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MODELING AND OPTIMIZATION OF A DYNAMIC SEPARATION PROCESS USING MIXED INTEGER NONLINEAR PROGRAMMING

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Abstract. In the present paper a chromatographic separation problem is modeled and solved using Mixed Integer Nonlinear Programming (MINLP) techniques. The problem is a complex process design problem that can be solved with the presented techniques. The objective is to maximize the profit for continuous cyclic operation, and at the same time, to find the optimal configuration for the separation column system.

The dynamics of the chromatographic separation process is modeled as a boundary value problem which is solved, repeatedly within the optimization, using a relatively fast and numerically robust finite difference method. Parameters within the model enable the control of the dynamic behavior of the chromatographic separation process. The optimization problem is solved using the Extended Cutting Plane (ECP) method. The purity demands of the separated products are modeled as constraints using control parameters.

A fructose-glucose example is solved using the presented techniques. The obtained results are promising. It is shown that the production planning can be done efficiently for different purity requirements, in such a way that all the output of a system can be utilized. Using a process design that is optimized it is thus possible to use existing complex systems, or to design new systems, more efficiently and also to reduce the energy costs or the costs in general.

Key words. Process design, Boundary value problem, Mixed Integer Nonlinear Programming, Extended Cutting Plane Method

AMS subject classifications. 90C90, 65N06, 90C11

1. Introduction. The problem of efficiently separating products of a multicomponent mixture is a complex challenge for many industries. The objective is to, within reasonable costs, separate products of a mixture as efficiently as possible retaining the preset purity requirements. The costs to be considered are, for instance, raw-material, equipment, machines, energy, waste costs etc. The energy consumption and/or the amount of waste are also important environmental costs that can be reduced using efficient mathematical optimization techniques.

The modeling and the design of different chromatographic separation processes have been addressed for example in [5], [1], [8] and [4]. The optimization of separation processes has been adressed in the pertinent literature in, for example, [2]. A sequentially simulated moving bed (SSMB) chromatographic separation process problem was recently modeled and solved mathematically as an MINLP problem in [6]. A brief introduction to the SSMB technique and the underlying physical and chemical processes is also given in [6]. Comparisons of solving the MINLP problem in [6] using the ECP method and a BB method was carried out in [3].

2. Chromatographic separation. The technique of separating components from a solution by differential migration during passage through a porous medium, e.g. through a bed in a column, is called *chromatographic separation*. The chromatographic separation technique was introduced already in 1906, [11], by Mikhail

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Semyonovich Tswett, a Russian botanist. Later on, in the 40's, 50's, and 60's, the chromatography was also applied within the gas industry. In the 70's the techniques of chromatographic separation were developed within oil industries and also within biotechnological industries. In the past decades the technique has been utilized and further developed within, for instance, the chemical and the pharmaceutical industries.

2.1. Process design issues. A two column separation system is illustrated in Fig. 1. At the inlet of a column it is possible to feed the mixture to be separated (e.g. molasses) or the eluent (e.g. water). The components of the mixture will flow down through the column in such a way that some components will get faster through the column than will others. At the outlet of the column one can thus collect the separated products, provided that they are pure enough. The logical decisions regarding the investment and/or the existence of a column, the input of feed mixture/eluent, the outtake of products, and the possible recycling connections are modeled using binary variables. The modeling and the notations used in this paper are illustrated in Fig. 1.

Note, that if the mixture is fed during a relatively long period the outflow will be less separated. The outflows that can not be separated can, for instance, be temporarily collected in a wastebin. The unpure outflows can, thus, be recycled into the same column or into another column for further separation. The production planning questions of a column system concern, for instance, the scheduling of the feeds, the outflows, and the possible recycling. There are many parameters (e.g. column height, column width, and flowrates) that affect the separation of each column. The process design problem of a separation column system is, thus, to find the optimal parameters for each column.

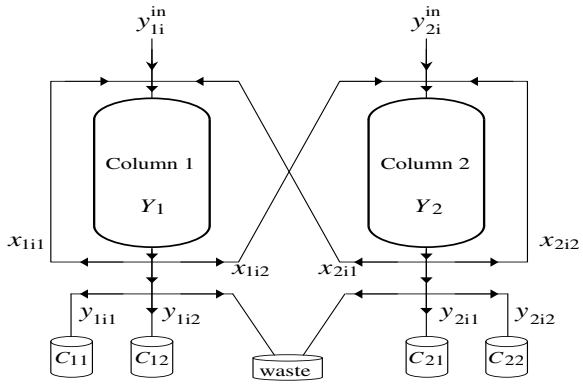

FIG. 1. *A two-column system with two components.*

The responses of feeding a glucose/fructose mixture into a column is illustrated in Fig. 2. Each component of the mixture have equal concentration (15 g/100ml). From Fig. 2 it can be seen that the glucose, c_1, flows through the column faster than the fructose, c_2. Note, that the outflowing products may have a low concentration but a high purity in some intervals. It can further be seen from Fig. 2, that there is a

time interval around 205 minutes when the outflow is relatively unpure. The unpure outflows should thus be recycled and a more complex system with more columns and/or recycling possibilities is needed. The purpose is to periodically repeat the decisions regarding the feed inputs and the handling of the outflows in such a way that a column system could be as efficiently used as possible.

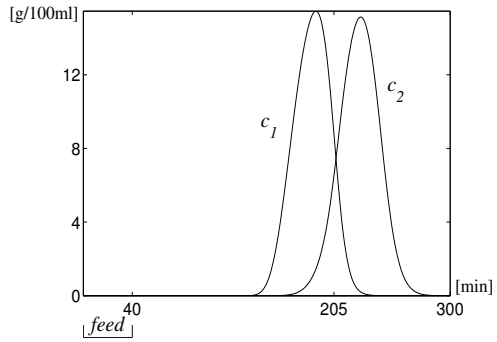

FIG. 2. *The responses of a short feed of a glucose (c_1)/fructose (c_2) mixture.*

3. A dynamic model of the separation process. The changes in the concentrations of the components during the separation process are mathematically modeled here using two-dimensional partial differential equations where the coordinates are given by the time and the height-position in the column.

The concentration of component j at the time $t \geq 0$ and at the height-position z within column k is denoted by $c_{kj}(t,z)$. The height of a column is denoted by z_H, and hence $0 \leq z \leq z_H$. The dynamics of the responses of the concentrations within each column can be modeled with the following system of PDEs [4]:

$$(1) \qquad (1+F\beta_j)\,\frac{\partial c_{kj}}{\partial t} + F \cdot \sum_{l=1}^{C} \beta_{jl} \left(c_{kl}\frac{\partial c_{kj}}{\partial t} + c_{kj}\frac{\partial c_{kl}}{\partial t} \right) + u\frac{\partial c_{kj}}{\partial z} = D_j \frac{\partial^2 c_{kj}}{\partial z^2}$$

where F, β_j, β_{jl}, u, and D_j for $j,l = 1,\ldots,C$, and $k = 1,\ldots,K$ are parameters that can be estimated, for example, from laboratory data. The parameters for a system consisting of two components (fructose and glucose), presented in [6], were used in the present paper.

3.1. Boundary conditions. The feed and the recycling decisions provide the following boundary conditions (at the inlet of column k):

$$(2) \qquad c_{kj}(t,0) = y_k^{in}(t) \cdot c_j^{in} + \sum_{l=1}^{K} x_{lk}(t) \cdot c_{lj}(t,z_H)$$

where c_j^{in} is the concentration of component j in the feed mixture. The logical functions $y_k^{in}(t)$ and $x_{lk}(t)$ in Eq. (2) are modeled using the following stepwise-linear functions:

$$(3) \qquad y_k^{in}(t) = \sum_{i=1}^{T} y_{ki}^{in} \cdot \delta_i(t)$$

$$(4) \qquad x_{lk}(t) = \sum_{i=1}^{T} x_{lik} \cdot \delta_i(t)$$

where the $\delta_i(t)$-function is defined as

$$\delta_i(t) = \begin{cases} 1 & \text{if } t \in [t_{i-1}, t_i],\ i = 1, \ldots, T \\ 0 & \text{otherwise.} \end{cases} \tag{5}$$

Note, that the beginning of a period can be declared by defining some of the feed variables within the first interval in advance. Here the cycle was defined to begin with a feed to the first column (i.e., $y_{11}^{in} = 1$, $y_1^{in}(0) = 1$, and $x_{k1}(0) = 0$). One of the main ideas in the modeling is that the decisions could be made in periods of τ. That is, the system should be in a so-called *steady state* condition [6]. Mathematically, the steady state condition of the system can simply be modeled as periodical boundary conditions as follows:

$$c_{kj}(0, z) = c_{kj}(\tau, z) \tag{6}$$

That is, the concentrations within a column should be equal at the start and at the end of a period. Conditions on the derivatives of the concentration functions can be formulated as follows:

$$\frac{\partial c_{kj}}{\partial t}(0, 0) = \frac{\partial c_{kj}}{\partial t}(\tau, 0) \tag{7}$$

$$\frac{\partial c_{kj}}{\partial t}(0, z_H) = \frac{\partial c_{kj}}{\partial t}(\tau, z_H) \tag{8}$$

$$\frac{\partial c_{kj}}{\partial z}(0, 0) = \frac{\partial c_{kj}}{\partial z}(\tau, 0) \tag{9}$$

$$\frac{\partial c_{kj}}{\partial z}(0, z_H) = \frac{\partial c_{kj}}{\partial z}(\tau, z_H) \tag{10}$$

3.2. Solving the boundary value problem. An analysis of solving the boundary value problem using orthogonal collocation, neural networks, and finite differences was conducted in [6]. The finite difference method was reported in to be the most robust one. The periodical behavior of the solution was achieved by solving the nonlinear PDEs (1) iteratively until the changes in the concentrations of two successive iterations resided within a given tolerance [3].

4. Formulation of the optimization problem. The objective function to maximize the profit for continuous cyclic operation and to optimize the configuration of the column system can be expressed as follows:

$$\max \frac{1}{\tau} \sum_{k=1}^{K} \sum_{i=1}^{T} \left[\left(\sum_{j=1}^{C} p_j y_{kij} \int_{t_{i-1}}^{t_i} c_{kj}(t, z_H) dt \right) - w y_{ki}^{in} (t_i - t_{i-1}) \right] - \sum_{k=1}^{K} r_k Y_k \tag{11}$$

where p_j and w are parameters that denote the prices of the feed inputs and the collected products. The annualized investment costs of the columns are modeled in the last sum in (11), where the parameter r_k is given by the annuity of the investment cost of column k. The binary variables y_{kij} and y_{ki}^{in} in (11) indicate when products are collected and feeds are input, respectively. Note, that the objective function in (11) is highly nonlinear, since the concentrations, $c_{kj}(t, z_H)$, are functions of all the time variables and the input and recycling variables. Hence, the formulation in Eq. (11)

is not very suitable to be used as such within a local optimization method. Denoting the outtaken products with s_{kij}, and the length of the feeds with d_{ki}, the following objective can be used:

$$\max \left\{ \frac{1}{\tau} \sum_{k=1}^{K} \sum_{i=1}^{T} \left[\left(\sum_{j=1}^{C} p_j s_{kij} \right) - w d_{ki} \right] - \sum_{k=1}^{K} r_k Y_k \right\} \tag{12}$$

The products, s_{kij}, and the feeds, d_{ki}, can be modeled using linear constraints, as will be described in the following.

Firstly, that the time points are, in increasing order:

$$t_{i-1} \leq t_i, \ i = 1, \ldots, T \tag{13}$$

The variables regarding the feed inputs and the handling of the outflows are restricted by the variables that indicate the existence of each column as follows:

$$y_{ki}^{in} - Y_k \leq 0 \tag{14}$$

$$y_{kij} - Y_k \leq 0 \tag{15}$$

$$x_{lik} - Y_k \leq 0 \tag{16}$$

That is, if $Y_k = 0$, then the corresponding binary variables, y_{ki}^{in}, y_{kij} and x_{lik} must also be zero. The outflow of column k during the time interval $[t_{i-1}, t_i]$ can be collected as a product, recycled, or put in a waste-bin. This can be formulated as follows:

$$\sum_{j=1}^{C} y_{kij} + \sum_{l=1}^{K} x_{kil} \leq 1 \tag{17}$$

Hence, if the left hand side of (17) is zero, then the outflow can be considered as waste. Within each interval, it is also possible to require that the outflow of each column should either be collected as a product or be recycled further. This can be managed by rewriting (17) as an equality constraint:

$$\sum_{j=1}^{C} y_{kij} + \sum_{l=1}^{K} x_{kil} = 1 \tag{18}$$

Put feed, recycle, or eluent into column k:

$$y_{ki}^{in} + \sum_{l=1}^{K} x_{lik} \leq 1 \tag{19}$$

The volume of the feed that is put into column k within interval i, that is used in the objective function in (12), is modeled using the variable d_{ki} with the following "big-M" formulation:

$$(t_i - t_{i-1}) - M_1(1 - y_{ki}^{in}) \leq d_{ki} \tag{20}$$

where $M_1 \geq \max\{t_i - t_{i-1}\}$. The volumes of the collected products, s_{kij}, in (12) are similarly modeled as follows:

$$s_{kij} \leq m_{kij} \tag{21}$$

$$s_{kij} \leq M_2 \cdot y_{kij} \tag{22}$$

where $M_2 \geq \max\{s_{kij}\}$. Hence, if $y_{kij} = 0$, then $s_{kij} = 0$, otherwise $s_{kij} \leq m_{kij}$. Because the collected products will be maximized in (12), the constraint in (21) will become active (i.e., $s_{kij} = m_{kij}$) when $y_{kij} = 1$. The m_{kij}-variable above is defined as the mass of product j within interval i at the outlet of column k. This can be formulated as an equality constraint as follows:

$$m_{kij} = \int_{t_{i-1}}^{t_i} c_{kj}(t, z_H)dt \tag{23}$$

where the concentrations $c_{kj}(t, z)$ are obtained by solving the boundary value problem. The purity constraints were formulated as the fraction of the collected product in the total mass of all components:

$$\frac{\sum_{k=1}^{K}\sum_{i=1}^{T} s_{kij}}{\sum_{k=1}^{K}\sum_{i=1}^{T} q_{kij}} \geq R_j \tag{24}$$

where $R_j \leq 1$ denotes the purity requirement of component j. The q_{kij}-variables in (24) are used for measuring the volume of all components within interval i if the component j is collected from column k:

$$\sum_{j=1}^{C} m_{kij} - M_3 y_{kij} \leq q_{kij} \tag{25}$$

In general, nonlinear equalities of the type in (23) might cause problems in many optimization methods, for example, difficulties in convergence. Furthermore, it is unnecessarily strict to require (23) to hold also when no products are collected. Assume that component j is collected from column k during interval i. The equality in (23) can be relaxed as follows:

$$m_{kij} \leq \int_{t_{i-1}}^{t_i} c_{kj}(t, z_H)dt + M \cdot (1 - y_{kij}) \tag{26}$$

where $M \geq \max\{c_{kj}(t, z_H)(t_i - t_{i-1})\}$. The maximization of variable s_{kij} in (12) will, through (21), also maximize variable m_{kij} whenever $y_{kij} = 1$. On the contrary, the masses of the other products, $m_{kil}, l \neq j$, within the outflow from column k during interval i should satisfy the following constraints:

$$m_{kil} \geq \int_{t_{i-1}}^{t_i} c_{kj}(t, z_H)dt - M \cdot (1 - \sum_{j=1,\ l\neq l}^{J} y_{kij}) \tag{27}$$

Note that the masses of the unpure fractions, m_{kil}, in (27) only affect the denominator of the purity constraint in (24) and will thus be minimized during the optimization. That is, the masses of the collected products that are to be maximized will be underestimated in (26) and the masses of the unpure fractions will be overestimated through (27).

4.1. The ECP method. The optimization problem was solved using the Extended Cutting Plane (ECP) method that is an extension of Kelley's Cutting Plane (CP) method [7] for solving convex NLP problems. The comparisons in [9] and [3] revealed that the ECP method generally requires magnitudes fewer function evalutions than a nonlinear BB-method. This property of the ECP method is a major advantage in the chromatographic separation problem, because each time the nonlinear contraints are evaluated, the integrals have to be calculated and hence the boundary value problem has to be solved.

The ECP method was first extended in order to enable the solving of convex MINLP problems [12]. The method was then developed in [13] to cover pseudo-convex MINLP problems. In [10], the convergence properties of both MINLP and NLP problems with quasi-convex constraints were analyzed. The method was further developed in [14] in order to enable the solving of problems consisting of both a pseudo-convex objective function and pseudo-convex constraints.

The general MINLP problems to be solved with the ECP method can be formulated as follows:

$$\begin{aligned} \min_{\mathbf{z}\in\mathbf{N}\cap\mathbf{L}} \quad & f(\mathbf{z}) \\ & \begin{cases} N = \{\mathbf{z}|\mathbf{g}(\mathbf{z}) \leq \mathbf{0}\} \\ L = \{\mathbf{z}|\mathbf{A}\mathbf{z} \leq \mathbf{a},\ \mathbf{B}\mathbf{z} = \mathbf{b}\} \cap \mathbf{X} \times \mathbf{Y} \end{cases} \end{aligned} \tag{28}$$

The variable vector, $\mathbf{z}$, consists of both a continuous part and an integer part that are bound by the X and Y sets, respectively. The objective function, $f(\mathbf{z})$, and the nonlinear constraints, $\mathbf{g}(\mathbf{z})$, should be differentiable pseudo-convex functions defined on the set L. If the functions $\mathbf{g}$ and f are pseudo-convex and if the set X is a compact subset of $\Re^n$ and if Y is a finite discrete set in Z^m, then the ECP algorithm will ensure convergence to the global optimal solution.

Assuming that the objective function is a pseudo-convex function, the generalized ECP method solves the problem (28) by solving the following sequence of MINLP subproblems:

$$\begin{aligned} \min_{\mathbf{z}\in\mathbf{N_r}\cap\mathbf{L_r^n}} \quad & \mu \\ & \begin{cases} N_r = \{\mathbf{z} \in \mathbf{N}|\mathbf{f}(\mathbf{z}) - \mathbf{f_r} \leq \mathbf{0}\} \\ L_r^n = \{\mathbf{z} \in \mathbf{L}|\mu \leq \mathbf{f_r};\ \mathbf{f_r} + \nabla\mathbf{f}(\mathbf{z_r^l})^{\mathbf{T}}(\mathbf{z} - \mathbf{z_r^l}) \leq \mathbf{0};\ \mathbf{l} = \mathbf{1}, \mathbf{2}, \ldots, \mathbf{n}\} \end{cases} \end{aligned} \tag{29}$$

where f_r is a valid upper bound on the objective function, $f(\mathbf{z})$. Note, that the subproblem (29) has a linear objective function and pseudo-convex constraints. Each subproblem (29) is solved with the ECP method that solves the following sequence of Mixed Integer Linear Programming (MILP) problems:

$$\min_{(\mu,\mathbf{z})\in\mathbf{\Omega_k}} \mu(P_k) \tag{30}$$

where the set Ω_k is defined by

$$\Omega_k = L \cap \{\mathbf{z} \mid \mathbf{l_j}(\mathbf{z}) \leq \mathbf{0}, \mathbf{j} = \mathbf{1}, \mathbf{2}, \ldots, \mathbf{J_k}\} \tag{31}$$

This iterative procedure begins with $\Omega_0 = L$. Note, that $l_j(\mathbf{z}) \in \mathbf{\Omega_k}$ are cutting planes underestimating the entire feasible region of (P) and J_k is the number of cutting planes in Ω_k at iteration k. After each iteration, a new MILP subproblem is generated by adding and/or modifying old cutting planes of the most violating

nonlinear constraints. The generated cutting planes, with respect to the constraints, are of the following type:

$$g_i(\mathbf{z}) + \alpha_{\mathbf{k}}^{\mathbf{r}'} \nabla \mathbf{g_i}(\mathbf{z})^{\mathbf{T}} (\mathbf{z} - \mathbf{z_k}) \leq \mathbf{0} \tag{32}$$

where $\mathbf{z_k}$ is the solution to the previous MILP problem (P_k). The scalar, $\alpha_k^{r'}$, is initially one but can be updated in subsequent iterations in order to guarantee that no part of the feasible region is cut off. Convergence to the global solution is ensured when the sequence of points converges to a solution in the feasible region of the problem (P), defined by the set $N \cap L$, where $N \cap L$ is a subset of Ω_k. For a more detailed description of the ECP algorithm, see [14].

Note, that the ECP-method does not require any second order information of the nonlinear functions. Only one single value of each nonlinear constraint, and one single gradient (of the most violating constraint) need to be calculated in each iteration. In the present paper, the gradients of the integrals were approximated using finite differences in a similar way as in the solving of the PDEs.

5. Numerical results. The results of solving the separation problem for different purity requirements will be presented in the following. For simplicity, the investment costs for the columns were neglected and the binary variables, Y_k, denoting the existence of each column, were predefined. The following parameters were used for the costs in (12): $p_1 = 1.0$, $p_2 = 1.4$, $w = 4.5$, and $r_1 = r_2 = 0.0$. The costs of the products and the feeds are normalized in such a way that product 1 has unit price, while product 2 is 40% more valuable. Thus, in some problems, higher purity was required for the second product. The feed cost can be interpreted as 30% of the value of product 1 and 21.4% (i.e., 0.3/1.4) of product 2. The problem was modeled and solved for a simple one-column system with no recycling, and a two-column system with recycling possibilities from column 1 to column 2. The one-column system was modeled for periods consisting of up to four intervals, while the two-column problem was modeled for up to seven time intervals. Note, that the complexity of the optimization problem increases with the number of intervals, as more intervals imply more variables and more constraints.

The obtained results when solving a one-column system for different purity requirements are presented in Table 1. Table 1 contains the obtained objective value, f^*, the obtained purity, the number of solved MILP subproblems, and the number of evaluations of the functions and the gradients. Furthermore, the total number of times the system of PDEs were solved and the CPU-times (on a 2.53 GHz Pentium 4 PC) are also presented in the table. The profiles of the concentrations of a solution at the outlet of the column are illustrated in Fig. 3. The obtained purities within each interval are also presented in the figure, while the actual purities of the total sum of each product are given in Table 1. These are in some cases slightly higher than the purity requirement because of the underestimation of the products and the over-estimation of the non-products. The value of the objective, f^*, that is given in Table 1, was calculated from (11) using the obtained solution.

Fig. 3 indicates that if the purity demand is low all the outflows can be collected as separated products. However, for the purity requirement $(0.90, 0.95)$ an additional column is needed in order to enable further separation of the unpure outflow.

Higher purity requirements were used in the separation problem of two-column systems where recycling was possible. The results are presented in Table 2 and the concentration profiles of the solution to one of the problems is illustrated in Fig. 4. Note, that the gradients of the nonlinear constraints, ∇g, were approximated using

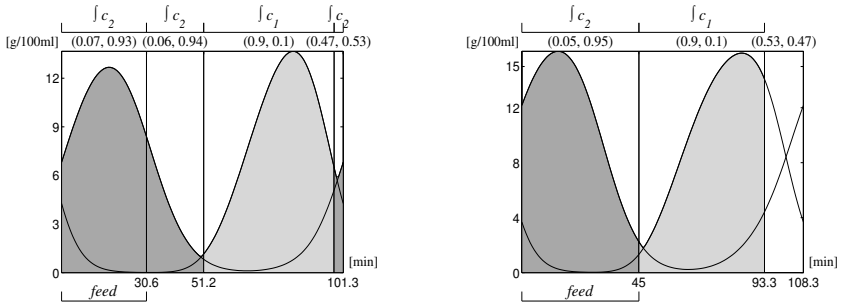

FIG. 3. *Profiles of the obtained solutions to a one-column problem.*

forward and/or backward differences. Hence, the total number of times of solving the PDEs (Table 2) increases with the number of evaluations of the nonlinear constraints and with the number of evaluations of the gradients of these.

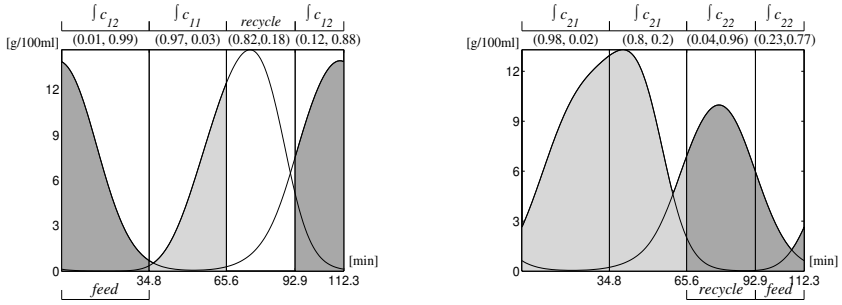

FIG. 4. *A solution to the two-column problem for the purity demand* $(0.90, 0.90)$, $f^* = 14.01$.

6. Conclusions. In the present paper, techniques for solving a chromatographic separation problem were presented. The separation process was modeled as a boundary value problem containing both design and control variables for optimal cyclic operation, of an optimized column system. The presented MINLP formulation enables a solving of the process design problem of chromatographic separation column system. The presented techniques can be applied, with low computational costs, to

TABLE 1
Results of a one-column system for different purity demands.

	Purity requirement			
	$(0.80, 0.90)$	$(0.85, 0.90)$	$(0.90, 0.90)$	$(0.90, 0.95)$
f^*	12.28	10.48	8.62	9.56
purity	$(0.81, 0.90)$	$(0.86, 0.91)$	$(0.90, 0.90)$	$(0.90, 0.95)$
# MILP	124	90	136	114
# f-eval.	124	111	205	114
# g-eval.	2000	1408	2144	1840
# ∇f	33	14	14	17
# ∇g	90	72	118	96
# PDE sol.	1385	1096	1786	1459
CPU [sec]	72.5	40.2	78.8	64.5

TABLE 2
Results of a two-column separation system.

	Purity requirement			
	(0.90, 0.90)	(0.90, 0.95)	(0.95, 0.95)	(0.95, 0.99)
f^*	14.01	12.01	11.54	7.96
purity	(0.90, 0.93)	(0.91, 0.95)	(0.97, 0.95)	(0.96, 0.99)
# MILP	150	105	146	152
# f-eval.	150	105	146	175
# g-eval.	4800	3360	4672	4832
# ∇f	10	7	11	15
# ∇g	139	96	134	135
# PDE sol.	3408	2296	3142	3065
CPU [sec]	780.0	192.2	395.48	261.1

improve the efficiency of already existing column systems.

An illustrative fructose-glucose example was solved using the presented formulations. The MINLP problem was numerically solved using the ECP-method that has been proven efficient on many complex engineering problems. The ECP-method requires relatively few non-linear function evaluations (in this particular case, evaluations of integrals), which is a great advantage in the presented separation problem where a boundary value problem is solved in each evalutaion.

It was shown that, for a lower purity demand, all the outflow of a one-column system could be utilized as products. For a higher purity demand, a more complex system with two or more columns was needed in order to enable the recycling of unpure outflows for further separation.

Improvements in the solving of the boundary value problem, the MINLP problem, and also in the modeling and design are challenges in future research. Some of the design variables of the column system, for instance the size of each column and the flowrates in each column, could be included as variables into the MINLP problem.

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