parameter variations. The current work concentrates on the low-frequency, deterministic type of model parameter and process variable variations.

The proposed sensitivity analysis method is based on the observation that a sensitivity matrix of the design optimization problem around a base operating point reflects the variability of the process variables in response to changes in the model parameters. Analysis of the deterministic sensitivity information via singular-value decomposition results in a set of orthogonal vectors (dominant directions), each one representing a unique mode of excitation for the process variables. Considering the response of the process to variations along directions aligned with the small number of dominant directions, the sensitivity analysis can be performed in a parameter/disturbance space of much smaller dimensionality, resulting in substantial computational savings. Usually, the dominant directions lump the effects of multiple parameters on the optimal solution and account for the most significant phenomena in the plant, so that they can be viewed as worst-case disturbance scenarios. Exploration of the process behavior focuses on directionality in the parameter/disturbance variations, which might magnify the effects on the process variables and thus increase the chance that operating constraints are violated. Such directional information provides a compact way of evaluating the characteristics of the process behavior under multiple parameter variations.

Furthermore, the process sensitivity is utilized to adaptively modify the design characteristics in order to enhance the process behavior and the process economics under the influence of disturbances. The most sensitive design variables are identified via a singular-value decomposition of the local sensitivity information with respect to the fixed structural design variables along the disturbance trajectory curve. An extra capacity is then introduced to the process flowsheet by preferably altering the most sensitive design parameters that will assist the plant in alleviating the detrimental effects of the process disturbances. The procedure aims at quantifying the possible tradeoff between the competing investment and operating costs for complex reactive distillation units under multiple parameter variations.

Design Problem Statement

The design problem of reactive distillation processes can be summarized as follows.

Given:

    a set of components and chemical reactions

    the characteristics of the feed streams

    a set of different modes of operation for the process

    a set of product specifications and safety and operational constraints for each mode of operation

    data regarding the process economics based on prices of the products and the reactants, as well as correlation relations for the investment and utility costs

    ranges of possible values for the major model parameters and ranges of variation for key process variables

Determine:
    the total number of stages in the reactive column

    the locations of the feed stages

    the distribution over the trays of the liquid-
        phase holdup for homogeneous reactions in the
            liquid phase or of the catalyst load for
                heterogeneous catalytic reactions

    the operating conditions

that optimize the economic objective function
        (e.g., total costs,plant profit) while satisfying
        the product specifications and the safety and
           operational constraints for the process

A steady-state model for staged reactive distillation processes is required to ensure an accurate representation of the underlying physical and chemical phenomena. The economic objective consists of a term that accounts for the annualized capital investment cost, a term that represents the annual operating costs of the process, and a term for the value of the products.

The mathematical representation of the stated design optimization problem is

$$\max_{\mathbf{x},\mathbf{d}} \quad f(\mathbf{x},\mathbf{d},\epsilon)$$

$$\begin{aligned} \text{s.t.} \quad &\mathbf{h}(\mathbf{x},\mathbf{d},\epsilon) = 0 \\ &\mathbf{g}(\mathbf{x},\mathbf{d},\epsilon) \leq 0 \\ &\mathbf{x}^{\mathbf{l}} \leq \mathbf{x} \leq \mathbf{x}^{\mathbf{u}}, \mathbf{d}^{\mathbf{l}} \leq \mathbf{d} \leq \mathbf{d}^{\mathbf{u}} \end{aligned} \qquad \text{(DP1)}$$

where $\mathbf{x}$ denotes the process (state and control) variables; $\mathbf{d}$ the vector of the design variables, which consists of equipment capacity variables or structural design variables (e.g., number of stages in a column); and ϵ the vector of model parameters and process disturbances, which will be called the parameter vector.

The process design derived from the solution of DP1 should ensure that the operating specifications (product purity levels, load constraints on process equipment), safety regulations, and environmental constraints are satisfied during plant operation and, in addition, that good economic performance is maintained for the plant under the presence of model- and process-related uncertainty. Multiple low-frequency model parameter and process variable variations that can be handled by either the operator or an on-line optimization system are considered, as it is assumed that a properly tuned control system will compensate for the high-frequency stationary process disturbances. The major aim is not to examine the behavior of the designed process over the entire model parameter−disturbance space but rather to focus on the effects of the directionality of the disturbances and model parameter variations on the feasible operation of the process. The optimal solution trajectory is traced with varying model parameters along dominant directions in the parameter space evaluated from local sensitivity information for the optimal solution of problem DP1. The next phase involves modification of the process design by proper adjustments of the design variables, so that a feasible operation is achieved under a given magnitude of parameter variations along the dominant directions of variation for the process.

Model Formulation for Staged Reactive Distillation Processes

The steady-state model is based on the MESH (material, equilibrium, summation, and enthalpy) equations.[18] The main modeling assumptions are (a) complete mixing of each phase at each stage; (b) constant liquid holdup and no vapor-phase holdup at each stage; (c) no liquid entrainment from stage to stage; (d) adiabatic stages, with no heat loss from each stage; and (e) thermal equilibrium between the leaving liquid and vapor streams from each stage.

Additional assumptions that might apply to specific cases will be stated as the details for the given reactive distillation process model are described. Following the work by Seferlis and Hrymak,[15] the column is separated into sections, with each section defined as the part of the column between two streams entering (feed streams) or leaving (product draw streams) the column. Each column section is divided into smaller subdomains, namely, the finite elements. For each finite element, a number of collocation points is specified. The main principle of the OCFE formulation is that material and energy balances are satisfied exactly only at the collocation points. The number of collocation points determines the order of the polynomial approximation of the composition and enthalpy profiles in the column. The collocation points are chosen as the roots of the discrete Hahn family of orthogonal polynomials. The roots of the discrete Hahn polynomials coincide with the location of the actual trays when the order of the polynomial (e.g., number of collocation points) is equal to the number of actual stages for any given column section.[14] Hence, the complete tray-by-tray model is fully recovered. Lagrange interpolation polynomials are used within each finite element to approximate the liquid- and vapor-component and total stream flow rates, as well as the liquid and vapor stream enthalpies, as follows:

$$\tilde{l}_m(s) = \sum_{j=0}^{n} W_j^L(s_j)\tilde{l}_m(s_j) \qquad 0 \leq s \leq NT, \quad m = 1, ..., NC \tag{1}$$

$$\tilde{v}_m(s) = \sum_{j=1}^{n+1} W_j^V(s_j)\tilde{v}_m(s_j) \qquad 1 \leq s \leq NT + 1, \\ m = 1, ..., NC \tag{2}$$

$$\tilde{L}(s)\tilde{H}^L(s) = \sum_{j=0}^{n} W_j^L(s_j)\tilde{L}(s_j)\tilde{H}^L(s_j) \qquad 0 \leq s \leq NT \tag{3}$$

$$\tilde{V}(s)\tilde{H}^V(s) = \sum_{j=1}^{n+1} W_j^V(s_j)\tilde{V}(s_j)\tilde{H}^V(s_j) \qquad 1 \leq s \leq NT + 1 \tag{4}$$

where $\tilde{L}(s)$ and $\tilde{V}(s)$ are the total liquid and vapor stream flow rates, respectively.

The functions W^L and W^V are Lagrange interpolation polynomials of order $n + 1$ given by the expressions

$$W_j^L(s) = \prod_{\substack{k=0 \\ k \neq j}}^{n} \frac{s - s_k}{s_j - s_k} \quad j = 0, ..., n \quad (5)$$

$$W_j^N(s) = \prod_{\substack{k=1 \\ k \neq j}}^{n+1} \frac{s - s_k}{s_j - s_k} \quad j = 1, ..., n+1 \quad (6)$$

The polynomials W^L and W^N are equal to zero at collocation points s_k when $k \neq j$ and to unity when $k = j$. Within each finite element, a Lagrange polynomial of different order can be used. The shape and characteristics of the approximated variable profiles determine the order of the interpolation polynomials (e.g., linear or irregularly shaped profiles, steep fronts).

The MESH modeling equations at the collocation points are as follows:

Component material balance

$$\tilde{l}_m(s_j-1) + \tilde{v}_m(s_j+1) - \tilde{l}_m(s_j) -$$

$$\tilde{v}_m(s_j) + M^L \sum_{k=1}^{Nr} \nu_{k,m} r_k^L[\tilde{l}(s_j), \tilde{T}(s_j)] +$$

$$M^N \sum_{k=1}^{Nr} \nu_{k,m} r_k^V[\tilde{v}(s_j), \tilde{T}(s_j), \tilde{P}(s_j)] = 0$$

$$m = 1, ..., NC \text{ and } j = 1, ..., n \quad (7)$$

Equilibrium relation

$$\frac{\tilde{v}_m(s_j)}{\tilde{V}(s_j)} - K_m[\tilde{T}(s_j), \tilde{P}(s_j), \tilde{l}(s_j), \tilde{v}(s_j)] \frac{\tilde{l}_m(s_j)}{\tilde{L}(s_j)} = 0$$

$$m = 1, ..., NC \text{ and } j = 1, ... n \quad (8)$$

Enthalpy balance

$$\tilde{L}(s_j-1)\tilde{H}^L(s_j-1) + \tilde{V}(s_j+1)\tilde{H}^N(s_j+1) - \tilde{L}(s_j)\tilde{H}^L(s_j) -$$

$$\tilde{V}(s_j)\tilde{H}^N(s_j) = 0 \quad j = 1, ..., n \quad (9)$$

A large variety of kinetic reaction models described as a set of algebraic equations can be easily accommodated within the framework of the OCFE model formulation. Furthermore, OCFE models can be tailored to allow reactive and nonreactive sections in the column. The rate of reaction is evaluated at the conditions prevailing at the collocation points. Stages that are connected to streams entering or leaving the column are treated as discrete equilibrium stages so that the effects of discontinuities in composition and temperature do not influence the continuity and smoothness of the interpolating polynomial schemes within the elements. This implies that the feed stages, the product removal stages, the reboiler, and the condenser are treated as discrete stages where the MESH equations apply. For a complete description of the governing equations around the feed and the end stages, refer to the work of Seferlis and Hrymak.[15]

The size of each column section (equivalent to the number of stages), NT, is not fixed but rather is a continuous decision variable (degree of freedom) in the design optimization problem. This means that the section length and, consequently, the length of each finite element can vary within real-valued bounds. The only constraint that applies refers to the size of each column section in terms of real column stages, which must be equal to or greater than the number of colloca-

tion points included in that section (i.e., $s_{n+1} > n$). An important issue in the OCFE formulation of the MESH equations is that a sufficient number of collocation points should be used to obtain a solution of desired resolution. The shape of the approximated profiles and the complexity of the thermodynamic models used (activity models, enthalpy calculation models) affect the minimum number of collocation points required for an accurate representation of a set of stages.[15] Adaptive placement of the finite element boundaries on the basis of the material and energy balance residuals results in a distribution of collocation points in the column domain so that the accuracy of the prediction is increased.[19]

Lagrange interpolating polynomials might give rise to oscillatory behavior in the composition profile of components that appear in very small amounts in some parts of the column. In such a case, composition might become negative or otherwise reach a specified lower bound and thus reduce the accuracy of the model. Huss and Westerberg[20] proposed a transformation of the molar fractions for components exhibiting very small concentrations to increase the accuracy of OCFE models for non-key components. However, such a transformation, usually expressed as a highly nonlinear function for composition values near zero, adds to the complexity and the nonlinearity of the model. A similar approach is taken here but the variable transformation is applied only for those non-key components with very low compositions near the endpoints of the column. The transformation is described by the expression

$$\hat{l}_m = \ln(\tilde{l}_m) \quad (10)$$

The transformed variable, $\hat{l}_m$, is allowed to take negative values, and the Lagrange interpolating function has more room to accommodate very low composition values for non-key components. However, the material and energy balances (eqs 7−9) are expressed in terms of the original component flow rates.

An alternative approach that enhances the stability of the OCFE scheme is also examined. The approach is based on the removal of inert components with low concentrations from the material and energy balances in particular column sections. This implies that different component slates are carried within the column. The disappearing components should not play a significant role in the product specifications or operating constraints. The remedy does not increase the accuracy of the OCFE formulation but rather improves the stability and robustness of the solution. Selection of the removed components should be performed carefully in order to avoid significant increases in the prediction error of the steady-state behavior. The elimination approach generally is easy to implement and significantly simplifies the modeling equations. However, the presence of disturbances that strongly affect the trace-component composition would make the use of the variable transformation approach the preferred choice.

Design of Ethyl Acetate Production via Reactive Distillation

The proposed methodology for the design of staged reactive distillation processes is tested on the production of ethyl acetate.[21−23] Ethanol and acetic acid form ethyl acetate through a reversible endothermic liquid-phase esterification reaction in the presence of sulfuric acid

that acts as the catalyst.

$$C_2H_5OH + CH_3COOH \leftrightarrow CH_3COOC_2H_5 + H_2O$$
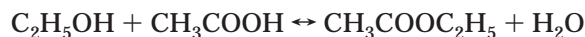
Pure ethanol and acetic acid are fed separately into a column that operates at atmospheric pressure. The reaction is assumed to take place only in the liquid phase. Under these conditions, acetic acid is the heaviest of the components and moves toward the bottom of the column. Ethyl acetate is the lightest, but its relative volatility with respect to that of ethanol is small. The rate of reaction is generally low, which implies that it is favored by long residence times in each stage. Ethanol, a reactant, has a relatively high volatility and prefers the vapor phase rather than the liquid phase where the reaction takes place, thus maintaining a low composition in the liquid phase and reducing the production rate of ethyl acetate. The Arrhenius expression for the rate of reaction is given by

$$r = k_{01} \exp(-A_1 R/T)[\text{ACOOH}][\text{EtOH}] - \\ k_{02} \exp(-A_2 R/T)[\text{EtAc}][\text{H}_2\text{O}] \quad (11)$$

The system consisting of ethanol, ethyl acetate, acetic acid, and water is nonideal and can form four binary azeotrope mixtures and one ternary azeotrope. In addition, Barbosa and Doherty[2] posited the existence of a reactive azeotrope when they used the Wilson activity model to describe the nonideality of the liquid phase. An unfavorable physical equilibrium makes the production of high-purity ethyl acetate impossible from a single distillation column. However, the use of a second recovery column operating at a higher pressure or a feed with a large excess of acetic acid would lead to the production of the desired purity.[23] A double-column production flowsheet is therefore selected. The main reason for this choice is to test the proposed OCFE model formulation in the coupled system of a reactive column with a conventional distillation unit. The second option, which involves a large excess of acetic acid, leads to a column with large internal streams and a high reflux ratio, which would require very large tray holdups and increased operating costs. However, for an industrial application, it would be necessary to investigate the economic potential of both possible flowsheet configurations.

The recovery distillation column is introduced next to the reactive column operating at a higher pressure (350 kPa) to break the azeotrope and produce high-purity ethyl acetate, as shown in Figure 1. The distillate stream from the reactive column is fed directly to the recovery column. At the increased pressure of 350 kPa, ethyl acetate becomes heavier than water and ethanol, so that it appears as the bottoms product. The target purity level of ethyl acetate at the bottoms stream of the recovery column is set at 99.5%. The effect of the reaction in the recovery column is considered negligible because the column operates without any catalyst (sulfuric acid) and the stages have small liquid-phase holdups. Another specification is imposed on the maximum allowable concentration of acetic acid in the distillate of the reactive column, because acetic acid appears as the bottoms product of the recovery stream and therefore directly affects the purity of the final ethyl acetate product. The control of the concentration of acetic acid in the distillate is achieved through a reduction of the liquid-phase holdup in the upper section

Table 1. Reactive and Recovery Column Specifications

reactive column	recovery column
condenser type: partial	condenser type: partial
two feed stages	one feed stage
acetic acid level in distillate	ethyl acetate in bottoms
< 0.8%	> 99.5%

of the reactive column to suppress the extent of the reverse reaction. A small purge stream in the recycle stream is intended to remove the accumulated impurities in the system.

The OCFE model implementation divides the reactive column into three sections, rectifying (from the condenser down to the acetic acid feed), the reactive (between the two feeds), and stripping (from the ethanol feed down to the reboiler). The reaction occurs in all three sections, but each column section has a uniform liquid-phase holdup. The OCFE formulation uses a single element with four collocation points in the rectifying section, three elements with three collocation points per element in the reactive section, and two elements with two collocation points per element in the stripping section. In the recovery column, the OCFE model uses two elements in each column section with three collocation points per element. The Wilson activity model is used for the liquid phase, while an ideal gas phase is assumed. Regressed equations are used for the liquid and vapor molar enthalpies.

An accurate OCFE representation of the process requires that a sufficient number of collocation points be placed within each column section. This number depends on the shape and slope of the approximated profiles in the particular column section and the actual size of the column section, in terms of number of discrete equilibrium stages. However, the variable profiles and the column size are not available unless the optimal solution is known, and it is advisable that a careful inspection of the optimal solution be performed to identify sections where more collocation points might be necessary. On the basis of extensive simulations, a ratio of the total number of discrete stages in a column section to the total number of collocation points of around 2 is judged adequate for the system under consideration. The ratio compromises between the accuracy of the prediction of the stage-by-stage optimal solution by the OCFE model formulation and achieved model size reduction and compactness. The operating specifications for the flowsheet are shown in Table 1. The entire flowsheet has 13 degrees of freedom, including the number of stages in the five column sections (counting the column sections in both the reactive and the recovery columns), the stage holdup in the three column sections of the reactive column, the four operating variables (two for each column), and the flow of the ethanol feed stream.

Capital and operating cost data for the objective function are taken from Douglas.[24] A penalty term equal to $0.017/kg of EtAc is introduced in the objective function to account for the losses of ethyl acetate in the bottoms stream of the reactive column. A price of $0.112/kg of EtAc is used for the 99.5% purity product. The design optimization is performed using MINOS 5.5,[25] an augmented Lagrangian projected gradient type of algorithm. Derivatives of the balance equations at the collocation points with respect to the total length (number of equivalent stages) of the column are necessary. Direct differentiation of the Lagrange interpolating polynomials and expression of the roots of the Hahn
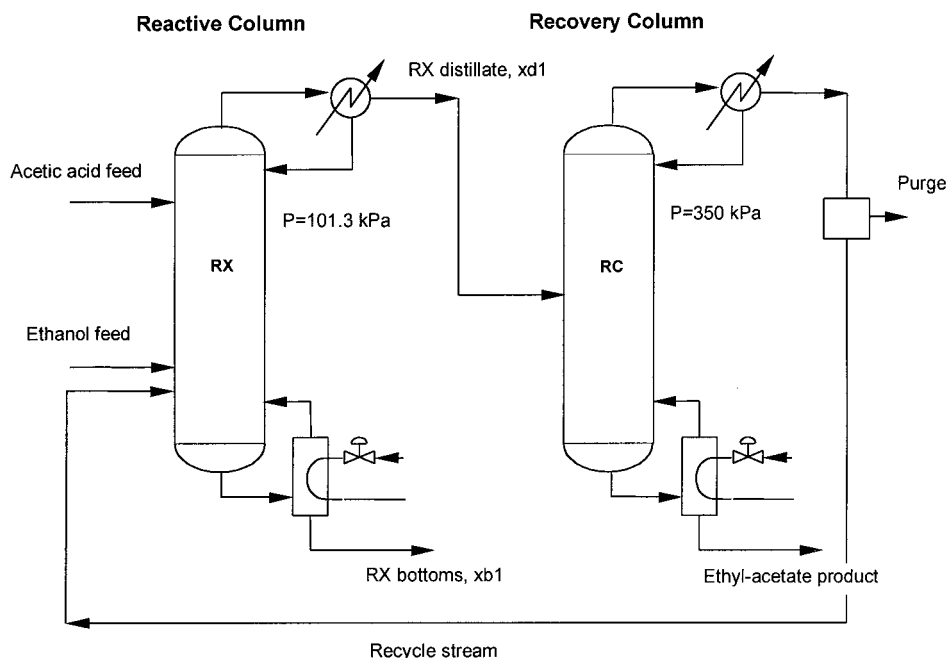
Figure 1. Schematic of the ethyl acetate reactive distillation production flowsheet.

polynomials with respect to the element sizes provide the analytical relations for the Jacobian matrix.

Acetic acid usually appears in very low concentrations in the rectifying section of the recovery column. Possible oscillatory behavior of the Lagrange interpolating polynomials when the composition profile for acetic acid close to the top of the recovery column is approximated can be avoided by following one of the two approaches described in the previous section: (A) A variable transformation for the liquid and vapor molar flow rates of acetic acid can be performed for the top element of the rectifying section in the recovery column, leading to model OCFE A. (B) The component slate can be modified, and acetic acid can be taken out of consideration in the formation of the mass and energy balances in the rectifying section of the recovery column, leading to model OCFE B.

Table 2 shows the optimal designs obtained from models OCFE A and B. The results from both models are very similar, implying that the omission of acetic acid in the rectifying section of the recovery column does not have a significant impact on the final optimal design. The production of ethyl acetate is strongly favored by large liquid-stage holdups in the reactive and stripping sections because of the relatively low rate of reaction. The optimal design attempts to enrich the distillate of the reactive column with ethyl acetate and reduce the intensity of the reverse reaction by requiring about six stages in the rectifying section and a small stage holdup. The large recycle stream (distillate stream of the recovery column) increases the interactions between the two columns and the operating costs in general. Figure 2 shows the oscillatory behavior of the Lagrange interpolating polynomials when applied to the original component molar flow rates. Oscillations become more severe as the size of the element increases for the same number of collocation points and might cause the interpolating polynomial to reach the lower bound for composition, a totally undesirable situation. Such a situation might generate serious convergence problems for the optimization solver and restrict the minimum density of collocation points that would

Table 2. Design Optimization Results for Alternative OCFE Model

model	reactive column		recovery column	
	OCFE A[a]	OCFE B[b]	OCFE A[a]	OCFE B[b]
number of stages				
rectifying section	6.01	6.00	7.76	7.63
reactive section	10.06	10.06	−	−
stripping section	6.09	6.09	8.44	8.59
stage holdup (m³)				
rectifying section	0.150	0.150	−	−
reactive section	1.750	1.750	−	−
stripping section	1.634	1.658	−	−
distillate flow (kmol/h)	17.396	17.392	14.491	14.483
bottoms flow (kmol/h)	3.439	3.436	2.909	2.909
reflux ratio (R/D)	0.843	0.842	1.071	1.067
distillate product composition (molar fraction)				
ethanol	0.2383	0.2383	0.2856	0.2856
acetic acid	0.0004	0.0004	0.0000	−
ethyl acetate	0.5520	0.5520	0.4630	0.4630
water	0.2093	0.2093	0.2514	0.2514
bottoms product composition (molar fraction)				
ethanol	0.0249	0.0249	0.0024	0.0025
acetic acid	0.0876	0.0876	0.0025	0.0025
ethyl acetate	0.0008	0.0008	0.9950	0.9950
water	0.8867	0.8867	0.0001	0.0000
heat duty (MJ/h)				
condenser	−530.08	−529.72	−534.12	−531.47
reboiler	482.58	482.34	516.38	514.32

	OCFE A[a]	OCFE B[b]
ethanol feed (kmol/h)	3.145	3.145
annual profit ($1000)	1028.10	1029.58

[a] OCFE A: full component slate; variable transformation in rectifying section of RC column. [b] OCFE B: no acetic acid in rectifying section of recovery column.

provide accurate model predictions. On the other hand, transformed variables result in a monotonically decreasing interpolating curve that serves the physical requirements for the system under study.

The optimal steady-state design results obtained using the OCFE model formulations are compared with those obtained by a full tray-by-tray model. The tray-by-tray model is constructed with the number of stages
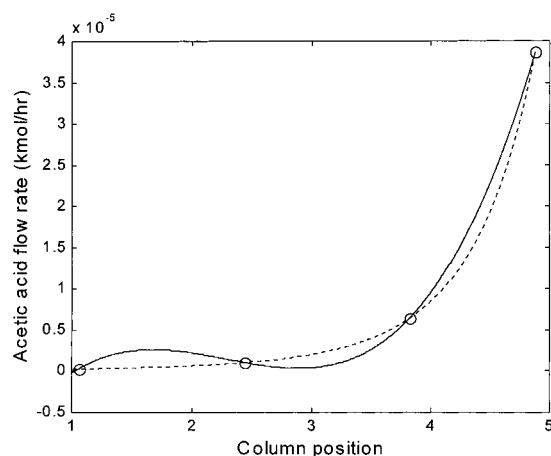
Figure 2. Lagrange interpolating polynomials applied to the original (solid curve) and transformed (dashed curve) liquid acetic acid flow rates in the rectifying section of the recovery distillation column (○ marks the collocation points).

Table 3. Comparison of Optimization Results between the Tray-by-Tray and OCFE Models[a]

	reactive column		recovery column	
	tray-by-tray	OCFE[b]	tray-by-tray	OCFE[b]
stage holdup (m³)				
rectifying section	0.150	0.150	–	–
reactive (middle) section	1.750	1.750	–	–
stripping section	1.650	1.658	–	–
distillate flow (kmol/h)	17.373	17.402	14.467	14.493
bottoms flow (kmol/h)	3.446	3.437	2.906	2.909
reflux ratio (R/D)	0.8445	0.843	1.044	1.043
distillate product composition (molar fraction)				
ethanol	0.2395	0.2392	0.2871	0.2867
acetic acid	0.0004	0.0004	0.0000	–
ethyl acetate	0.5512	0.5513	0.4621	0.4623
water	0.2089	0.2091	0.2508	0.2510
bottoms product composition (molar fraction)				
ethanol	0.0275	0.0251	0.0025	0.0025
acetic acid	0.0881	0.0876	0.0025	0.0025
ethyl acetate	0.0009	0.0008	0.9950	0.9950
water	0.8835	0.8865	0.0000	0.0000
heat duty (MJ/h)				
condenser	−530.74	−530.36	−519.52	−519.85
reboiler	483.34	482.96	502.35	502.73

	tray-by-tray	OCFE[b]
ethanol feed (kmol/h)	3.152	3.146
annual profit ($)	1027.35	1028.71
number of variables	587	449

[a] Both models with equal number of stages per column section.
[b] OCFE B stage values rounded up to closest integer.

per column section equal to those calculated by the OCFE model for the optimum solution and rounded up to the closest integer value. Table 3 compares the optimized solutions between tray-by-tray and OCFE B models with equivalent column structures (OCFE B column section stages are also rounded to the closest integer). The approximation of the tray-by-tray solution by the OCFE scheme seems to be very good. Furthermore, the number of stages in each column section for the tray-by-tray model is slightly perturbed from the fixed value. A comparison of the objective functions between the nominal (see Table 3) and perturbed problems for the tray-by-tray model formulation verifies the existence of a local maximizer for the number of stages in each column section and the location of the feed streams. Hence, the design optimization results also seem to be in very good agreement between the
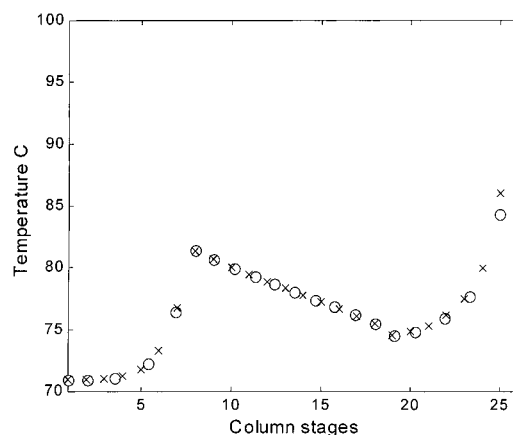

Figure 3. Optimal temperature profile in the reactive distillation column for the tray-by-tray (×) and OCFE (○) model formulations.

tray-by-tray and OCFE model formulations. A 23.5% reduction in the number of equations is achieved using the OCFE formalism, but this is a conservative result, as an excess of collocation points is used in order to ensure an accurate prediction of the steady-state optimal design. Figure 3 compares the temperature profiles obtained at the optimum by both the tray-by-tray and OCFE models. An interesting observation is that temperature within the reactive (middle) section of the reactive column decreases, mainly because of the endothermic nature of the occurring reaction.

Design Sensitivity Analysis

Initially, a set of optimal design variables is obtained that optimizes an economic objective for a nominal set of parameter values, which is considered the base operating point for the plant (i.e., solution of DP1). However, model parameter variations and disturbance changes will perturb the plant away from its base operating point. A local sensitivity analysis is performed at the optimal nominal point of problem DP1 with a fixed set of design variables. The resulting sensitivity matrix represents the effects of small model parameter perturbations on the operating conditions (e.g., stream flow rates, column temperatures, heat duties, and so forth). The sensitivity matrix, considering constant design variables, $\mathbf{d}$, can easily be calculated at the solution of the design optimization problem by solving the system of equations[26]

$$
\begin{bmatrix}
\nabla_{\mathbf{x}}^2 \mathbf{L} & \nabla_{\mathbf{x}} \mathbf{h}^T & \nabla_{\mathbf{x}} \mathbf{g}_{\mathbf{J}_0}^T \\
\nabla_{\mathbf{x}} \mathbf{h} & 0 & 0 \\
\nabla_{\mathbf{x}} \mathbf{g}_{\mathbf{J}_0} & 0 & 0
\end{bmatrix}
\begin{bmatrix}
\nabla_{\epsilon} \mathbf{x}^* \\
\nabla_{\epsilon} \lambda^* \\
\nabla_{\epsilon} \mu^*
\end{bmatrix}
=
\begin{bmatrix}
\nabla_{\mathbf{x}\epsilon}^2 \mathbf{L} \\
\nabla_{\epsilon} \mathbf{h} \\
\nabla_{\epsilon} \mathbf{g}_{\mathbf{J}_0}
\end{bmatrix}
\quad (12)
$$

where $\nabla_{\epsilon} \mathbf{x}^*$, $\nabla_{\epsilon} \lambda^*$, and $\nabla_{\epsilon} \mu^*$ are the local gradients, or local sensitivities, of the process variables and the Lagrange multipliers with respect to ϵ at point ($\mathbf{x}^*$, $\mathbf{d}^*$, ϵ^*). The gradients of the Lagrangian, $\mathbf{L}$, and the active constraints of eq 12 are evaluated at point ($\mathbf{x}^*$, $\mathbf{d}^*$, ϵ^*), which denotes the base operating point. Vectors $\nabla_{\epsilon} \lambda^*$ and $\nabla_{\epsilon} \mu^*$ are not required for the local sensitivity analysis of the process variables and are therefore omitted. Several matrix decomposition methods[27] eliminate the need for the evaluation of the full Hessian of the Lagrangian in eq 12, allowing a quick and efficient calculation of the sensitivity matrix, $\mathbf{P}_{\epsilon}$ (only in terms of the process variables, keeping the design variables constant).

$$\mathbf{P}_\epsilon = \nabla_\epsilon \mathbf{x}^* = \begin{bmatrix} \dfrac{\partial x_1}{\partial \epsilon_1} & \cdots & \dfrac{\partial x_1}{\partial \epsilon_p} \\ \vdots & \ddots & \vdots \\ \dfrac{\partial x_n}{\partial \epsilon_1} & \cdots & \dfrac{\partial x_n}{\partial \epsilon_p} \end{bmatrix} \qquad (13)$$

The sensitivity matrix $\mathbf{P}_\epsilon$ can be viewed as a measure of the variability of the process variables under the influence of parametric changes in the neighborhood of the nominal point, ϵ^*. However, the number of model parameters and disturbances that are involved in the design of a process unit or a multi-unit flowsheet might become very large, thus prohibiting an easy interpretation of the sensitivity information. The sensitivity information can be decomposed into a set of dominant modes of variation for the process using a singular-value decomposition (SVD) of $\mathbf{P}_\epsilon$. A small perturbation in ϵ along the direction of the eigenvector that corresponds to the largest-magnitude singular value of matrix $\mathbf{P}_\epsilon$, $\mathbf{v_1}$, reveals the dominant direction of variability in the system that causes the largest change in the process variables in a least-squares sense (Appendix I). Similarly, the eigenvector direction that corresponds to the second-largest-magnitude singular value, $\mathbf{v_2}$, denotes the second most important direction of variability and so forth. The orthogonality of the eigenvectors of $\mathbf{P}_\epsilon^{\mathrm{T}}\mathbf{P}_\epsilon$ ensures the independence of the modes of variation. Therefore, the sensitivity of the process with respect to all parameters can be projected into a low-dimensional space defined by the dominant directions. The entries of the normalized eigenvectors $\mathbf{v}$ denote the relative importance of each parameter to the given direction.

The calculation of the singular values is scale-dependent; therefore, the entries of the matrix $\mathbf{P}_\epsilon$ are scaled for the SVD according to the following scheme:

$$\frac{\partial x_i}{\partial \epsilon_j} \frac{\epsilon_j^*}{x_i^*} \qquad i = 1, ..., n \quad j = 1, ..., p \qquad (14)$$

However, the importance of certain variables that are closely associated with inequality process constraints, product specifications, or cost-related quantities in the determination of the dominant directions can be increased by selectively weighting the corresponding row of the sensitivity matrix.

The ability of the process with fixed design characteristics to anticipate changes in the parameter set is investigated for changes along the dominant directions. The structural design variables (number of stages in each section, stage holdup, or catalyst distribution) are set constant at the optimal values for the nominal parameter case. The operating degrees of freedom are allowed to vary to compensate for the imposed parametric changes in a manner dictated by the process economics. The trajectory of the optimal solution is traced for changes in the parameters ϵ by solving the parametrized set of first-order Karush–Kuhn–Tucker (KKT) optimality conditions for problem DP1.[28]

$$F(\mathbf{x},\mathbf{d},\lambda,\mu,\epsilon,\zeta) = \begin{bmatrix} \nabla_{\mathbf{x},\mathbf{d}} L(\mathbf{x},\mathbf{d},\lambda,\mu,\epsilon) \\ \mathbf{h}(\mathbf{x},\mathbf{d},\epsilon) \\ \mathbf{g}_{J_0}(\mathbf{x},\mathbf{d},\epsilon) \\ \Delta\epsilon(\epsilon,\zeta) \end{bmatrix} = 0 \qquad (15)$$

$\Delta\epsilon(\epsilon,\zeta)$ in eq 15 governs the variation of the parameter set ϵ, along the predefined direction (e.g., dominant directions) in the multidimensional parameter space. Variable ζ is an auxiliary variable that represents the size of the perturbation at any given point in the solution path. The solution of eq 15 is performed using a continuation method as implemented in PITCON.[29] PITCON is a predictor–corrector type of continuation method with embedded step-size adaptation. The feasibility of inactive inequality constraints and variable bounds and the sign of the Lagrange multipliers for active inequalities are examined at every continuation point to identify possible active set changes. Computationally, the solution of the nonlinear system in eq 15 is not very demanding as an approximation to the optimal solution path is sufficient and large steps can be taken along the optimal solution path. A limiting factor is the required evaluation of the second-order derivative for the Lagrangian. Multiple solutions for eq 15 are possible, but the current method does not have the capability of identifying a bifurcation point and tracing all solution paths.

Following the path of the optimal solution along the dominant directions represents the most severe case of change (worst-case scenario) for the process variables around the base operating point. A desired magnitude for the normalized eigenvector is determined, which will define the size of variation. Bounds on the values of the parameters confine the magnitude of variation for each individual parameter. As the magnitude of the perturbation increases, the optimal point moves toward the boundaries of the feasible window for the current process design and eventually reaches a fully constrained optimal point.[28] The feasible region can only be further extended by either relaxation of the process specifications or alteration of the process design variables.

The process design modifications are based on sensitivity analysis information. More specifically, a sensitivity matrix, $\mathbf{P_d}$, is derived along the perturbed optimal trajectory that contains as elements the partial derivatives of the process variables with respect to the otherwise constant, in this phase of the analysis, design variables $\mathbf{d}$. The singular-value decomposition of $\mathbf{P_d}$ reveals the relative importance of the design variables in affecting the process operation. Therefore, adjustments in the most influential design variables would provide the greatest impact in alleviating the detrimental effects of the parameter variation. Consequently, proper adjustments in the key design variables as dictated by the dominant directions of $\mathbf{P_d}$ near the fully constrained point will expand the feasible region of the process. The allowable level of additional investment costs mainly determines the size of changes in the design variables (e.g., addition of extra stages). The entire procedure is repeated starting from the modified design as the new base operating point, with a new disturbance trajectory calculated along the new dominant directions. The procedure terminates when the design remains feasible for the desired parameter level variation while obeying an upper level for the total annualized investment costs. There is usually a point at which a small expansion in the feasible region can only be achieved at an enormous expense of resources and equipment capacity. The complete design algorithm is shown schematically in Figure 4.

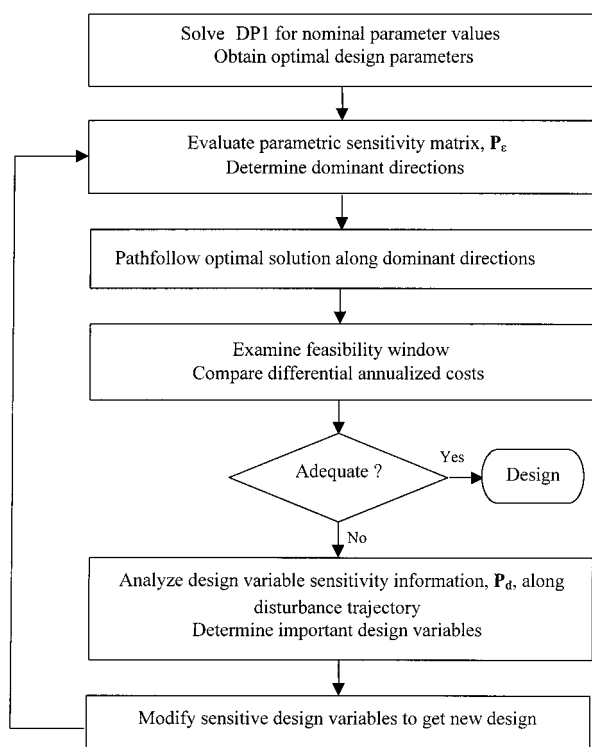The proposed procedure reveals the behavior of the

Figure 4. Block diagram of the algorithm for the sensitivity analysis in the design of the reactive distillation process.

Table 4. Nominal Parameter Values and Bounds

parameter symbol	value	allowable variation
RX column pressure (kPa)	101.3	
k_{01}	1.0	$\pm 35\%$
k_{02}	1.0	$\pm 35\%$
RC column pressure (kPa)	350.0	
$x_{F\ ACOOH}(H_2O)$	0.0	0.20
$x_{F\ EtOH}(H_2O)$	0.0	0.20

optimal operating point for different designs and a wide range of variations along the dominant directions. It also pinpoints the critical constraints that will be more susceptible to violations along a given direction of perturbation. Furthermore, the path-following problem determines the sequence in which the operating constraints become active. Such information will provide useful insight into the behavioral aspects of the process system under uncertainty. In addition, the level of variation for important process variables is derived (e.g., heat exchanger thermal duty variation), which can be utilized in the final adjustment of the capacity requirements for process equipment.

Design Sensitivity Analysis of the Ethyl Acetate Production Flowsheet

The behavior of the design for ethyl acetate production using reactive distillation under the influence of multiple parameter variations is investigated. The perturbation scenario involves variations in the column pressure for both columns, in the kinetic parameters in the expression for the reaction rate (eq 11), and in the purity level of the acetic acid and ethanol feed streams. Based on the optimal design (Table 2) for the nominal parameter values (Table 4) the sensitivity matrix, $\mathbf{P}_\epsilon$, is evaluated. Table 5 shows the individual entries for the dominant (eigenvector) directions of $\mathbf{P}_\epsilon^T \mathbf{P}_\epsilon$ that correspond to the three largest singular values of $\mathbf{P}_\epsilon$. Column pressure in both columns makes the greatest contribution in the first dominant direction, while the kinetic parameters contribute the most in the second dominant direction. The first dominant direction implies that a simultaneous increase in the pressure of the reactive column and decrease in the pressure of the recovery column will cause the largest changes in the process variables. The second dominant direction emphasizes the effects of the forward and reverse kinetic parameters and the third the effects from the column pressure and the purity in the acetic acid feed. All directions would cause unfavorable effects on the optimal operating point for the process.

The optimal solution path for the initial design A (Table 6) is calculated for positive changes along the first two dominant directions subject to the variable bounds described in Table 7. Figures 5 and 6 show the behavior of a number of key process variables and model parameters, respectively, plotted against the overall perturbation magnitude, the independent continuation parameter, ζ. Following the variation along the first dominant direction, the optimizer tries to compensate for the parameter changes by forcing the production flow toward the lowest allowable level. Simultaneously, the reboiler's heat duties in the reactive and recovery columns increase in order to anticipate the reduced column pressure that makes the separation more difficult. At a specific perturbation magnitude, the upper bound for the reboiler heat duty in the recovery column becomes active. The system loses a degree of freedom, which makes the effects of variation for the process variables more severe beyond this point. As the perturbation magnitude further increases, the bottoms product flow rate in the recovery column reaches the lower bound specified by production requirements, thus consuming an additional degree of freedom. Immediately, the heat requirements in the reboiler for the reactive column become extremely sensitive to small parameter changes along the dominant direction until they also reach their upper limit. Such a point can easily be recognized by the sharp change in the slope of the solution trajectory due to the active set change (see Figure 5a). On the other hand, the Lagrange multiplier associated with the purity specification of the ethyl acetate product increases dramatically as soon as the upper bound for the reboiler duty becomes active, denoting the critical nature of the purity specification in the current disturbance scenario. The system is deprived of degrees of freedom, and no feasible solution

Table 5. Contribution of Model Parameters to the Dominant Directions of Variation Based on Sensitivity Information around the Nominal Operating Point for Design A

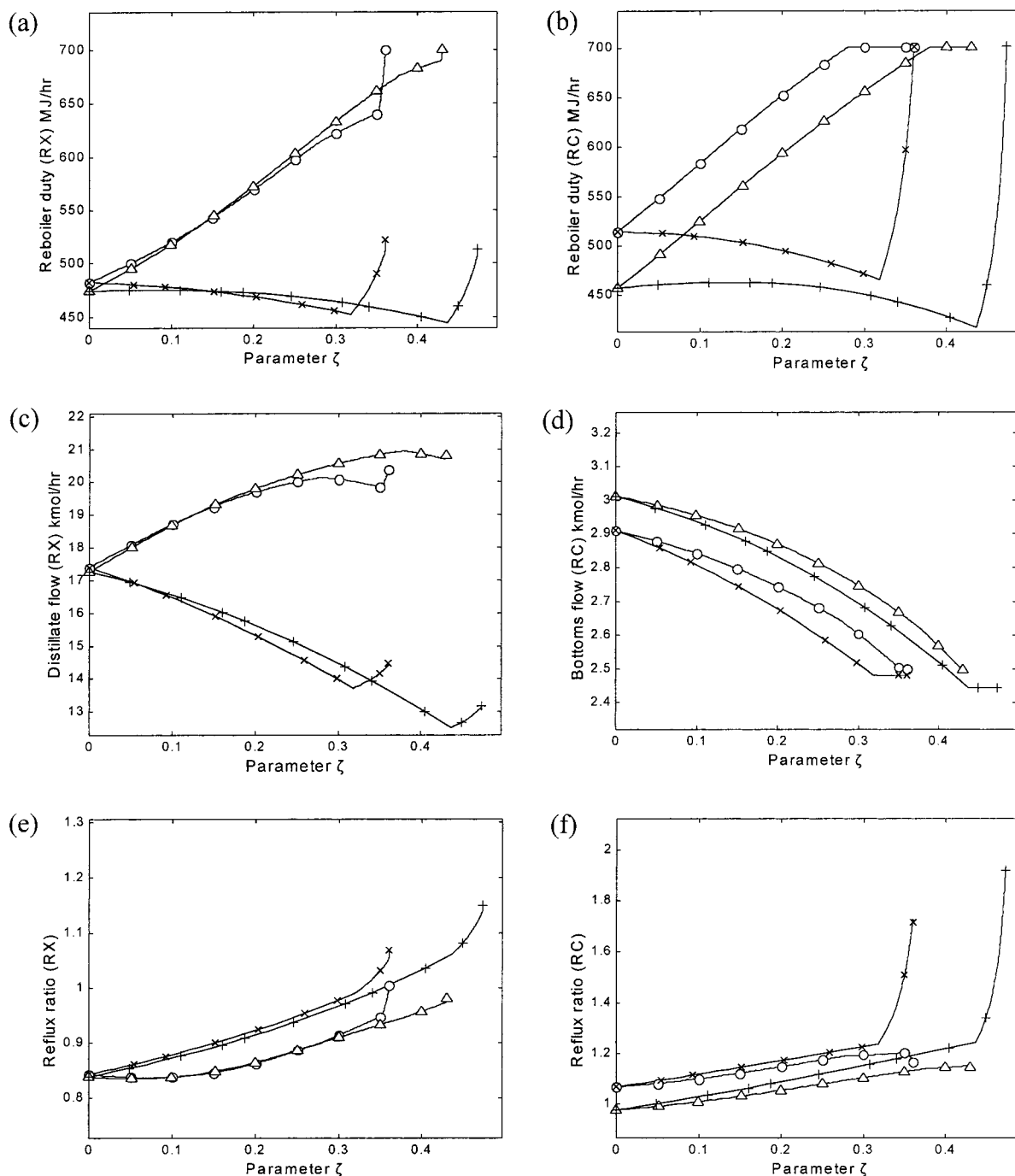|	first direction	second direction	third direction
RX column pressure	0.6280	−0.5820	0.3800
kinetic parameter k_{01}	−0.3050	−0.7500	−0.1620
kinetic parameter k_{02}	0.2220	0.2970	0.5580
RC column pressure	−0.6450	−0.0970	0.4470
acetic acid purity level in feed $x_{F\ ACOOH}(H_2O)$	−0.2170	−0.0380	0.5630
ethanol purity level in feed $x_{F\ EtOH}(H_2O)$	−0.0290	−0.0240	0.0430

Figure 5. Optimal trajectory for designs A (○ and ×) and B (Δ and +) for variations along the first (○ and Δ) and second (× and +) dominant directions.

Table 6. Values of Structural Design Variables for Designs A, B, and C

	design A	design B	design C
number of stages			
RX rectifying section	6.0	5.9	5.8
RX reactive section	10.1	11.8	12.6
RX stripping section	6.1	6.5	6.7
RC rectifying section	7.6	8.0	8.2
RC stripping section	8.6	9.5	9.7
stage holdup			
rectifying section	0.150	0.149	0.149
reactive section	1.750	1.943	2.023
stripping section	1.633	1.722	1.755

Table 7. Variable Bounds during Optimal Solution Trajectory Calculations

variable	lower bound	upper bound
RC bottoms product flowrate (kmol/h)	2.50	–
RX, RC condenser heat duty (MJ/h)	−750.0	–
RX, RC reboiler heat duty (MJ/h)	–	700.0

in the optimal trajectory in terms of values for the perturbation parameter ζ and the type of constraint that becomes active. The point at which the third consecutive variable bound becomes active signals the end of the feasibility region for each design.

Analysis of the sensitivity information with respect to the process design structure $\mathbf{P_d}$ close to the fully
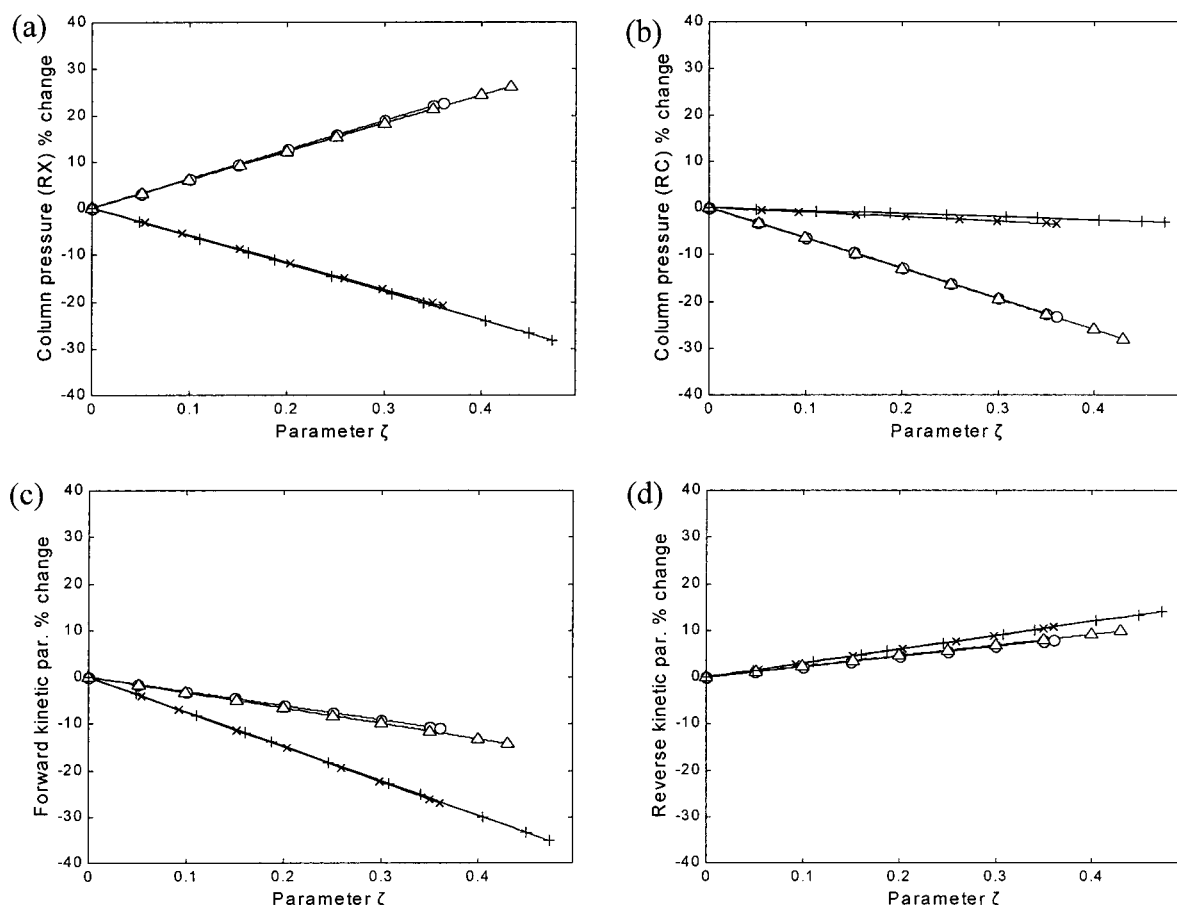
exists that can satisfy the process specifications for larger perturbations. Table 8 reports the critical points

Figure 6. Model parameter variation for designs A (○ and ×) and B (△ and +) along the first (○ and △) and second (× and +) dominant directions.

Table 8. Critical Points in the Optimal Solution Path

	design A		design B		design C	
	1st	2nd	1st	2nd	1st	2nd
1	0.280^a	0.319^b	0.380^a	0.437^b	0.441^a	0.487^b
2	0.352^b	0.360^a	0.429^b	0.474^a	0.447^b	0.520^a
3	0.361^c	0.361^d	0.431^c	0.475^d	0.447^c	0.520^d

^{a} RC reboiler's heat duty upper bound. ^{b} RC bottoms product flow rate lower bound. ^{c} RX reboiler's heat duty upper bound. ^{d} RC condenser's heat duty upper bound.

constrained point in the optimal trajectory reveals the most important design variables, whose changes will affect the operating conditions the most. It should be noted at this point that, in the OCFE model formulation for the distillation column, the optimal solution is expressed as a continuous function of the number of stages for each column section, therefore facilitating the easy evaluation of $\mathbf{P_d}$. The modified design B (Table 6) has about two additional stages and a larger stage holdup in the middle section of the reactive column, where most of the reaction takes place, than design A to account for the reduction of the kinetic parameters in the overall production rate of ethyl acetate. Furthermore, design B requires a larger recovery column to compensate for the reduced column pressure.

Starting at the nominal parameter values, the optimal trajectory for design B is determined (Figure 5) for variations along the dominant directions of the new parameter sensitivity matrix $\mathbf{P}_\epsilon$ that are quite similar to the directions obtained by design A (Figure 6). The general shape of the optimal solution trajectories is similar to those of design A, but the feasible region for

the process is further extended, as indicated by a comparison of the final value for the perturbation parameter ζ in Table 8. The procedure is repeated once more, leading to design C (Table 6). Design C does not extend the feasible region along the first dominant direction significantly compared to design B, but it does result in a definite improvement along the second dominant direction.

An economic analysis of the alternative designs reveals some very interesting conclusions. Annual profit generally declines as a result of the increased operating costs and the reduction of the production level under the influence of the parametric variations. However, from a comparison of the profit curves obtained from designs A, B, and C, it appears that the decline in the profit for designs B and C is slower than the decline for design A for perturbations along the first and second dominant directions, as shown in Figure 7a and 7b, respectively. Specifically, for perturbations along the second dominant direction, the difference is even more significant. In addition, the process remains profitable for a larger range of parametric variation for designs B and C than for design A. Even though design B and subsequently design C involve larger investment costs, they require much lower operating costs to cope with the model parameter perturbations, thus increasing the overall profitability of the process. In conclusion, designs B and C become more favorable options than design A, especially when the type of disturbance examined is expected to disrupt the normal operation of the process. Further increases in the investment costs will not provide significant economic benefits for the process, as
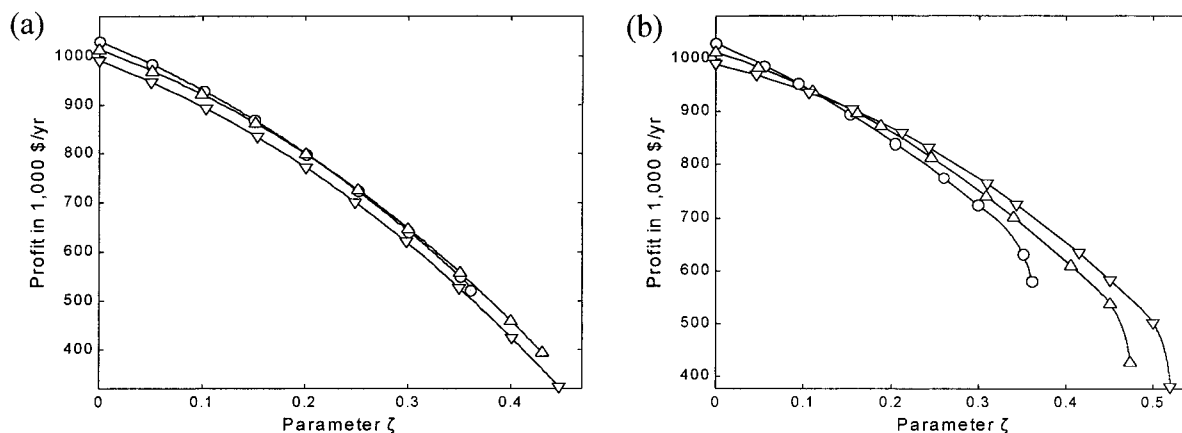
Figure 7. Profit for parametric variation along the (a) first and (b) second dominant directions for designs A (○), B (△), and C (▽).

investment costs will increase exponentially for a very small gain in the feasible window of the process. Larger variations can only be accommodated if the constraining process specifications, especially the product purity level and the production level, are relaxed with all implications arising from such a policy.

Conclusions

The economic design of an ethyl acetate production flowsheet consisting of two columns in series determines the number of reactive and nonreactive stages and the liquid-phase holdup per stage in every column section, the location of the feed stages, and the optimal operating conditions. The ability of the process design to compensate for the effects of multiple model parameter and process variable variations on the operating conditions is investigated. The optimal solution path of the process is calculated with fixed structural design characteristics for parametric variations along the dominant directions of variability, obtained from a decomposition of the process sensitivity matrix.

Detailed stage models with full account for the reaction kinetics throughout the column are developed, and OCFE techniques are used to approximate the tray-by-tray model. The OCFE model formulation transforms the discrete nature of staged columns into a continuous analogue. The main advantages of the OCFE formulation are that a more compact model, in terms of a smaller number of modeling equations, still provides an accurate representation and eliminates the need for integer variables in the model, thus resulting in considerable model simplifications without loss of accuracy and facilitating the solution of the design optimization problem and the sensitivity analysis. A variable transformation of the composition for minor components or the selective removal from the component slate of those inert components that appear in very small concentrations in certain column sections are two viable modifications that enhance the stability and convergence robustness of the OCFE formulation.

The varying model parameters include the column pressures, the kinetic parameters, and the feed purity levels. The behavioral characteristics of the process are explored for a wide range of parameter values with easily identified critical constraints that limit the feasible operating window of ethyl acetate production. The analysis thus provides to the engineer a tool for a fast and accurate investigation of the impact of parametric variations and disturbances in the plant. Design modifications utilizing sensitivity information along the

optimal operating condition trajectories are able to extend the feasibility window and improve the overall economic performance of the process.

Notation

d = vector of design variables
f = objective function
g = vector of inequality constraints
H = stream molar enthalpy, MJ/kmol
h = vector of equality constraints
K = equilibrium K value
k_0 = preexponential kinetic parameters
l = liquid-component molar flowrate, kmol/h
L = liquid-stream flow rate, kmol/h
L = vector of Lagrangian function
M = liquid-phase stage holdup, m³
n = number of collocation points on an element
NC = number of components
Nr = number of reactions
NT = number of stages
P = pressure, kPa
P = sensitivity matrix
r = reaction rate, kmol/(m³ h)
s = continuous position in the column
T = temperature, °C
v = vapor-component molar flowrate, kmol/h
V = vapor-stream flow rate, kmol/h
W = Lagrange interpolating polynomial
x = vector of process variables

Greek Letters

ϵ = vector of model parameter
ζ = auxiliary continuation parameter, overall magnitude of perturbation
λ = vector of Lagrange multipliers
μ = vector of Lagrange multipliers
ν = stoichiometric coefficients

Superscripts

L = liquid state
V = vapor state

Symbols

EtOH = ethanol
ACOOH = acetic acid
EtAc = ethyl acetate
H_2O = water

RX = reactive column
RC = recovery column

Appendix I. Dominant directions of the sensitivity matrix

Let **P** be the ($n \times p$) first-order sensitivity matrix at the reference point ($\mathbf{x}^*$, ϵ^*). The local behavior of the optimal values for the process variables for variations in the parameter values can be approximated using a Taylor series expansion with the expression

$$\mathbf{x}(\epsilon) = \mathbf{x}(\epsilon^*) + \mathbf{P}(\epsilon - \epsilon^*) + O(||\epsilon||) \quad (A1)$$

where $O(||\epsilon||)$ is the approximation error estimate, which is proportional to the magnitude of the variation in parameter space. The change in the variable space can be defined as $\mathbf{x}(\epsilon) - \mathbf{x}(\epsilon^*) = \Delta\mathbf{x}(\epsilon)$. Without any loss of generality, it is assumed that $\epsilon^* = 0$ at the nominal point.

The objective is to determine the direction in the parameter space that causes the greatest change in the optimal values of the process variables. If the measure of variation in the variable space is defined to be the sum of squares of deviation from the reference optimal solution ($\mathbf{x}^*$, ϵ^*), the problem takes the following form:

$$\max_{\epsilon} \quad \Delta\mathbf{x}^T\Delta\mathbf{x} = \epsilon^T\mathbf{P}^T\mathbf{P}\epsilon$$
$$\text{s.t. } \epsilon^T\epsilon = 1 \quad (A2)$$

The constraint imposes a bound on the magnitude of the parameter perturbation. The solution to problem A2 is given by forming the Lagrangian and setting its derivative with respect to ϵ equal to zero

$$\frac{d}{d\epsilon}[\epsilon^T\mathbf{P}^T\mathbf{P}\epsilon - \lambda(\epsilon^T\epsilon - 1)] = 0 \quad (A3)$$

where λ is the scalar Lagrange multiplier associated with the constraint. The differentiation in eq A3 results in

$$\mathbf{P}^T\mathbf{P}\epsilon - \lambda\epsilon = 0 \quad (A4)$$

The optimality conditions in eq A4 imply that ϵ is an eigenvector of matrix $\mathbf{P}^T\mathbf{P}$ with λ being the corresponding eigenvalue. Hence, the maximum value for the objective function in problem A2 is attained when ϵ is selected to be the eigenvector of $\mathbf{P}^T\mathbf{P}$ that corresponds to the eigenvalue with the largest magnitude.

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