

# **A Unified Modeling Framework for the Design of Complex Separation Processes**

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## Abstract

A unified modeling approach that combines rigorous rate-based balance equations with the model-order reduction properties of orthogonal collocation on finite elements (OCFE) approximation techniques is employed for the design and optimization of complex staged separation processes. The process model involves the rigorous description of mass and heat transfer phenomena, phase equilibrium, and chemical reactions in both gas and liquid phases in a sufficient number of selected collocation points which are less than the number of stages in the column. In this way a significant degree of detail is maintained that is absolutely necessary for the accurate representation of complex reactive absorption and distillation processes but in a more compact form than the equivalent full-order (tray-by-tray) model representation. The unified modeling framework has been proved particularly efficient in the optimal design of single or multiple columns, the optimization of operating conditions and the dynamic simulation of complex staged separation units mainly due to the elimination of integer variables associated with the column stages and the accurate representation of the process.

Results from the implementation of the compact model formulation to the design optimization and the dynamic simulation of the reactive absorption of nitrogen oxides ( $\text{NO}_x$ ) from a gas stream by a weak  $\text{HNO}_3$  aqueous solution as used in an industrial nitric acid production process are reported. Optimal column configurations with multiple side feed and draw streams are obtained.

## Introduction

Reactive absorption and distillation processes are gaining strong interest in many industrial applications mainly due to the significant reduction in the overall investment costs that can be achieved through the combination of reaction steps with the separation of products. Common applications of reactive absorption can be found in the manufacture of nitric and sulfuric acid, soda ash, the purification of synthesis gases and the recovery of solvents. Another important application is found in air pollution control and the cleaning of process gas streams from pollutants and toxic gases. Reactive distillation is used in the production of a number of ether solvents and gasoline additives. Both reactive absorption and distillation are complex unit operations characterized by coupled equilibrium, mass and heat transfer and reactive phenomena. Therefore, the use of detailed models that account for the interactions between chemical reactions and multicomponent mass and heat transfer for the simulation and optimal design of the units has been proved necessary<sup>1-3</sup>.

Detailed rate-based nonequilibrium (NEQ) models for reactive separation involve the simultaneous consideration of mass and heat transfer phenomena, phase equilibrium relations and chemical reactions in both gas and liquid phases in a number of equivalent stages<sup>1</sup> associated with the actual stages in the column. Mass and heat transfer resistance is considered to occur within a thin film region adjacent to the vapor-liquid interface<sup>1-2</sup>. Coupled multicomponent mass and heat transfer is described in the form of the Maxwell-Stephan equations, while chemical reactions may be considered both in the bulk and film regions and become a significant source of non-linearity in the systems behavior.

The design of staged reactive separation processes involves the calculation of the column configuration, the design parameters and operating conditions that optimize an economic criterion and further meet the safety, environmental and operating constraints. The operating conditions in reactive absorption involve decisions about the flow rate and concentration of the solvent feed streams in the column, the location in the column of the side solvent feed, recycle and product draw streams, and the temperature profile in the

column. For distillation units these conditions become the reflux and boilup ratios and the location of feed and draw side streams. In addition, stage holdups play an important role as they manipulate the reaction extent in the stages. Whilst some of these decision variables can be represented as continuous variables (e.g., operating conditions) some others associated with the structural configuration of the column (e.g., total number of stages, location of the side streams in a plate column) are of discrete nature.

NEQ stage balance equations introduce a considerable degree of detail that is absolutely necessary for an adequately accurate representation of the column behavior. In optimization-based approaches with integer-valued variables representing the existence of each column stage, a large number of stages in the column results in the introduction of an equally large number of integer variables. Therefore, the design optimization of single or multiple unit flowsheets therefore becomes quite tedious as the solution effort for a full-order rate based model is quite heavy.

Orthogonal collocation on finite elements (OCFE) techniques transform the discrete number of stages in the column into a continuous variable thus eliminating the need for integer variables associated with the column stages. Composition and temperature are subsequently 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 staged model with significant savings in computational time<sup>4</sup>. Furthermore, an OCFE formulation of the model allows for the use of conventional nonlinear programming methods for the calculation of the optimal number of stages as only continuous variables are involved in the model. The achieved model size reduction results in increased efficiency of the method, especially when the simultaneous design of more than one column is performed<sup>5</sup>.

In all previous works regarding OCFE techniques in staged separation units<sup>4-6</sup> the associated process model assumed instant equilibrium between phases. The present work combines the sophisticated and accurate NEQ balance equations with the model reduction properties of the OCFE formulation. The greatest advantage is that the model maintains the necessary degree of complexity and detail but employ an efficient and accurate approximation technique that requires the solution of a much smaller set of modeling equations. This is achieved through the continuous representation of the staged column and the polynomial approximation along the column domain. Moreover, the OCFE formulation provides a unified modeling framework for a wide variety of unit operations ranging from staged to packed separation columns and from reactive absorption to reactive distillation.

In the next two sections, a description of the design problem and its formulation for staged reactive absorption and distillation units is presented. The unified NEQ/OCFE formulation is applied in the reactive absorption of  $\text{NO}_x$  gases by a weak nitric acid aqueous solution used in the industrial production of nitric acid.

## **Design problem statement**

The design of reactive separation processes involves the determination of the column configuration expressed in total number of stages in the column, the locations of side feed and draw streams and the operating conditions that optimize an economic criterion, while satisfying the product specifications and the safety and operational constraints for the process. The economic criterion usually involves the annualized investment costs, the cost of raw materials, the operating costs, and the revenues from the sale of the products. The behavior of the units is obtained using detailed process model that accurately describe the underlying physical and chemical phenomena (e.g., NEQ model). In addition, operating

(e.g., flooding), safety and environmental constraints are effective and should be satisfied by the optimal design.

The mathematical representation of the design optimization problem is:

$$\begin{aligned}
 & \text{Max}_{\mathbf{x}, \mathbf{d}} \quad f(\mathbf{x}, \mathbf{d}, \boldsymbol{\varepsilon}) \\
 & \text{s.t.} \quad \mathbf{h}(\mathbf{x}, \mathbf{d}, \boldsymbol{\varepsilon}) = \mathbf{0} \\
 & \quad \quad \mathbf{g}(\mathbf{x}, \mathbf{d}, \boldsymbol{\varepsilon}) \leq \mathbf{0} \\
 & \quad \quad \mathbf{x}^l \leq \mathbf{x} \leq \mathbf{x}^u, \quad \mathbf{d}^l \leq \mathbf{d} \leq \mathbf{d}^u
 \end{aligned} \tag{1}$$

where  $\mathbf{x}$  denotes the process (state and control) variables,  $\mathbf{d}$  the vector of the design variables that comprises equipment capacity variables and structural design variables (e.g., number of stages in a column) and  $\boldsymbol{\varepsilon}$  the vector of model parameters and process disturbances.

The process design derived from the solution of (1) should ensure that the operating specifications, safety regulations, and environmental constraints are satisfied during plant operation and in addition, good economic performance is maintained for the plant under the presence of model and process related uncertainty. The optimal solution is calculated for multiple model parameter and process variables variations system along the dominant directions of variability for the system<sup>5</sup>.

## Model formulation for staged reactive separation processes

The rate-based model for reactive absorption processes<sup>1-3,7-8</sup>, involves the rigorous description of mass and heat transfer phenomena, phase equilibrium relations and chemical reactions in both the gas and liquid phase calculated in a number of equivalent stages. Mass transfer is described by the thin-film model<sup>7</sup>, which assumes that mass transfer resistance is limited in the two film regions adjacent to the gas-liquid interface. Gas and liquid bulk phases are in contact only with the corresponding films, while thermodynamic phase equilibrium is assumed to occur only at the interface. Chemical reactions are considered to take place in both the film and bulk regions. The basic assumptions of the model are: (i) no axial dispersion along the column, (ii) one-dimensional mass transport normal to the interface and (iii) gas and liquid bulk phases are perfectly mixed with uniform temperature and composition.

The present formulation combines the rigorous rate-based modeling equations with the model reduction properties of the OCFE technique. According to the principles of OCFE technique<sup>4,6</sup>, the column is separated into sections, with each section defined as the part of the column between two streams entering or leaving the column. Each column section is divided into smaller sub domains, namely, the finite elements. For each finite element, a number of collocation points are specified. The main principle of the OCFE formulation is that material and energy balances as resulted from the rate-based model 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 within each element. 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 stages 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. Hence, the complete model is fully recovered. Lagrange interpolation polynomials are used within each finite element to approximate the liquid and vapor component molar flow rates, as well as the liquid and vapor stream enthalpies.

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). 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 feed and product draw stages are treated as discrete stages.

The size of each column section (equivalent to the number of stages) 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 collocation points included in that section. The conditions at the element boundaries obey zero-order continuity. While this is a plausible assumption for staged units where the actual profiles are discontinuous, in packed columns smoothness conditions for the concentration and enthalpy profiles may be employed.

Mass and energy balances as resulted from the NEQ model are satisfied exactly only at the collocation points. The mass balances for collocation point  $s_j$ , considering potential accumulation of mass in the gas and liquid bulk phases, are described by the following equations:

$$\frac{dm_i^L(s_j)}{dt} = \tilde{L}_i(s_j - 1) - \tilde{L}_i(s_j) + (f^L(s_j)R_i^{Lb}(s_j) + N_i^{Lb}(s_j)\mathbf{a}^{int})A^{col}\Delta h \quad i=1,\dots,nc, j=1,\dots,NC \quad (2)$$

$$\frac{dm_i^G(s_j)}{dt} = \tilde{G}_i(s_j + 1) - \tilde{G}_i(s_j) + (f^G(s_j)R_i^{Gb}(s_j) - N_i^{Gb}(s_j)\mathbf{a}^{int})A^{col}\Delta h \quad i=1,\dots,nc, j=1,\dots,NC \quad (3)$$

The terms on the left-hand-side of the equations account for the component molar hold-up in the liquid and gas bulk phase, respectively. These are related to the available liquid and vapour volumes corresponding to an equivalent stage by the following equations:

$$m_i^L(s_j) = f^L(s_j)d^L(s_j)\frac{\tilde{L}_i(s_j)}{\tilde{L}_i(s_j)}A^{col}Dh \quad i=1,\dots,nc, j=1,\dots,NC \quad (4)$$

$$m_i^G(s_j) = f^G(s_j)d^G(s_j)\frac{\tilde{G}_i(s_j)}{\tilde{G}_i(s_j)}A^{col}Dh \quad i=1,\dots,nc, j=1,\dots,NC \quad (5)$$

In Eq (4) and (5),  $d^L(s_j), d^G(s_j)$  denote the liquid and gas phase density and  $f^L(s_j), f^G(s_j)$  the liquid and gas phase volumetric holdup, respectively, calculated at conditions prevailing at each collocation point  $[\tilde{L}_i(s_j), \tilde{G}_i(s_j), \tilde{T}(s_j), \tilde{P}(s_j)]$ , while  $\Delta h$  stands for the height of an equivalent stage.

The diffusion molar flux term  $N_i(s_j)$  in Eq. (2) and (3) is estimated by the Maxwell-Stefan equations for multicomponent mixtures. Assuming ideal gas phase, the Maxwell-Stefan equations for the gas and the liquid phase respectively take the following form:

$$\frac{\partial y_i^{Gf}(s_j)}{\partial \eta^{Gf}} = - \sum_{\substack{k=1 \\ k \neq i}}^{NC} \frac{y_k^{Gf}(s_j)N_i^{Gf}(s_j) - y_i^{Gf}(s_j)N_k^{Gf}(s_j)}{(\tilde{P}(s_j))/RT(s_j)}E_{ik}^G \quad i=1,\dots,nc, j=1,\dots,NC, 0 < \eta^{Gf} \leq \delta^{Gf}(s_j) \quad (6)$$

$$\sum_{k=1}^{NC-1} \Gamma_{i,k}(s_j) \frac{\partial x_i^{Lf}(s_j)}{\partial \eta^{Lf}} = - \sum_{\substack{k=1 \\ k \neq i}}^{NC} \frac{(x_k^{Lf}(s_j) N_i^{Lf}(s_j) - x_i^{Lf}(s_j) N_k^{Lf}(s_j))}{c_t(s_j) D_{ik}^L} \quad i=1, \dots, nc, \quad j=1, \dots, NC, \quad 0 < \eta^{Lf} \leq \delta^{Lf}(s_j) \quad (7)$$

where

$$G_{ik}(s_j) = \delta_{ik} + x_i(s_j) \left. \frac{\partial \ln g_i(s_j)}{\partial x_k(s_j)} \right|_{\tilde{T}(s_j), \tilde{P}(s_j), x_k(s_j), k \neq i=1, \dots, NC-1} \quad (8)$$

The dynamic mass balances in the gas and liquid films, considering the effect of chemical reactions on the mass transfer through the film regions, as well as the boundary conditions connecting the gas and liquid bulk phases with the respective films are also satisfied exactly only at the collocation points. The mass balances in the films therefore become:

$$\frac{\partial c_i^{Gf}(s_j)}{\partial t} + \frac{\partial N_i^{Gf}(s_j)}{\partial \eta^{Gf}} - R_i^{Gf}(s_j) = 0 \quad i=1, \dots, NC \quad j=1, \dots, n \quad 0 < \eta^{Gf} \leq \delta^{Gf}(s_j) \quad (9)$$

$$\frac{\partial c_i^{Lf}(s_j)}{\partial t} + \frac{\partial N_i^{Lf}(s_j)}{\partial \eta^{Lf}} - R_i^{Lf}(s_j) = 0 \quad i=1, \dots, NC, \quad j=1, \dots, n \quad 0 < \eta^{Lf} \leq \delta^{Lf}(s_j) \quad (10)$$

The boundary conditions for Eq (9) and (10) are as follows:

$$N_i^{Gb}(s_j) = N_i^{Gf}(s_j) \Big|_{\eta^{Gf}=0} \quad y_i^{Gb}(s_j) = y_i^{Gf}(s_j) \Big|_{\eta^{Gf}=0} \quad i=1, \dots, nc, \quad j=1, \dots, NC \quad (11)$$

$$N_i^{Lf}(s_j) \Big|_{\eta^{Gf}=\delta^{Gf}(s_j)} = N_i^{Lb}(s_j) \quad x_i^{Lf}(s_j) \Big|_{\eta^{Gf}=\delta^{Gf}(s_j)} = x_i^{Lb}(s_j) \quad i=1, \dots, nc, \quad j=1, \dots, NC \quad (12)$$

At the gas-liquid interface at each collocation point, the thermodynamic equilibrium was described by the following equation:

$$y_i^{int}(s_j) = K_i(s_j) x_i^{int}(s_j) \quad i=1, \dots, nc, \quad j=1, \dots, NC \quad (13)$$

while the boundary equations between the gas and liquid films and the interface are:

$$N_i^{Gf}(s_j) \Big|_{\eta^{Gf}=\delta^{Gf}(s_j)} = N_i^{int}(s_j) = N_i^{Lf}(s_j) \Big|_{\eta^{Lf}=0} \quad i=1, \dots, nc, \quad j=1, \dots, NC \quad (14)$$

$$y_i^{Gf}(s_j) \Big|_{\eta^{Gf}=\delta^{Gf}(s_j)} = y_i^{int}(s_j) \quad x_i^{int}(s_j) = x_i^{Lf}(s_j) \Big|_{\eta^{Lf}=0} \quad i=1, \dots, nc, \quad j=1, \dots, NC \quad (15)$$

Neglecting the heat transfer effects along the film regions the overall dynamic energy balance at each collocation point becomes:

$$\frac{dU(s_j)}{dt} = \tilde{L}_t(s_j - 1) \tilde{H}^L(s_j - 1) + \tilde{G}_t(s_j + 1) \tilde{H}^G(s_j + 1) - \tilde{L}_t(s_j) \tilde{H}^L(s_j) - \tilde{G}_t(s_j) \tilde{H}^G(s_j) - Q(s_j) \quad j=1, \dots, NC \quad (16)$$

where

$$U(s_j) = \sum_{i=1}^{NC} (m_i^L(s_j) u_i^L(s_j) + m_i^G(s_j) u_i^G(s_j)) \quad j=1, \dots, NC \quad (17)$$

Terms  $R_i^{Gb}(s_j)$  and  $R_i^{Lb}(s_j)$  denote the total component reaction rate of the  $i$ th component in the gas and liquid bulk phases and are estimated at the conditions prevailing at each collocation point by the following equations:

$$R_i^{Gb}(s_j) = \sum_r n_{i,r}^G r_r^{Gb}(s_j) \quad i=1, \dots, nc, \quad j=1, \dots, NC \quad (18)$$

$$R_i^{Lb}(s_j) = \sum_r n_{i,r}^L r_r^{Lb}(s_j) \quad i=1,\dots,nc, \quad j=1,\dots,NC \quad (19)$$

where  $r_r^{Gb}(s_j)$  and  $r_r^{Lb}(s_j)$  denote the rates of the reactions taking place in the gas and liquid phases, respectively. OCFE formulation can be easily tailored to allow reactive and non-reactive sections in the column through the manipulation of the stage holdup. Similar expressions are employed for the calculation of the total component reaction rates  $R_i^{Gf}(s_j)$  and  $R_i^{Lf}(s_j)$  in the films.

Pressure drop in the column, liquid hold-up, specific interfacial area, and gas and liquid film thickness are calculated from correlations that account for the column internals and hydraulics.

## Reactive absorption of NO<sub>x</sub>

The reactive absorption of nitrogen oxides (NO<sub>x</sub>) from a gas stream by a weak HNO<sub>3</sub> aqueous solution<sup>3, 9-11</sup> was modeled using the NEQ/OCFE formulation. This process is an efficient way to remove the nitrogen oxides from gas streams released to the atmosphere, while it is used for the industrial production of nitric acid. Chemical reactions play an important role in the system because they allow the absorption of otherwise insoluble components (e.g., NO) through their chemical transformation (oxidation) to more soluble components (e.g., NO<sub>2</sub>). Furthermore, nitric acid is produced through subsequent reactions in the gas and liquid phase. The mechanism of NO<sub>x</sub> absorption in weak nitric acid aqueous solutions is very complicated and the selected reaction scheme involves five gas-phase and four liquid-phase reactions<sup>9</sup> (Table 1). The oxidation of NO to NO<sub>2</sub> (RR1) is kinetically the slowest and thus the limiting step in the mechanism<sup>10</sup>. The remaining gas-phase equilibrium reactions (RR2)-(RR5) were considered as reversible kinetic reactions. The reaction rate constants of reactions (RR2) and (RR3) were estimated as 10<sup>4</sup> times the value of  $k_1$ <sup>10</sup>. Liquid phase reactions (RR6) and (RR7) are kinetically controlled, while reactions (RR8) and (RR9) were considered as reversible kinetic reactions. The temperature dependency expressions of the equilibrium constants for all the reactions in the kinetic mechanism are shown in Table 2<sup>9-11</sup>.

The gas-phase diffusion coefficients used for the calculation of the component diffusion molar fluxes through the Maxwell-Stefan equations were estimated using the Chapman-Enskog-Wilke-Lee model<sup>12</sup>, while the liquid-phase diffusion coefficients were estimated using the method proposed by Siccidi and Lucas<sup>13</sup>. The NRTL activity model was used for the calculation of the liquid phase activity coefficients. All other necessary thermodynamic calculations (enthalpy, density and so forth) were based on the SRK equation of state.

Table 1. Reactions in NO<sub>x</sub> removal process

Gas phase	Liquid phase
RR1    2 NO + O <sub>2</sub> → 2 NO <sub>2</sub>	RR6    N <sub>2</sub> O <sub>4</sub> + H <sub>2</sub> O → HNO <sub>2</sub> + HNO <sub>3</sub>
RR2    2 NO <sub>2</sub> ↔ N <sub>2</sub> O <sub>4</sub>	RR7    3 HNO <sub>2</sub> → HNO <sub>3</sub> + H <sub>2</sub> O + 2 NO
RR3    3 NO <sub>2</sub> + H <sub>2</sub> O ↔ 2 HNO <sub>3</sub> + NO	RR8    N <sub>2</sub> O <sub>3</sub> + H <sub>2</sub> O → 2 HNO <sub>2</sub>
RR4    NO + NO <sub>2</sub> ↔ N <sub>2</sub> O <sub>3</sub>	RR9    2 NO <sub>2</sub> + H <sub>2</sub> O → HNO <sub>2</sub> + HNO <sub>3</sub>
RR5    NO + NO <sub>2</sub> + H <sub>2</sub> O ↔ 2 HNO <sub>2</sub>	

Table 2. Reaction constants in NO<sub>x</sub> removal process

	Equilibrium and Rate Constants
RR1	$\log_{10}k_1 = 652.1/T - 0.7356 \text{ (atm s)}^{-1}$
RR2	$\log_{10}k_2 = 2993/T - 9.226 \text{ atm}^{-1}$
RR3	$\log_{10}k_3 = 2003.8/T - 8.757 \text{ atm}^{-1}$
RR4	$\log_{10}k_4 = 2072/T - 7.234 \text{ atm}^{-1}$
RR5	$\log_{10}k_5 = 2051.17/T - 6.7328 \text{ atm}^{-1}$
RR6	$\log_{10}k_6^c = -4139/T + 16.3415 \text{ s}^{-1}$
RR7	$\log_{10}k_7^c = -6200/T + 20.1979 \text{ (m}^3/\text{kmol)}^2\text{atm/s}$
RR8	$k_8^c = 3.3 \cdot 10^2 \text{ (kmol /m}^3\text{)}^{-1}$
RR9	$k_9^c = 3.8 \cdot 10^9 \text{ (kmol/m}^3\text{)}^{-1}$

A gas stream with high concentration of NO<sub>x</sub> enters the bottom of the staged counter-current reactive absorption column, a liquid water stream enters from the top of the column, and a feed stream of weak solution of nitric acid enters the side of the column. The bottom liquid stream is mainly consisted of an aqueous nitric acid solution of portion of which is recycled in the column. The nitric acid concentration in the liquid product, leaving the column as a side draw stream, is subject to quality constraints while the concentration of NO<sub>x</sub> gases in the gas stream in the top of the column is subject to specifications due to environmental constraints.

The column comprises 44 trays with an internal diameter of 3.6 m. The distance between the trays is equal to 0.9 m, except for the five trays closer to the bottom, where oxidation reactions mostly take place and higher spacing is used to increase the gas phase holdup. Cooling was provided in the column stages for the removal of the reaction heat and the control of the column temperature, since reactions are highly exothermic and the NO<sub>2</sub> absorption is strongly favored by low temperature. Empirical correlations for sieve plates are used for the calculation of the column pressure drop, the liquid phase holdup, the film thickness, and the stage interfacial area<sup>14-15</sup>.

Table 3. Feed stream specifications

Gas inlet stream (bottom)		Liquid inlet stream (top)	
NO	21.83 mol/s	H <sub>2</sub> O	4.55 mol/s
NO <sub>2</sub>	58.08 mol/s	Temperature	293 K
N <sub>2</sub> O <sub>4</sub>	20.11 mol/s	Side stream	
O <sub>2</sub>	82.74 mol/s	H <sub>2</sub> O	34.62 mol/s
N <sub>2</sub>	1016.44 mol/s	HNO <sub>3</sub>	6.02 mol/s
Temperature	332 K	NO <sub>2</sub>	0.41 mol/s
Pressure	5.6 bar	Temperature	306 K
		Recycle stream	
		Flow	4.55 mol/s



The reactive absorption column was separated into three sections as divided by the two side feed streams. The modular representation of the  $\text{NO}_x$  reactive absorption column can be seen in Figure 1. The stage where the liquid product is removed as well as the five-oxidation stages are treated as discrete stages because for each stage in that section a different holdup is defined. Gas and liquid stream flow rates, temperature and pressure were selected as shown in Table 3. The model was implemented in gPROMS<sup>®16</sup>, an integrated process modeling environment, while the partial differential equations describing mass transfer in the films were discretized using OCFE techniques in gPROMS.

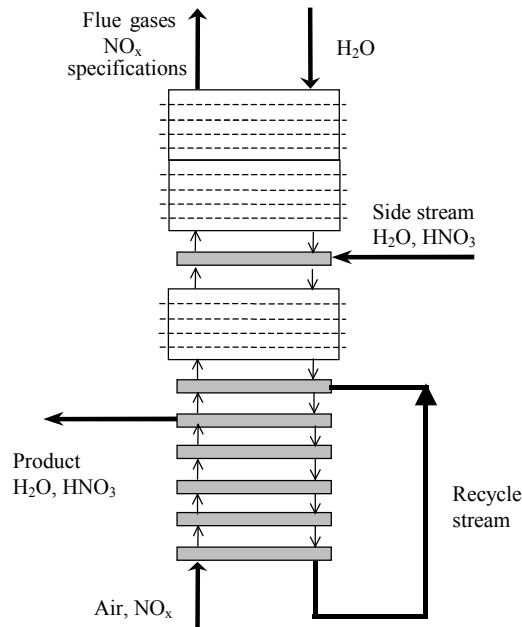


Figure 1. Column configuration

## Model validation

The steady-state design results using the NEQ/OCFE model were compared with those obtained by a full-order (tray-by-tray) rate-based model. The full-order model validation was achieved with steady-state bibliographical data for an industrial  $\text{NO}_x$  removal reactive absorption column<sup>10</sup>.

Table 4. Comparison between full-order and NEQ/OCFE models

Model	Model description				No Eq	CPU ratio	% max dev
	Top Section		Middle Section				
Full-order	29		8		42,680	1.0	-
	NE	NC	NE	NC			
OCFE A	4	4	2	3	28,790	0.73	2.26
OCFE B	2	4	1	2	16,720	0.33	2.30
OCFE C	2	2	1	2	12,580	0.14	2.32

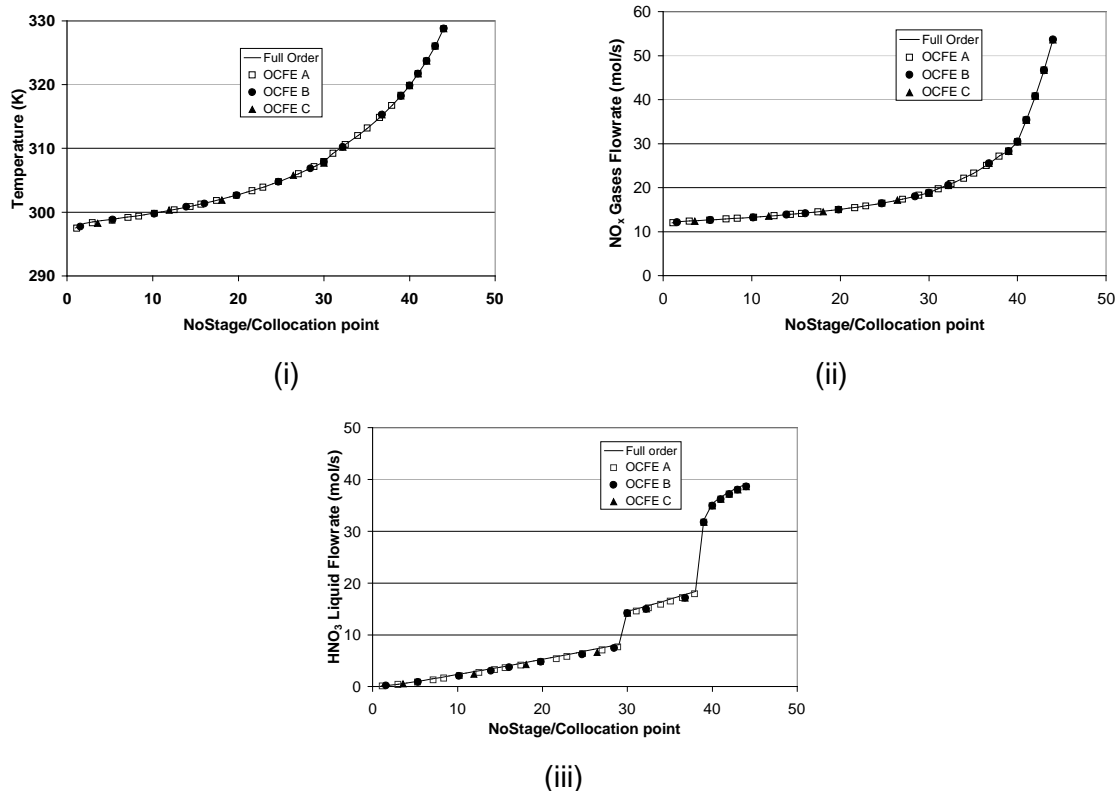


Figure 2. Steady-state model validation: (i) Column temperature (ii) NO<sub>x</sub> gases flow rate in outlet stream (iii) HNO<sub>3</sub> liquid product flow rate.

A sufficient number of collocation points should be placed within each column section, to ensure that the OCFE formulation corresponds to an accurate representation of the process. The sufficient total number of collocation points in each column section depends on the shape and slope of the approximated profiles and the actual size of the column section, in terms of number of discrete column stages<sup>4</sup>. The effect of the number of elements and the order of the polynomials used for the approximation of the two column sections previously described, can be seen in Figure 2 as well as in Table 4. The steady-state temperature profiles, NO<sub>x</sub> gas phase and HNO<sub>3</sub> liquid phase profiles (in terms of flow rates) in the column, for different numbers of finite elements and collocation points in each element, are compared with the results obtained by the full order model (Figure 2). The lines represent the profiles for the full-order rate-based model, while the data points in the NEQ/OCFE model correspond to the position of the collocation points. Figure 2 shows the very good agreement between the profiles calculated with the full-order order and the three OCFE schemes. The maximum deviation that however remained well within acceptable limits, from the full-order profiles was observed in OCFE C. The model size reduction percentage in the case of OCFE C was 70%. The CPU time required for the solution of the full-order model was sevenfold the solution time for case OCFE C. It is obvious that the NEQ/OCFE models retained the ability to accurately approximate complex behavior in the column with a significantly more compact model formulation.

The comparison between the dynamic behavior predicted from both the NEQ/full-order and the NEQ/OCFE model formulations showed excellent agreement as shown in Figure 3 for a 10% increase of the inlet gas stream flow rate. The OCFE approximation of the rate-based reactive absorption model also retains the ability to accurately represent the dynamic

behavior of the process with good tracking of the observed overshoot and inverse response and excellent prediction of the overall settling time.

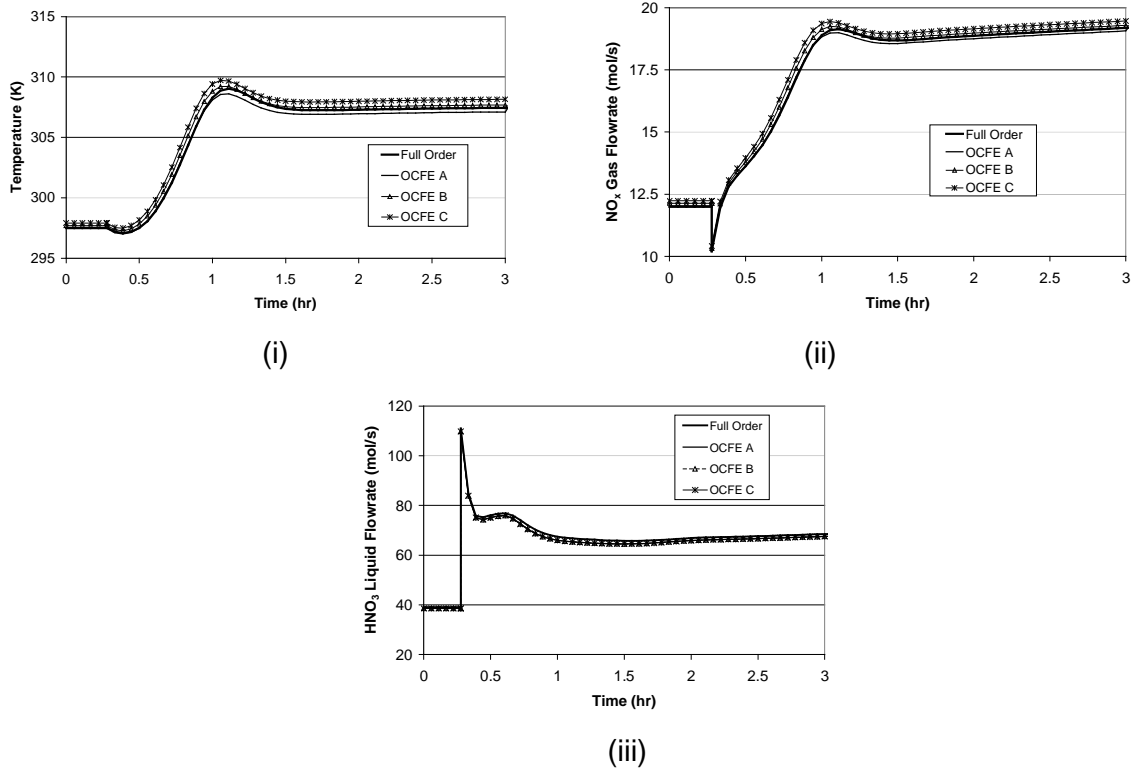


Figure 3. Dynamic model validation: (i) Column temperature (ii) NO<sub>x</sub> gases flow rate in outlet stream (iii) HNO<sub>3</sub> liquid product flow rate.

## Design optimization of NO<sub>x</sub> removal

The NEQ/OCFE model formulation was used for the design optimisation of the NO<sub>x</sub> reactive absorption column. The main objective was the calculation of the operating conditions that optimise an economic criterion and further ensure the satisfaction of the product quality and environmental constraints. The optimization problem has seven degrees of freedom that include the number of stages in the top and the middle section of the column, the flow rate of solvent (water) in the top of the column, the flow rate of the side feed stream, and the cooling water requirements in the column sections. These are common decisions that the operators of the column have to make in a frequent basis as the operating conditions change. The operating and environmental specifications in the column are the nitric acid concentration in the liquid product as well as the NO<sub>x</sub> gases concentration in the top of the column (Table 5). The objective function that has to be minimized includes a term for the capital cost of the column, as well as terms for the cost of the solvent and the necessary cooling water.

$$\text{TotalCost} = 26.25 * D * h^{0.805} + 0.5 * L + 0.2 * L_s - 1.24e^{-4} Q \quad (20)$$

where  $D$  is the diameter and  $h$  the height of the column,  $L$  the solvent flow rate entering the top of the column and  $L_s$  (mol/s) the feed side stream flow rate, while  $Q$  is the amount

of heat removed from the column. Capital and operating cost data were taken from Douglas<sup>17</sup>.

Table 5. Design specifications for the NO<sub>x</sub> removal process

NO <sub>x</sub> in gas outlet (molar fraction)	< 0.0125
HNO <sub>3</sub> in liquid product (molar fraction)	> 0.25

Table 6 shows the design optimization results for two different cases in the NO<sub>x</sub> reactive absorption column. In Design A, the total number of stages of the column remained fixed. In Design B, the number of stages in both the top and middle sections of the column were additional degrees of freedom in the optimization problem. Comparison of Designs A and B shows that the size of the column can be reduced by more than 10 stages for the same set of column specifications. To achieve this reduction the solvent and side stream flow rates are accordingly increased. Furthermore, higher cooling requirements were necessary, especially in the top section of the column. This can be attributed to the fact that absorption is favored by low temperature and the amount of the solvent in the upper part of the column becomes relatively small. The total annualized costs for Design A are larger than those of Design B because the savings in the operational costs do not counter balance the increase of the capital investment costs.

Table 6. Design optimization results

Design	A	B
Number of stages		
Top section	16	16.7
Middle section	21	10
Entire column	44 (fixed)	33.7
Liquid feed streams flow rates (mol/s)		
Solvent (top)	27	36.38
Side stream	37.57	45
Cooling water flow rates (mol/s)		
Side stream position	10	80
Middle section	157.9	160
Bottom part	350	350
Outlet streams concentration		
NO <sub>x</sub> in gas outlet (molar fraction)	0.01165	0.01249
HNO <sub>3</sub> in liquid product (molar fraction)	0.25001	0.25003
Total cost (1,000 \$/yr)	1,844	1,457

## Conclusions

A unifying modeling framework, combining a rigorous nonequilibrium rate-based model and orthogonal collocation on finite elements techniques is employed for the optimal design of staged reactive absorption and distillation processes. NEQ/OCFE models have been proved accurate for steady-state and design optimization and dynamic simulations. The efficiency of the NEQ/OCFE model is enhanced through the elimination of discrete decision variables and the significant model size reduction.

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## Notation

$A^{col}$	= column cross section, $m^2$
$a^{int}$	= specific gas-liquid interfacial area, $m^2/m^3$
$c$	= molar concentration, $mol/m^3$
$\mathbf{d}$	= vector of design variables
$d$	= molar density, $mol/m^3$
$D$	= column diameter, $m$
$\mathcal{D}$	= Maxwell-Stephan diffusion coefficient, $m^2/s$
$f$	= objective function
$\mathbf{g}$	= vector of inequality constraints
$G$	= gas molar flow rate, $mol/s$
$h$	= column height, $m$
$H$	= stream molar enthalpy, $J/mol$
$\mathbf{h}$	= vector of equality constraints
$K$	= equilibrium K value
$L$	= liquid molar flow rate, $mol/s$
$m$	= component molar holdup, $mol$
$nc$	= number of components
$N$	= molar flux, $mol/m^2s$
$NC$	= number of collocation points
$NE$	= number of elements
$NT$	= number of stages
$P$	= pressure, $Pa$
$Q$	= specific heat loss, $J/s$
$r$	= reaction rate, $mol/m^3 s$
$R$	= reaction rate of component, $mol/m^3s$

$s$  = continuous position in the column  
 $t$  = time, s  
 $T$  = temperature, K  
 $u$  = component internal energy, J  
 $U$  = stream internal energy, J  
 $W$  = Lagrange interpolating polynomial  
 $\mathbf{x}$  = vector of process variables  
 $x$  = liquid phase mole fraction  
 $y$  = gas phase mole fraction

#### *Greek Letters*

$\delta$  = film thickness, m  
 $\Delta h$  = height of an equivalent stage, m  
 $\mathbf{e}$  = vector of model parameters  
 $f$  = volumetric holdup,  $\text{m}^3/\text{m}^3$   
 $\eta$  = dimensionless film coordinate

#### *Superscripts*

$L$  = liquid phase  
 $L_f$  = liquid film  
 $G$  = gas phase  
 $G_f$  = gas film  
 $s$  = side stream  
 $t$  = total

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