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# A reduced order rate based model for distillation in packed columns: Dynamic simulation and the differentiation index problem

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ABSTRACT

This paper presents a rigorous dynamic rate based model suitable for simulation of distillation of mixtures in packed columns. The model equations are described in detail considering structure exploitation at simulation level in order to alleviate the large number of states involved in the model description. Moreover, this kind of model may leads to differential-algebraic equations with a differentiation index higher than one. Here this issue is analyzed and a differentiation-index reduction procedure based on the incidence of model states in the Jacobian and the properties of the model dynamics is proposed. This procedure allows for a simplified index-1 model with a reduced stiffness so that dynamic simulation can be performed with off-the-shelf solvers.

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## 1. Introduction

The classical approach for modeling stage-wise distillation columns employs models where the stages are considered in thermodynamic equilibrium. However, this equilibrium-stage approach is not completely valid since, in general, vapor and liquid leaving a stage are not at the same temperature (Seader and Henley, 2006). To cope with this problem the concept of stage efficiency is introduced. Nevertheless, the stage efficiency is an artificial concept and still deficient when multicomponent processes are analyzed or the efficiency is relatively low (Seader and Henley, 2006). To this end, mass and heat transfer considerations are used to better model the interaction between vapor and liquid phases along the column (Taylor and Krishna, 1993). In this approach each stage is assumed in mechanical but not thermal equilibrium and the bulk phases, e.g., liquid and vapor, are in contact at the stage interface. Fig. 1 illustrates a non-equilibrium stage, with vapor and liquid bulk phases, as considered by the rate based model (RBM) (Khrishnamurthy and Taylor, 1985). Mass and energy transfer are performed between the phases through the interface due to temperature and composition gradients. Although this kind of model provides a rigorous description of the separation, it poses challenges at the level of numerical and computational requirements:

- Non-equilibrium models involve a considerable number of variables when compared with equilibrium models.
- Distillation models normally lead to differential-algebraic equations (DAEs) that may exhibit high differentiation index (Pantelides et al., 1988).
- The physical interaction among, e.g., vapor and liquid, implies fast and slow dynamics generating stiff DAEs.

Consequently, the model needs to be formulated so that the simulation task can be easily performed, i.e., the large number of variables used has to be alleviated by e.g., structure exploitation, while stiffness and the differentiation index problem should be treated by looking into the physical features of the model.

### 1.1. Contributions

The contributions of this paper can be summarized as follows: (i) a reduced order model rate based model for distillation in packed columns is presented. (ii) The structure of the proposed model is exploited to alleviate the computational demand for simulation due to the considerable number of model states. (iii) The high-index problem is analyzed and a model simplification based on structural properties of the model Jacobian is proposed. It is noted that this simplification not only solves the

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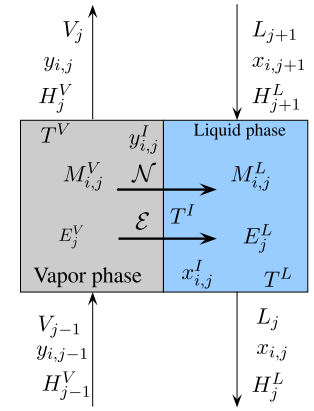



**Fig. 1.** Non-equilibrium stage in the rate based model.

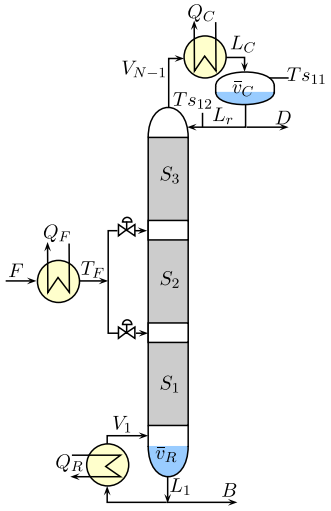



**Fig. 2.** Distillation column layout. Packing material has been distributed in three segments along the main body of the column.

index problem but also reduces the stiffness of the model equations, allowing for simulation with off-the-shelf dynamic equation solvers. (iv) In addition, a dynamic sensitivity analysis is performed in order to identify model parameters that can be estimated from temperature measurements coming from a plant.

## 2. The rate based model

A dynamic model is presented here, based on the work of Khrishnamurthy and Taylor (1985) and Kooijman (1995). The model is referred in this paper as the *Full Rate Based Model* (FRBM), and contains the original equations presented in Khrishnamurthy and Taylor (1985) obtained from mass, equilibrium, component summation and heat (MESH) balances. The packed column studied here is divided in three sections, i.e., (i) reboiler, (ii) structured packing material, subdivided in three sections, and (iii) condenser plus reflux drum as illustrated in Fig. 2.

The column is not thermally insulated, hence, heat loss flows $Q^V$ and $Q^L$ need to be included in the formulation. Moreover, four manipulated variables are considered in the column namely, reboiler duty $Q_R$, recirculation flow $L_r$, top product flow $D$ and bottom product flow $B$. Although feed flow and temperature can be changed in the studied setup, they are not considered as control variables here. The removed heat at the top $Q_C$ is not considered as a degree of freedom neither and it is determined by the model equations due to the constant pressure in the condenser. The following assumptions are made to simplify the model.

- A binary mixture is considered, i.e., $i=1,2$.
- Bulk phases are assumed to be perfectly mixed.
- Vapor–liquid equilibrium is only assumed at the vapor–liquid interface.
- The coupling of heat flux to the mass fluxes across the interface is neglected.
- The reboiler and condenser are assumed to be in thermodynamical equilibrium.
- Each stage is in mechanical equilibrium.
- The condenser is at atmospheric pressure.

In the following paragraphs each one of the mentioned column sections is modeled using dynamic and algebraic equations.[1]

### 2.1. Reboiler

A partial reboiler is considered, assuming thermal and mechanical equilibrium. Under these conditions, the equilibrium stage is modeled by the following mass, energy balances and equilibrium equations:

$$\dot{M}_{1,1}^L = L_2 x_{1,2}^I - B x_{1,1}^I - V_1 y_{1,1}^I, \tag{1}$$

$$\dot{M}_{2,1}^L = L_2 x_{2,2}^I - B x_{2,1}^I - V_1 y_{2,1}^I, \tag{2}$$

$$\dot{E}_1^L = L_2 H_2^L - B H_1^L - V_1 H_1^V + Q_R - Q_1^L, \tag{3}$$

$$g_{M_{t_1}^L} = M_{1,1}^L + M_{2,1}^L - M_{t_1}^L, \tag{4}$$

$$g_{E_1^L} = M_{t_1}^L H_1^L - E_1^L, \tag{5}$$

$$g_{M_{v_1}^L} = B - B^{\mathrm{ref}}, \tag{6}$$

$$g_{K_{1,1}} = y_{1,1}^I - K_{1,1} x_{1,1}^I, \tag{7}$$

$$g_{K_{2,1}} = y_{2,1}^I - K_{2,1} x_{2,1}^I, \tag{8}$$

$$g_{S_{y,1}} = y_{1,1}^I + y_{2,1}^I - x_{1,1}^I - x_{2,1}^I, \tag{9}$$

$$g_{P_1} = P_2 + \Delta P_2 - P_1. \tag{10}$$

Note that $B^{\mathrm{ref}}$ in (6) is used as a control variable and helps to determine the volumetric holdup of the reboiler. This model of the reboiler leads to three differential and seven algebraic equations involving 10 local[2] variables. The system of equations and the vector of variables can be summarized as

$$F_1 = [\dot{M}_{1,1}^L \;\; \dot{M}_{2,1}^L \;\; \dot{E}_1^L g_{M_{t_1}^L} \;\; g_{M_{v_1}^L} \;\; g_{E_1^L} \;\; g_{K_{1,1}} \;\; g_{K_{2,1}} \;\; g_{S_{y,1}} \;\; g_{P_1}]^T \tag{11}$$

and

$$\mathbf{x}_1 = [M_{1,1}^L \;\; M_{2,1}^L \;\; E_1^L \;\; M_{t_1}^L \;\; B \;\; T_1^L \;\; y_{1,1}^I \;\; y_{2,1}^I \;\; V_1 P_1]^T, \tag{12}$$

[1] Here, g is used to represent the algebraic equations.

[2] The term local here refers to variables that are uniquely determined by the set of equations describing the stage. Although there are more than 10 variables involved, the extra ones are determined by the stages linked to the reboiler by incoming and outgoing flows.

respectively. Liquid and vapor compositions $x$ and $y$, respectively, are calculated from molar holdups using expressions such as

$$x_{i,j} = \frac{M^L_{i,j}}{M^L_{t_j}}, \quad \text{with } j = 1,\ldots,N, \tag{13}$$

$$y_{i,j} = \frac{M^V_{i,j}}{M^V_{t_j}} \quad \text{with } j = 2,\ldots N-1. \tag{14}$$

### 2.2. Non-equilibrium stages

The dynamic equations for the stages $j = 2,\ldots,N-1$ are described by the energy and mass balances over the bulk phases for the components $i = 1,2$

$$\dot{M}^L_{1,j} = L_{j+1}x_{1,j+1} - L_j x_{1,j} + F^L_j x^F_{1,j} + \mathcal{N}_{1,j}, \tag{15}$$

$$\dot{M}^L_{2,j} = L_{j+1}x_{2,j+1} - L_j x_{2,j} + F^L_j x^F_{2,j} + \mathcal{N}_{2,j}, \tag{16}$$

$$\dot{M}^V_{1,j} = V_{j-1}y_{1,j-1} - V_j y_{1,j} + F^V_j y^F_{1,j} - \mathcal{N}_{1,j}, \tag{17}$$

$$\dot{M}^V_{2,j} = V_{j-1}y_{2,j-1} - V_j y_{2,j} + F^V_j y^F_{2,j} - \mathcal{N}_{2,j}, \tag{18}$$

$$\dot{E}^L_j = L_{j+1}H^L_{j+1} - L_j H^L_j + F^L_j H^L_{f,j} - Q^L_j + \mathcal{E}^L_j, \tag{19}$$

$$\dot{E}^V_j = V_{j-1}H^V_{j-1} - V_j H^V_j + F^V_j H^V_{f,j} - Q^V_j - \mathcal{E}^V_j. \tag{20}$$

Total holdups are calculated from the geometry of the packing section and the component holdups are given as

$$g_{M^L_{t_j}} = M^L_{1,j} + M^L_{2,1} - M^L_{t_j}, \tag{21}$$

$$g_{M^V_{t_j}} = M^V_{1,j} + M^V_{2,j} - M^V_{t_j}, \tag{22}$$

$$g_{M^L_{t_j}} = M^L_{t_j} - \frac{\pi}{4}d^2 l h^L_{t_j} c^L_{t_j}, \tag{23}$$

$$g_{M^V_{t_j}} = M^V_{t_j} - \frac{\pi}{4}d^2 l(\epsilon - h^L_{t_j})c^V_{t_j}, \tag{24}$$

$$g_{E^L_j} = E^L_j - \frac{\pi}{4}d^2 l h^L_{t_j} c^L_{t_j} H^L_j, \tag{25}$$

$$g_{E^V_j} = E^V_j - \frac{\pi}{4}d^2 l(\epsilon - h^L_{t_j})c^V_{t_j} H^V_j. \tag{26}$$

Mass and energy transfer rates between vapor and liquid bulk phases are modeled using gradient driven mass and energy flows along with mass and heat transfer coefficients as proposed in Khrishnamurthy and Taylor (1985). Although the Chilton–Colburn analogy for the calculation of heat transfer coefficients from mass transfer correlations is employed here due to its widely use, recent studies (Mendoza and Kjelstrup, 2011) have shown and improved calculation of heat fluxes when using non-equilibrium thermodynamics for the vapor-liquid interface. It has been shown that the use of more advanced models such as the one proposed in Van der Ham et al. (2010) leads to an improvement of the calculation of heat fluxes

$$g_{\mathcal{N}^L_{1,j}} = \mathcal{N}_{1,j} - a^I c^L_t k^L_j (x^I_{1,j} - x_{1,j}) - x_{1,j}(\mathcal{N}_{1,j} + \mathcal{N}_{2,j}), \tag{27}$$

$$g_{\mathcal{N}^V_{1,j}} = \mathcal{N}_{1,j} - a^I c^V_t k^V_j (y_{1,j} - y^I_{1,j}) - y_{1,j}(\mathcal{N}_{1,j} + \mathcal{N}_{2,j}). \tag{28}$$

The energy flow $\mathcal{E}_j$ is calculated from conductive and convective fluxes as

$$\mathcal{E}^V_j = h^V_j a^I_j (T^V_j - T^I_j) + \sum_{i=1}^{2} \mathcal{N}_{i,j}\overline{H}^V_{i,j}, \tag{29}$$

$$\mathcal{E}^L_j = h^L_j a^I_j (T^I_j - T^L_j) + \sum_{i=1}^{2} \mathcal{N}_{i,j}\overline{H}^L_{i,j}, \tag{30}$$

$$g_{\mathcal{E}_j} = \mathcal{E}^V_j - \mathcal{E}^L_j. \tag{31}$$

Equilibrium is only assumed at the interface and it is modeled using the $K$-values

$$g_{K_{1,j}} = y^I_{1,j} - K_{1,j}x^I_{1,j}, \tag{32}$$

$$g_{K_{2,j}} = y^I_{2,j} - K_{2,j}x^I_{2,j}, \tag{33}$$

$$g_{S_{x,j}} = x^I_{1,j} + x^I_{2,j} - 1, \tag{34}$$

$$g_{S_{y,j}} = y^I_{1,j} + y^I_{2,j} - 1. \tag{35}$$

Pressure at each stage is obtained by calculating pressure drops $\Delta P$ from particular correlations, such as the one proposed in Bravo et al. (1986), and incorporating them into

$$g_{P_j} = P_{j+1} + \Delta P_{j+1} - P_j. \tag{36}$$

A non-equilibrium stage with this formulation leads to 6 differential and 14 algebraic equations/variables. The system of equations and variables is summarized in the vectors

$$F_j = [\dot{M}^L_{1,j}\ \dot{M}^L_{2,j}\ \dot{E}^L_j\ g_{M^L_{t_j}}\ g_{M^L_{v,j}}\ g_{E^L_j} g_{K_{1,j}}\ g_{K_{2,j}}\ g_{S_{x,j}} g_{S_{y,j}}\ g_{\mathcal{E}_j}\ g_{\mathcal{N}^L_{1,j}}\ g_{\mathcal{N}^V_{1,j}}\ g_{E^V_j}\ g_{M^V_{t_j}}\ g_{M^V_{v,j}}\ \dot{M}^V_{1,j}\ \dot{M}^V_{2,j}\ \dot{E}^V_j\ g_{P_j}]^T \tag{37}$$

and

$$\mathbf{x}_j = [M^L_{1,j}\ M^L_{2,j}\ E^L_j\ M^L_{t_j}\ L_j\ T^L_j\ x^I_{1,j}\ x^I_{2,j}\ y^I_{1,j}\ y^I_{2,j}\ T^I_j\ N_{1,j}\ N_{2,j}\ T^V_j\ M^V_{t_j}\ V_j\ M^V_{1,j}\ M^V_{2,j}\ E^V_j\ P_j]^T, \tag{38}$$

$\forall j = 2,\ldots,N-1$, respectively.

### 2.3. Equilibrium condenser

To model the top stage, a total condenser is considered, i.e., $L_C = V_{N-1}$. $L_C$ is the liquid leaving the condenser at temperature $T^I_N$ with an associated enthalpy $H^L_C$. Moreover, the composition of the vapor leaving the last packing segment is considered in equilibrium with the liquid phase in the condenser as presented in (45). This static unit is modeled by the following set of equations:

*Energy balance*:

$$g_{E^L_{t,N}} = V_{N-1}H^V_N - L_C H^L_C + Q_C. \tag{39}$$

*Equilibrium*:

$$g_{K_{1,N}} = y^I_{1,N} - K_{1,N}x^I_{1,N}, \tag{40}$$

$$g_{K_{2,N}} = y^I_{2,N} - K_{2,N}x^I_{2,N}, \tag{41}$$

$$g_{S_1} = x^I_{1,N} + x^I_{2,N} - 1, \tag{42}$$

$$g_{S_2} = y^I_{1,N} + y^I_{2,N} - 1. \tag{43}$$

*Pressure*:

$$g_{P_N} = P_{\text{atm}} - P_N. \tag{44}$$

*Vapor composition*:

$$g_{y_{1,N}} = y_{1,N-1} - y^I_{1,N}, \tag{45}$$

Notice that no differential equation is used in this model formulation, leading to seven algebraic equations/variables.

#### 2.3.1. Reflux drum

The reflux drum model is described by the mass and energy balances and total holdup summations

$$\dot{M}^L_{1,N} = L_C x^I_{1,N} - (L_r + D)x_{1,N}, \tag{46}$$

$$\dot{M}^L_{2,N} = L_C x^I_{2,N} - (L_r + D)x_{2,N}, \tag{47}$$

$$\dot{E}^L_N = L_C H^L_N - (L_r + D)H^L_N, \tag{48}$$

$$g_{M^L_{t_N}} = M^L_{1,N} + M^L_{2,N} - M^L_{t_N}, \tag{49}$$

$$g_{E^L_N} = M^L_{t_N} H^L_N - E^L_N, \tag{50}$$

$$g_{M^L_{t_N}} = D - D^{\text{ref}}, \tag{51}$$

leading to three differential and three algebraic equations. The outflow $D^{\text{ref}}$ is a control variable that can be used to set the volumetric holdup in the reflux drum and $x^I_N$ represents the composition of the liquid leaving the condenser at temperature $T^I_N$. The model for the condenser and reflux drum leads to 3 differential and 10 algebraic equations and variables organized as follows:

$$F_N = [g_{y_{1,N}}\ \ \dot{M}^L_{1,N}\ \ \dot{M}^L_{2,N}\ \ \dot{E}^L_N\ \ g_{M^L_{t_N}}\ \ g_{E^L_N}\ \ g_{M^L_{t_N}}\ \ g_{K_{1,N}}\ \ g_{K_{2,N}}\ \ g_{S_{x_N}}\ \ g_{S_{y_N}}\ \ g_{P_j}\ \ g_{E^L_{t_N}}]^T \tag{52}$$

and

$$\mathbf{x}_N = [y^I_{1,N}\ \ y^I_{2,N}\ \ M^L_{1,N}\ \ M^L_{2,N}\ \ E^L_N\ \ M^L_{t,N}\ \ T^L_N\ \ Dx^I_{1,N}\ \ x^I_{2,N}\ \ T^I_N\ \ P_N\ \ Q_C]^T, \tag{53}$$

respectively.

There are a considerable number of thermodynamic correlations that need to be included to properly simulate the model. Here, for simplicity in the presentation of the model, those correlations are not presented but all references to them are listed in Table 1.

The presented model leads to $6N-6$ differential and $14N-8$ algebraic equations, where $N$ represents the number of stages including reboiler and condenser. The model equations can be used for steady state simulation in their current form. However, for dynamic simulation, the challenges for distillation models mentioned in Section 1 need to be carefully considered. In the following section a modification to the model equations is proposed in order to find an equivalent model representation with a smaller number of states variables. This representation preserves the physical meaning of the state vector and leads to a *Reduced Order Rate Based Model* (RORBM).

**Table 1**
References for physical properties of the mixture.

| Property | Source |
|---|---|
| Activity coefficients | Wilson (1964) |
| Diffusion coefficients | Fuller et al. (1966) and Reid et al. (1987) |
| Density | Daubert and Danner (1989) |
| Heat capacities | Sandler (1999) |
| Heat of vaporization | Daubert and Danner (1989) |
| Heat of mixing | Christensen (1982) |
| Heat transfer coeff. | Seader and Henley (2006) |
| Enthalpy | Seader and Henley (2006) |
| Mass transfer coeff. | Bravo et al. (1985) |
| Viscosity | Reid et al. (1987) |
| Pressure drop | Bravo et al. (1986) |
| Thermal conductivities | Daubert and Danner (1989) |
| Specific liquid holdup | Bravo et al. (1986) |
| Packing parameters | Kister (1992) and Sulzer Chemtech |

## 3. A reduced order rate based model

Here, a Reduced Order Rate Based Model (RORBM) is proposed which provides the same behavior as the presented FRBM. The model order reduction is performed by differentiation of enthalpy correlations and algebraic manipulation of energy and mass balance equations. If an expression such as $E^{\text{p}}_j = M^{\text{p}}_{t_j} H^{\text{p}}_j$ is substituted in the differential equations involving the change in energy per time unit for the bulk phase p, $\dot{E}^{\text{p}}_j$, relations of the form

$$M^{\text{p}}_{t_j}\frac{\partial H^{\text{p}}_j}{\partial t} + H^{\text{p}}_j\frac{\partial M^{\text{p}}_{t_j}}{\partial t} = \text{energy balance in stage } j, \text{ phase p}, \tag{54}$$

are obtained. On the one hand, expressions for the time derivative of total composition holdups are easily determined from individual component holdups. For the binary case

$$\dot{M}^{\text{p}}_t = \dot{M}^{\text{p}}_{1,j} + \dot{M}^{\text{p}}_{2,j}, \tag{55}$$

$$x_{2,j} = 1 - x_{1,j}, \tag{56}$$

$$y_{2,j} = 1 - y_{1,j}, \tag{57}$$

hold. On the other hand, expressions for the change of enthalpy with respect to time are obtained by applying rules of differentiation to the enthalpy correlations (Bonilla, 2011). This manipulation leads to a reduction in model equations and variables with respect to the FRBM. Note that since expressions such as (56) are used here, the RORBM equations are intended to be used in the binary distillation case. On the one hand, addressing the multicomponent case with the FRBM is straightforward (Taylor and Krishna, 1993). On the other hand, for the multicomponent case the RORBM equations need to be reformulated and the mass transfer coefficients need to be considered in a matrix form (Taylor and Krishna, 1993). In the following, the set of equations describing the dynamics of the column stages using the simplifications listed previously are presented.

### 3.1. Reboiler equations

The reduced model of the equilibrium reboiler is described by *Mass and energy balances*:

$$\dot{M}^L_{t_j} = L_{j+1} - B - V_j, \tag{58}$$

$$\dot{x}_j = \frac{L_{j+1}(x_{j+1} - x_j) + V_j(x_j - y_j)}{M^L_{t_j}}, \tag{59}$$

$$\dot{T}^L_j = \frac{L_{j+1}\left(H^L_{j+1} - H^L_j - \dfrac{\partial H^L_j}{\partial x}(x_{j+1} - x_j)\right)}{M^L_{t_j}\dfrac{\partial H^L_j}{\partial T^L}} + \frac{V_j\left(H^L_j - H^V_j + \dfrac{\partial H^L_j}{\partial x}(y_j - x_j)\right) + Q_R - Q_L}{M^L_{t_j}\dfrac{\partial H^L_j}{\partial T^L}}. \tag{60}$$

*Component equilibrium*:

$$g_{K_{x_1}} = y_j - K_{1,j}x_j, \tag{61}$$

$$g_{K_{y_1}} = (1 - y_j) - K_{2,j}(1 - x_j). \tag{62}$$

*Pressure drop*:

$$g_{P_1} = P_{j+1} + \Delta P_{j+1} - P_j. \tag{63}$$

*Bottom flow*:

$$g_{M^L_{t_{N_1}}} = B - B^{\text{ref}}. \tag{64}$$

This model of the reboiler leads to seven equations involving seven local[3] variables. The system of equations and the vector of variables can be summarized in

$$F_1 = [g_{M^L_{t_{N_1}}} \;\; \dot{M}^L_{t_1} \;\; \dot{x}_1 \;\; \dot{T}^L_1 \;\; g_{K_{x_1}} \;\; g_{K_{y_1}} \;\; g_{P_1}]^T \tag{65}$$

and

$$\mathbf{x}_1 = [B \;\; M^L_{t_1} \;\; x_1 \;\; T^L_1 \;\; y^I_1 \;\; V_1 \;\; P_1]^T. \tag{66}$$

respectively.

### 3.2. Non-equilibrium stages

The following set of equations are defined for the non-equilibrium stages in the RORBM, i.e., $j = 2, \ldots, N-1$.

#### 3.2.1. Mass and energy balance

$$\dot{M}^L_{t_j} = L_{j+1} - L_j + \mathcal{N}_{1,j} + \mathcal{N}_{2,j} + F^L_j, \tag{67}$$

$$\dot{x}_j = \frac{L_{j+1}(x_{j+1} - x_j) + F^L_j(x^F_j - x_j) + \mathcal{N}_{1,j} - (\mathcal{N}_{1,j} + \mathcal{N}_{2,j})x_j}{M^L_{t_j}}, \tag{68}$$

$$\dot{T}^L_j = \frac{L_{j+1}\left(H^L_{j+1} - H^L_j - \dfrac{\partial H^L_j}{\partial x}(x_{j+1} - x_j)\right) + \mathcal{E}^L_j - Q^L_j}{M^L_{t_j}\dfrac{\partial H^L_j}{\partial T^L}} + \frac{F^L_j\left(H^L_{F,j} - H^L_j - \dfrac{\partial H^L_j}{\partial x}(x^F_j - x_j)\right) - \dfrac{\partial H^L_j}{\partial x}\mathcal{N}_{1,j}}{M^L_{t_j}\dfrac{\partial H^L_j}{\partial T^L}} + \frac{(\mathcal{N}_{1,j} + \mathcal{N}_{2,j})\left(\dfrac{\partial H^L_j}{\partial x}x_j - H^L_j\right)}{M^L_{t_j}\dfrac{\partial H^L_j}{\partial T^L}}, \tag{69}$$

$$\dot{M}^V_{t_j} = V_{j-1} - V_j - (\mathcal{N}_{1,j} + \mathcal{N}_{2,j}) + F^V_j, \tag{70}$$

$$\dot{y}_j = \frac{V_{j-1}(y_{j-1} - y_j) + F^V_j(y^F_j - y_j) - \mathcal{N}_{1,j} + (\mathcal{N}_{1,j} + \mathcal{N}_{2,j})y_j}{M^L_{t_j}}, \tag{71}$$

$$\dot{T}^V_j = \frac{V_{j-1}\left(H^V_{j-1} - H^V_j - \dfrac{\partial H^V_j}{\partial y}(y_{j-1} - y_j)\right) - \mathcal{E}^V_j - Q^V_j}{M^V_{t_j}\dfrac{\partial H^V_j}{\partial T^V}} + \frac{F^V_j\left(H^V_{F,j} - H^V_j - \dfrac{\partial H^V_j}{\partial y}(y^F_j - y_j)\right) + \dfrac{\partial H^V_j}{\partial y}\mathcal{N}_{1,j}}{M^V_{t_j}\dfrac{\partial H^V_j}{\partial T^V}} + \frac{(\mathcal{N}_{1,j} + \mathcal{N}_{2,j})\left(H^V_j - \dfrac{\partial H^V_j}{\partial y}y_j\right)}{M^V_{t_j}\dfrac{\partial H^V_j}{\partial T^V}}. \tag{72}$$

#### 3.2.2. Mass holdups

$$g_{M^L_{t_j}} = M^L_{t_j} - \frac{\pi}{4}d^2 l h^L_{t_j} c^L_{t_j}, \tag{73}$$

$$g_{M^V_{t_j}} = M^V_{t_j} - \frac{\pi}{4}d^2 l(\epsilon - h^L_{t_j})c^V_{t_j}. \tag{74}$$

#### 3.2.3. Mass and energy transfer rates

$$g_{\mathcal{N}^L_j} = \mathcal{N}_{1,j} - a^I c^L_t k^L_j (x^I_j - x_j) - x_j(\mathcal{N}_{1,j} + \mathcal{N}_{2,j}), \tag{75}$$

$$g_{\mathcal{N}^V_j} = \mathcal{N}_{1,j} - a^I c^V_t k^V_j (y_j - y^I_j) - y_j(\mathcal{N}_{1,j} + \mathcal{N}_{2,j}). \tag{76}$$

The energy fluxes $\mathcal{E}_j$ are calculated from conductive and convective contributions as

$$\mathcal{E}^V_j = h^V_j a^I_j (T^V_j - T^I_j) + \sum_{i=1}^{2} \mathcal{N}_{i,j}\overline{H}^V_{i,j}, \tag{77}$$

$$\mathcal{E}^L_j = h^L_j a^I_j (T^I_j - T^L_j) + \sum_{i=1}^{2} \mathcal{N}_{i,j}\overline{H}^L_{i,j}, \tag{78}$$

$$g_{\mathcal{E}_j} = \mathcal{E}^V_j - \mathcal{E}^L_j. \tag{79}$$

#### 3.2.4. Interface equilibrium

$$g_{K_{x_j}} = y^I_j - K_{1,j}x^I_j, \tag{80}$$

$$g_{K_{y_j}} = (1 - y^I_j) - K_{2,j}(1 - x^I_j). \tag{81}$$

#### 3.2.5. Pressure

$$g_{P_j} = P_{j+1} + \Delta P_{j+1} - P_j. \tag{82}$$

Note that each non-equilibrium stage is modeled by 14 equations and 14 local variables. The system of equations and variables is summarized in the vectors

$$F_j = [\dot{x}_j \;\; \dot{T}^L_j \;\; \dot{M}^L_{t_j} \;\; g_{M^L_{t_{V_j}}} \;\; g_{K_{x_j}} \;\; g_{K_{y_j}} \;\; g_{\mathcal{E}_j} \;\; g_{\mathcal{N}^L_{1,j}} \;\; g_{\mathcal{N}^V_{1,j}} \;\; g_{M^V_{t_{V_j}}} \;\; \dot{M}^V_{t_j} \;\; \dot{y}_j \;\; \dot{T}^V_j \;\; g_{P_j}]^T \tag{83}$$

and

$$\mathbf{x}_j = [x_j \;\; T^L_j \;\; M^L_{t_j} \;\; L_j \;\; x^I_j \;\; y^I_j \;\; T^I_j \;\; N_{1,j} \;\; N_{2,j} \;\; V_j \;\; M^V_{t_j} \;\; y_j \;\; T^V_j \;\; P_j]^T, \tag{84}$$

$\forall j = 2, \ldots, N-1$, respectively.

### 3.3. Condenser

The model of the condenser keeps the same structure as the one presented for the FRBM.

*Energy balance*:

$$g_{E_{t,N}} = V_{N-1}H^V_N - L_C H^L_C + Q_C. \tag{85}$$

[3] The term local here refers to variables that are uniquely determined by the set of equations describing the stage. Although there are more than seven variables involved, the extra ones are determined by the stages linked to the reboiler by incoming and outgoing flows.

*Equilibrium*:

$$g_{K_{1,N}} = y_N^I - K_{1,N} x_N^I, \tag{86}$$

$$g_{K_{2,N}} = (1-y_N^I) - K_{2,N}(1-x_N^I), \tag{87}$$

$$g_{y_N} = y_{N-1} - y_N^I. \tag{88}$$

*Pressure*:

$$g_{P_N} = P_{\text{atm}} - P_N. \tag{89}$$

### 3.4. Reflux drum

Mass and energy balances in the reflux drum lead to

$$\dot{M}_{t_N}^L = L_C - L_N - D, \tag{90}$$

$$\dot{x}_N^L = \frac{L_C(x_N^I - x_N)}{M_{t_N}^L}, \tag{91}$$

$$\dot{T}_N^L = \frac{L_C\left(H_C^L - H_N^L - \dfrac{\partial H_N^L}{\partial x}(x_N^I - x_N)\right) - Q_N^L}{M_{t_N}^L \dfrac{\partial H_j^L}{\partial T^L}}, \tag{92}$$

**Table 2**
Summary of variables and equations involved in the RBM.

| Stage | Variables[a] | | | Associated |
|---|---|---|---|---|
| | Name | Units | Type[b] | equation |
| Reboiler $j=1$ | $M_{t_1}^L$ | mol | D | (58) |
| | $x_1$ | mol/mol | D | (59) |
| | $T_1^L$ | K | D | (61) |
| | $V_1$ | mol/s | A | (60) |
| | $B$ | mol/s | A | (64) |
| | $y_1^I$ | mol | A | (62) |
| | $P_1$ | Pa | A | (63) |
| Non-equilibrium $j=2,\ldots,N-1$ | $x_j$ | mol/mol | D | (68) |
| | $T_j^L$ | K | D | (69) |
| | $M_{t_j}^L$ | mol | D | (67) |
| | $y_j$ | mol/mol | D | (71) |
| | $T_j^V$ | K | D | (72) |
| | $M_j^V$ | mol | D | (70) |
| | $V_j$ | mol/s | A | (73) |
| | $L_j$ | mol/s | A | (74) |
| | $\mathcal{N}_{1,j}$ | mol/s | A | (75) |
| | $\mathcal{N}_{2,j}$ | mol/s | A | (76) |
| | $T_j^I$ | K | A | (79) |
| | $y_j^I$ | mol | A | (80) |
| | $x_j^I$ | mol | A | (81) |
| | $P_j$ | mol | A | (82) |
| Condenser $j=N$ | $T_N^I$ | K | A | (86) |
| | $Q_C$ | kW | A | (85) |
| | $y_N^I$ | mol/mol | A | (88) |
| | $x_N^I$ | mol/mol | A | (87) |
| | $P_N$ | Pa | A | (89) |
| Reflux drum $j=N$ | $x_N$ | mol | D | (91) |
| | $T_N^L$ | mol | D | (92) |
| | $M_{t_N}^L$ | kW | D | (90) |
| | $D$ | mol/s | A | (93) |

[a] Considering a binary mixture.
[b] D and A stand for differential and algebraic variables, respectively.

$$g_{M_{v_N}^L} = D - D^{\text{ref}}, \tag{93}$$

The equations and states for the condenser plus reflux drum are organized as follows:

$$F_N = [\dot{x}_N \;\; \dot{T}_N^L \;\; \dot{M}_{t_N}^L \;\; g_{E_{t_N}^L} \;\; g_{M_{v_N}^L} \;\; g_{K_{1,N}} \;\; g_{K_{2,N}} \;\; g_{P_j} \;\; g_{y_N}]^T \tag{94}$$

and

$$\mathbf{x}_N = [x_N \;\; T_N^L \;\; M_{t_N}^L \;\; Q_C \;\; D \;\; T_N^I \;\; x_N^I \;\; P_N \;\; y_N^I]^T. \tag{95}$$

Table 2 summarizes the variables and equations used in the proposed RORBM. On the one hand, the FRBM model in (1)–(51) uses a total of $6N-6$ differential and $14N-8$ algebraic equations/variables, leading to $20N-14$ equations/variables. On the other hand, the RORBM uses $6N-6$ differential and $8N-6$ algebraic equations/variables, i.e., a total of $14N-12$ equations/variables. Consequently, there is a reduction of $6N-5$ variables/equations, i.e., approximately 31% of the total number of variables for the original model.

## 4. Sparsity and structure exploitation

It is known that distillation systems lead to sparse models due to the cascade structure obtained by dividing the length of the column in stages (Seader and Henley, 2006; Taylor and Krishna, 1993). This structure is better exploited when the model equations are permuted such that algebraic and differential relations involved in one stage are grouped together. This procedure leads to a banded Jacobian matrix. The steady state RORBM is solved on its sparse form by reorganizing the model residuals $F^T = [F_1 F_2 \ldots, F_N]$ according to (65), (83) and (94), and the states $\mathbf{x}^T = [\mathbf{x}_1 \mathbf{x}_2, \ldots, \mathbf{x}_N]$ following the definitions in (66), (84) and (95).

The sparsity pattern[4] for the RORBM using two different vector structures is shown in Fig. 3. The second form presents numerical advantages if sparse linear-algebra solvers are used. Off-the-shelf solvers for nonlinear equations provide options so that the sparsity patterns for the Jacobian can be specified. Providing such patterns, leads to an improvement in the computation time, since first order derivatives can be computed in specific directions for each equation in the model, i.e, *sparse finite differences* (Dongarra et al., 1988).

Note that the bandwidth of the reorganized Jacobian does not change with the number of stages, and in this case corresponds[5] to 20. This bandwidth is employed when solving the linear algebra subproblem at each Newton step using, e.g., preconditioned conjugate gradient method PCG[6] (Nocedal and Wright, 2006). Table 3 summarizes the computational demand of the full rate based model without exploiting sparsity (FRBM-NSP) and the reduced order rate based model exploiting sparsity (RORBM-SP) in terms of solution time and memory usage. Note the significative improvement in execution time and memory usage when the FRBM-NSP and the RORBM-SP are compared. It has to be mentioned that the solution time for both cases, can be further reduced if the model equations are coded using a high level language, e.g., C or Pascal and precompiling the model. Obtaining a steady state solution is 93% more efficient in terms of function evaluations per iteration when the sparse RORBM is used instead of the original FRBM. Hence, the former model is selected for the

[4] The Jacobian in this representation exhibits four states more than in the model presented in Table 2. Those four states correspond to first order filters added to the actuators. The addition of these filters is justified in the following sections.
[5] This bandwidth is determined by the stage with the maximum number of variables acting on its equations.
[6] Here, an iterative method is used due to the reduced memory demands.

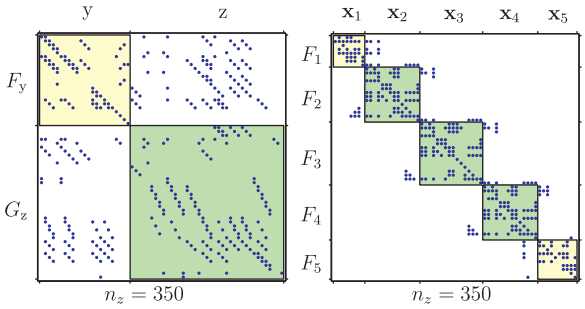



**Fig. 3.** System Jacobian for a 5 stages column, i.e., reboiler, three packing stages and condenser plus reflux drum, using the RORBM in its original form (left). Note the banded pattern in obtained when a proper ordering of vector and equations is performed (right).

**Table 3**
Performance comparison between the full rate based model and the reduced state rate based model when sparsity is exploited.

| Performance criterion | FRBM-NSP | RORBM-SP |
|---|---|---|
| Number of variables[a] | 383 | 272 |
| Function evaluations | 2688 | 108 |
| Execution time per iteration (s) | 2.93 | 0.17 |
| Memory used[b] (kB) | 1146 | 2.73 |

[a] For a column with 20 stages.
[b] Only the number of kilobytes to store the Jacobian in double precision format are considered as indication of the memory usage.

dynamic simulation since it alleviates the use of a considerable number of states.

## 5. Dynamic simulation of the RORBM

As mentioned previously, the RORBM described in Section 3 is used for dynamic simulation. Although the large scale issue has been alleviated by the model order reduction and the exploitation of the model structure, there is still a problem when the model is used for dynamic simulation. Off-the-shelf solvers (Shampine et al., 1999; Hindmarsh et al., 2005) are normally able to solve index-1 DAEs (Hairer and Wanner, 2002). The presented model does not lie in this category and it should be reformulated in order to be solved dynamically. In the following paragraphs the differentiation index problem is explained and analyzed for the reduced order RBM along with the inherent stiffness of the model.

### 5.1. Differentiation index in DAEs

Consider a semi-explicit differential algebraic equation of the form

$$\dot{y} = f(t,y,z), \tag{96}$$

$$0 = g(t,y,z), \tag{97}$$

with $y \in \mathbb{R}^{[n}_{y}$, $z \in \mathbb{R}^{[n}_{z}$, $f : \mathbb{R}^{[n}_{y} \times \mathbb{R}^{[n}_{z} \times \mathbb{R} \to \mathbb{R}^{[n}_{y}$ and $g : \mathbb{R}^{[n}_{y} \times \mathbb{R}^{[n}_{z} \times \mathbb{R} \to \mathbb{R}^{[n}_{z}$. The *differentiation index* $I$ is defined as the number of times the algebraic equations $g(y,z,t)$ have to be differentiated with respect to time in order to obtain an explicit expression for the time derivative of the algebraic variables $z$, i.e., $\dot{z}$. The differential index is a measure of how far a DAE lies from an Ordinary Differential Equation (ODE). In fact a DAE could be transformed into an ODE after $I$ differentiations with respect to time and algebraic manipulation, generating what is called the *underlying ODE* (Ascher and Petzold, 1998).

Numerical solvers find a solution to (96)–(97) by obtaining an expression for the time derivative of the algebraic variables $\dot{z}$. This set of ODEs can be obtained by differentiating the algebraic constraints with respect to time, leading to

$$\dot{z} = -\left(\frac{\partial g(y,z)}{\partial z}\right)^{-1} \frac{\partial g(y,z)}{\partial y} f(t,y,z). \tag{98}$$

It is possible to find a solution to $\dot{z}$ if the Jacobian of the algebraic equations with respect to the algebraic variables $\partial g(y,z)/\partial z$ is nonsingular (Hairer and Wanner, 2002). If that is not the case, the algebraic constraints are differentiated until an index-1 system is obtained, i.e., $I-1$ times. Off-the-shelf solvers are only capable of dealing with index-1 problems, i.e., $\partial g(y,z)/\partial z$ in (98) must be nonsingular. In general, the underlying ODE formed by (96) and (98) provides a family of solutions that do not necessarily satisfy the original algebraic equations. Hence, in order to achieve the required constraint satisfaction, the correct initialization must be done, i.e., the initialization of the underlying ODE must be performed considering the original constraints and the derivatives[7] that lead to the underlying ODE.

When a numerical method is applied to the integration of the underlying ODE, a common feature is the drift of the solution trajectories from the manifold defined by the hidden constraints, i.e., the solution of the ODE does not satisfy the original constraint and its $I-1$ derivatives (Hairer and Wanner, 2002). Hence, reducing the index by differentiation of the constraints is always accompanied by methods for stabilization of the error in the solution. Among the most widely used are Baumgarte's stabilization (Baumgarte, 1972) and projections of the solution on the manifold (Hairer and Wanner, 2002). If the differentiated constraints are just appended to the original set of constraints, the system becomes overdetermined. There exist other methods that attempt to solve the overdetermined system resulting from this index reduction procedure. However, differentiation of constraints can create new differential variables making the solution even more involved. Among the most used methods for overdetermined systems are the least squares minimization applied to the nonlinear equations (Hairer and Wanner, 2002) and the method of the dummy derivatives (Mattsson and Söderlind, 1993). All those methods depart from a DAE reduced to index-1 by differentiation. Pantelides (1988) proposes an algorithm that identifies the minimum set of equations from the DAE that need to be differentiated, so that an index-1 system can be obtained for further stabilization with one of the methods mentioned.

### 5.2. Index problem in distillation models

The DAEs high-index problem has been previously mentioned in several works for different kinds of distillation models, e.g., Pantelides et al. (1988), Gani and Cameron (1992), Kreul et al. (1998), Peng et al. (2003) among others. Kreul et al. (1998) explain that the high-index problem often arise from neglecting momentum balances and fluid dynamics equations from the model. There are basically two approaches to tackle the problem. On the one hand, the complexity of the model is reduced by making several assumptions that lead to an index-1 DAE. On the other hand, the constraints that need to be differentiated are detected by, e.g., *Pantelides algorithm* (Pantelides, 1988). The differentiated constraints are added to the system, leading to an overdetermined model that can be solved by one of the methods mentioned previously. Although this method preserves the original set of variables, it becomes involved. The method

[7] These constraints imposed by the derivatives with respect to time are called the underlying or *hidden constraints*.

requires: (i) the implementation of the graph-theory based Pantelides algorithm, (ii) tools to obtain the derivatives of the equations detected by the algorithm and (iii) procedures to solve the overdetermined model dynamically.

The approach used here lies in the first class of the mentioned methods. The index problem for the RORBM is analyzed and the proper assumptions are justified physically and numerically, highlighting the limitations of the resulting model.

Pantelides et al. (1988) traced back the index problem in distillation to the appropriate links between vapor flows and pressure drops. Kreul et al. (1998) refer to the index problem and confirm that this appears when there is no relation between pressure drops in a non-equilibrium stage and vapor or liquid flowing through the stage. As it is shown here, this is a necessary condition but it is not the only one that helps to avoid the problem. In general, from the numerical viewpoint, each algebraic variable must appear at least once in the algebraic equations. This avoids what is called *structural singularities*. The flows in a stage, algebraic variables, must appear in the algebraic equations either through the pressure drops or through the calculation of mass transfer coefficients.[8] Consequently, assuming pressure drops constant or transfer coefficients constant removes the flows from the algebraic equation. Since flows are algebraic variables, this leads to a singular Jacobian $\partial g/\partial z$ and to the high-index problem unless extra assumptions are considered. These extra assumptions must imply an extra algebraic equation involving the flows in a stage that were suppressed by assuming, e.g., constant pressure. This is illustrated in the following paragraphs.

### 5.3. Structural singularity detection

A particular procedure to detect structural singularity problems is proposed in Gani and Cameron (1992) by analyzing the incidence of algebraic variables in the algebraic equations. By analyzing this incidence matrix, it is possible to suggest modifications to the model that avoid the higher index problem. Note that this procedure is restricted to structural singularity, numerical singularities are in general more difficult to avoid by this method. Gani and Cameron (1992) propose to choose the variables that do not appear in the incidence matrix as degrees of freedom. This approach is certainly effective, however, in practical cases not always the variables that create the higher index problem can be assumed as given.

In order to trace back the origins of the higher index problem in the RORBM, a simple 3-stages system is analyzed, i.e., only one packing section is assumed and it is modeled using the non-equilibrium equations (67)–(82), along with the reduced models of reboiler (58)–(64) and condenser plus reflux drum (85)–(93). The Jacobian of the nonlinear set of equations, composed of dynamic and algebraic relations, is calculated numerically. Note that the numerical values of the Jacobian change as a function of the states value. However, the purpose of this calculation is to check the structure of the Jacobian and not its numerical values. The equations and states are organized as $F=[F_y\ g_z]^T$ and $\mathbf{x}=[y\ z]^T$, respectively, to clearly identify the dynamic and algebraic parts in the Jacobian in the analysis.[9]

The results are illustrated in Fig. 4. Note that, in this model, the pressure drops and the transfer coefficient are calculated as a function of the flows in the stage as suggested in Kreul et al. (1998). However, the DAE system still exhibits a differentiation index bigger than one. It is easy to see that the vapor flow in the reboiler $V_1$ does not appear in the algebraic constraints, causing the structural singularity problem. Any other algebraic variable missed in $\partial g/\partial z$ leads to the same structural singularity problem.

### 5.4. Higher index reduction

Once the structural singularity has been detected, there are some options to obtain an index-1 system. In order to reduce the differentiation index of the proposed model, it is required to include all the algebraic variables at least once in the algebraic equations. Hence, assumptions that lead to that inclusion avoid the structural singularity. In this particular case, assuming vapor molar holdup $M_2^V$, constant solves the problem. This common assumption transforms (70) into an algebraic constraint, i.e., shifts the row corresponding to $\dot{M}_2^V$, in Fig. 4, down to the algebraic part of the Jacobian, allowing for $V_1$ to appear once in the algebraic constraints. There exists a second effect of this assumption, since the fast dynamics associated with the vapor holdups are being neglected, the stiffness of the DAE is expected to be alleviated. This kind of common assumption reduces on the one hand, the index problem to one and, on the other hand, the stiffness of the whole DAEs system, facilitating the dynamic simulation task.

Detecting structural singularities can be generalized by analyzing the Jacobian of the algebraic constraints with respect to the algebraic variables. A procedure for reducing the index from structural singularity problems is proposed in Algorithm 1.

**Algorithm 1.** Index reduction from structural singularities.

1: Organize the DAE in the form (96)–(97).
2: Obtain the incidence matrix (sparsity pattern) of the problem by, e.g., numerical perturbation.
3: Detect the empty columns $i_e$ of the block corresponding to the incidence of algebraic variables $z$ into the algebraic equations $G$.
4: Identify the variables $z(i_e)$ from which the structural singularity is originated.
5: Scan the rows of the incidence matrix corresponding to the dynamic equations $f$ detecting the ones that contains the variables $z(i_e)$, i.e., $F(z(i_e))$.
6: Based on process insight of the process evaluate which ones of the $F(z(i_e))$ can be considered as algebraic equations.

### 5.5. Further simplifications to the RORBM and actuator dynamics

Once the index problem has been solved a simulation of the system, under the assumption of constant molar vapor holdup, can be performed. Note that the dynamic model has as degrees of freedom four manipulated variables, namely reflux flow $L_r$, bottom flow $B$, top flow $D$ and reboiler duty $Q_r$. By simple inspection, it is possible to note that the system is not BIBO (bounded input bounded output) stable (Ogata, 2010). If one of these variables is changed, the volumes in the reboiler and condenser can reach saturation. Starting from an equilibrium value, a step in the reboiler power $Q_r$ induces a higher vapor flow $V_1$. If $B$ is not changed, the reboiler volume decreases until it reaches its lower level, i.e., it saturates. At the top of the column, if $D$ and $L_r$ are kept constant, the level in the reflux drum increases since more vapor is flowing through the column. This excess of vapor condensates and induces an increase of liquid volume in the reflux drum until it saturates to its maximum volume. Consequently, the model with these four degrees of freedom is unstable. A very simple approach to avoid this kind of instability

[8] Note that both pressure drops and mass and heat transfer coefficients involve the vapor and liquid flows in a stage.

[9] Although, a different organization presents advantages when solving the system of equations, with this form of organizing variables, the analysis of the index problem is easily performed.

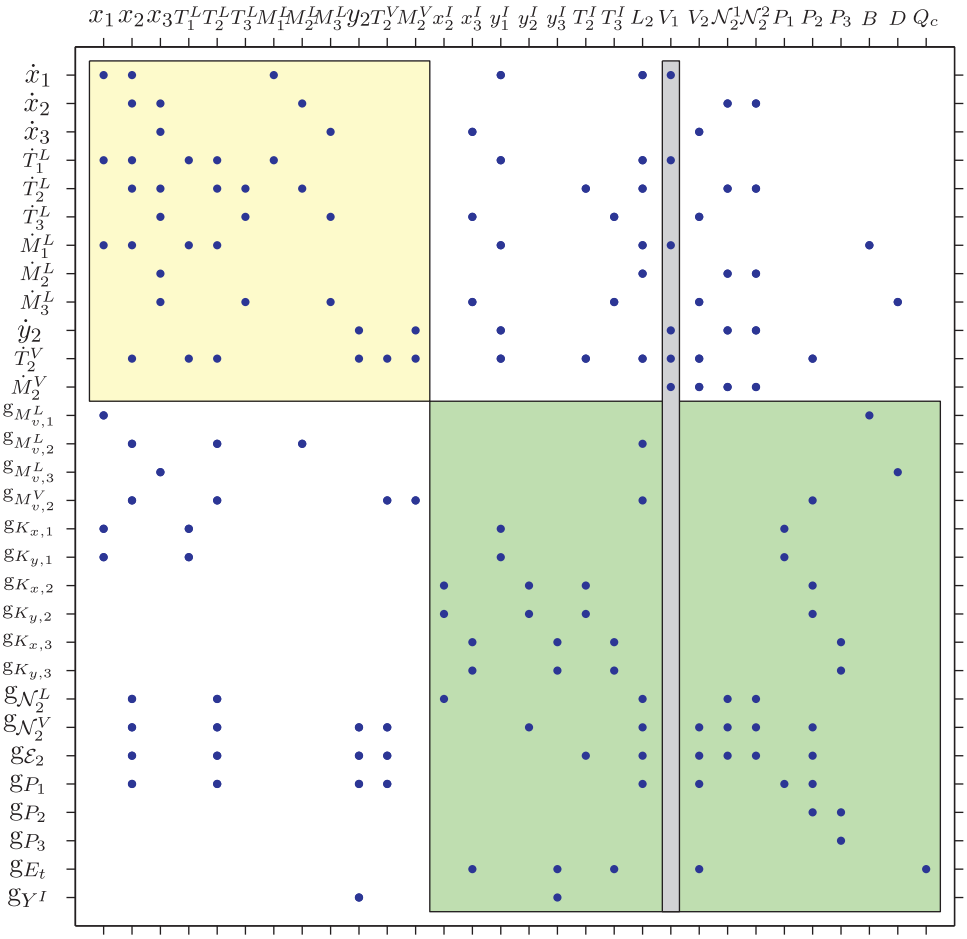



**Fig. 4.** Jacobian of a 3 stages distillation system using the RORBM. Note that the Jacobian of the algebraic equations with respect to the algebraic variables lacks of elements in the column corresponding to the reboiler vapor flow $V_1$, originating the singularity in $\partial g/\partial z$ and the higher index problem in the DAE.

is to close loops between liquid volumes in the reboiler and reflux drum with bottom and top flows, respectively (Skogestad, 1997). The dynamics of these liquid loops is, in general, faster than the one associated with temperature and composition. Hence, in many distillation models it is assumed that there exist perfect controllers that keep these volumes constant. In practice, simple PI controllers can be tuned so that correction for volume variations is rapidly achieved. Therefore, if the liquid volume in the reboiler is assumed constant, then (58) and (64) must be replaced by

$$g_{M_{t_1}^L} = v_{t_j}^L(L_{j+1}-B-V_j)+M_{t_j}^L\left(\frac{\partial v_{t_j}^L}{\partial x_j}\dot{x}_j+\frac{\partial v_{t_j}^L}{\partial T_j^L}\dot{T}_j^L\right), \tag{99}$$

$$g_{M_{v_1}^L} = v_{t_1}^L M_{t_1}^L-\overline{v}_R, \tag{100}$$

respectively. Likewise, if the volume in the reflux drum is assumed constant, (90) and (93) must be replaced by

$$g_{M_{t_N}^L} = v_{t_N}^L(L_c-D-L_r)+M_{t_N}^L\left(\frac{\partial v_{t_N}^L}{\partial x_N}\dot{x}_N+\frac{\partial v_{t_N}^L}{\partial T_N^L}\dot{T}_N^L\right) \tag{101}$$

and

$$g_{M_{v_1}^L} = v_{t_N}^L M_{t_N}^L-\overline{v}_D. \tag{102}$$

The advantages of incorporating these assumptions into the model are an easier simulation, avoiding saturation of variables without the need of considering control loops for the volumes in the top and bottom stages. However, the real dynamics of the liquid loops is merged with the dynamics of the temperature inside the column. As mentioned, if desired, the model can be used without this assumption. However, the proper control loops need to be designed and incorporated into the model.

The presented model does not consider the dynamics of the actuators. If a step change is performed in the reboiler duty, the extra heat applied directly propagates to the vapor flow, i.e., the extra heat added, generates an instantaneous change in the vapor flow since the liquid in the reboiler is saturated. Fig. 5 shows the response of some model states when changes of $\pm 10\%$ in the reboiler duty and the reflux are performed. Although part of the vapor dynamics have been neglected with the constant molar vapor holdup assumption, there is a very fast response due to the lack of proper modeling for the heat transfer between the actuator and the saturated liquid in the bulk phase.

A real setup exhibits a different behavior. The applied heat takes some time until it is transferred to the surroundings of the actuator and to the vapor due to the heat resistance in the liquid bulk phase, which has not been considered in the model. Similarly, the dynamics of the reflux pump, the feed pump and the feed heater are not considered. Hence, in order to provide a model closer to what is expected in a real setup, first order filters of the form

$$\dot{q}(t) = \frac{1}{\tau}(u(t)-q(t)), \tag{103}$$

are added to each one of the command signals. Here, $u(t)$ represents the command sent to the actuator while $q(t)$ accounts for the filtered command signal that reaches the process. The time constants for those filters are tuning parameters that can be

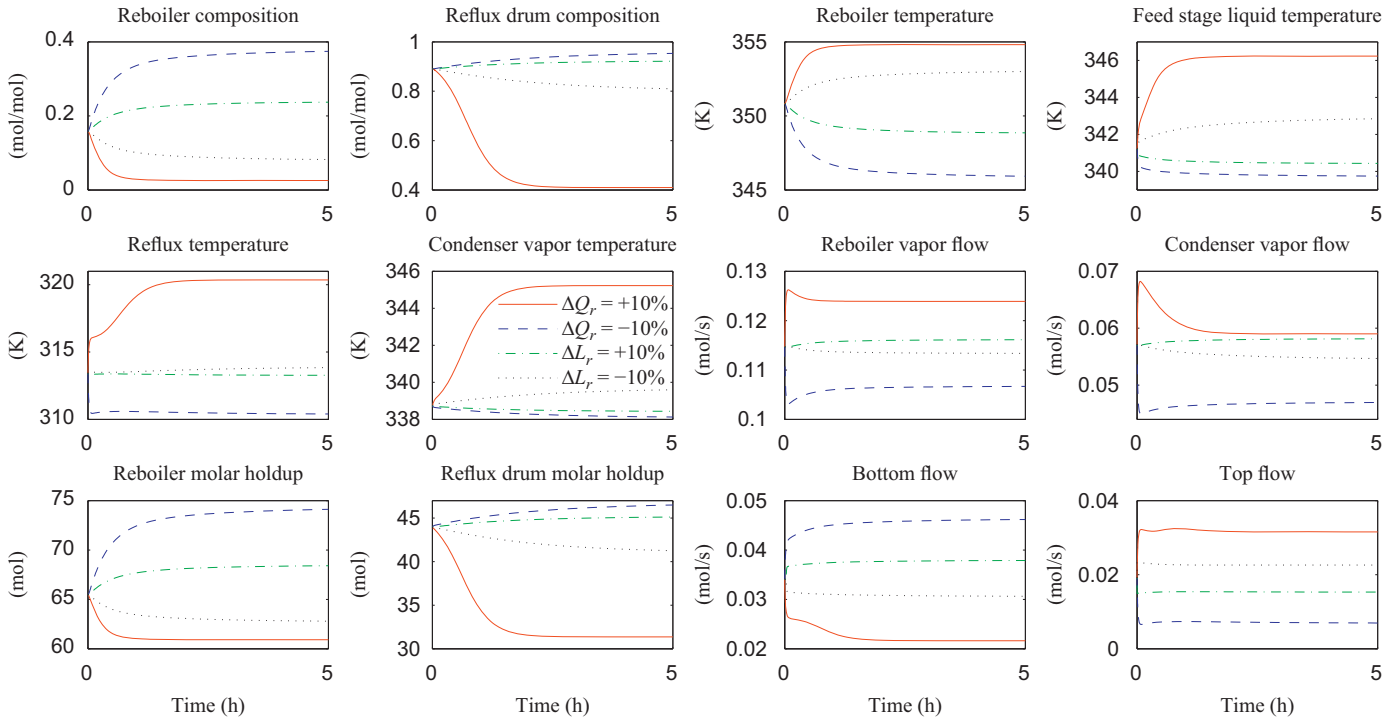



**Fig. 5.** RORBM response to $\pm 10\%$ changes in the reboiler duty and the reflux. First order filters have been added to the actuators to model the actuator dynamics.

estimated in the real setup since measurement of slave control loops is available.

## 6. Dynamic sensitivity analysis of the RORBM

As noted in Fig 5, the steady state value of model compositions for the top stage does not reach the one of a pure component. In a real setup top composition is approximately one. This mismatch between the dynamic simulation and the experimental setup is due to lack of tuned values for the model parameters. Hence, a dynamic parameter estimation problem needs to be formulated. The model formulated here uses the 16 parameters listed in Table 4. However, the number of parameters that can be estimated depends on the available state measurements. Note that the analysis performed here does not consider the identifiability of highly correlated parameters.

Since in this particular setup only measurements of temperatures are available, it is necessary to evaluate which parameters can be estimated from those measurements. Here, a parameter sensitivity analysis is performed. For the index-1 DAE

$$\dot{y} = f(y,z,p,t), \tag{104}$$

$$0 = g(y,z,p,t), \tag{105}$$

the sensitivities of states $\mathbf{x}^T = [y^T\ z^T]$ with respect to parameters $p$, i.e.

$$s^T = \frac{\partial \mathbf{x}^T}{\partial p} = \left[\frac{\partial y^T}{\partial p}\ \frac{\partial z^T}{\partial p}\right] = [s_y^T\ s_z^T], \tag{106}$$

are obtained by solving the DAE

$$\begin{bmatrix} \dot{s}_y \\ 0 \end{bmatrix} = \begin{bmatrix} \frac{\partial f}{\partial y} & \frac{\partial f}{\partial z} \\ \frac{\partial g}{\partial y} & \frac{\partial g}{\partial z} \end{bmatrix} \begin{bmatrix} s_y \\ s_z \end{bmatrix} + \begin{bmatrix} \frac{\partial f}{\partial p} \\ \frac{\partial g}{\partial p} \end{bmatrix}. \tag{107}$$

Although the required differentiation may be performed symbolically, the DAE solver with sensitivity generation capabilities presented in Hindmarsh et al. (2005) is used here to obtain and solve (107) together with the RORBM. The sensitivities of temperature trajectories at the top and the bottom of the column as a function of the 16 model parameters are obtained under a simulation test. A 10% perturbation is performed in the four possible manipulated variables of the setup,[10] i.e., $Q_r$, $L_r$, $F$ and $T_F$. The sensitivities can be seen as the gain $k$ in the linear approximation of the states

$$\mathbf{x}(p) = \mathbf{x}(\overline{p}) + k(p - \overline{p}). \tag{108}$$

Consequently, the higher the sensitivity the larger the effects of variation in $p$ over the analyzed state trajectories. On the contrary, lower sensitivities lead to almost no change in the measured

**Table 4**
Initial guess for parameters in the rate based model.

| Parameter | Value | Unit | Description |
|---|---|---|---|
| $\overline{v}_R$ | $5 \times 10^{-3}$ | $m^3$ | Reboiler liquid volume |
| $\overline{v}_D$ | $2 \times 10^{-3}$ | $m^3$ | Condenser liquid volume |
| $x_F$ | 0.7004 | mol/mol | Liquid feed composition |
| $\psi_L$ | 0.0 | kW/K | Heat loss coefficient liquid |
| $\psi_V$ | 0.0 | kW/K | Heat loss coefficient vapor |
| $\psi_R$ | 0.0215 | kW/K | Reboiler losses coefficient |
| $\psi_D$ | 0.0106 | kW/K | Condenser losses coefficient |
| $C_h$ | 1 | | Liquid holdup tuning coefficient |
| $C_{\Delta P}$ | 1 | | Pressure drop tuning coefficient |
| $C_{k^L}$ | 1 | | Mass transfer tuning coefficient |
| $C_{k^V}$ | 1 | | Mass transfer tuning coefficient |
| $\overline{M}^V_{t_j}$ | 0.018 | mol | Molar vapor holdup |
| $\tau_R$ | 180 | s | Heater time constant |
| $\tau_{L_r}$ | 20 | s | Reflux pump time constant |
| $\tau_F$ | 20 | s | Feed pump time constant |
| $\tau_{T^F}$ | 90 | s | Feed heater time constant |

[10] These signals can be manipulated when gathering data for model identification.

states trajectories with respect to changes in the parameters. Hence, parameters with lower sensitivities, i.e., low effect on measured trajectories is difficult to estimate from the variations of the available measurements.

In order to use the sensitivities to reduce the search space for the model parameters $p$, a criterion based on a 2-norm of the form

$$\|S_i\| = \sum_{i=1}^{4}\sum_{j=1}^{N}\sum_{k=0}^{k_f}\frac{\left\|\frac{\partial x_j}{\partial p_i}(k)\right\|_2^2}{4k_f N} \tag{109}$$

is proposed as an indicator for the relevance of parameters in the estimation procedure. $k_f$ is the number of values used for describing the numerical solution of the sensitivities. $N$ denotes the number of states analyzed, i.e., for the temperature of the liquid or vapor $N$ corresponds to the number of stages and $m=4$ input variables perturbed. This criterion adds all the contributions of the sensitivities associated to a set of $N$ states with respect to the parameter $p_i$ along one simulation test for the four tests. Fig. 6 illustrates $\|S_i\|$ for the 16 parameters proposed, when the temperature of the vapor phase, liquid phase and top and bottom concentration are assumed to be measurable.

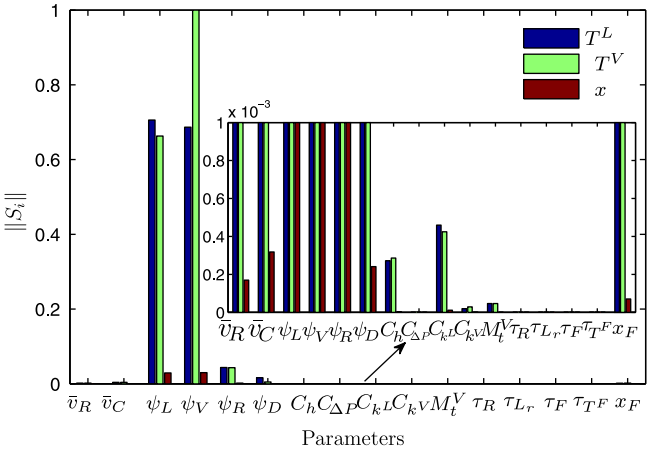



**Fig. 6.** Norm on the sensitivity of vapor temperature, liquid temperature and liquid composition with respect to the 16 model parameters when changes of 10% are performed on the four manipulated variables of the model.

**Table 5**
RORBM parameters and its influence on the dynamic and static response.

| Parameter | Dynamic | Static | $p_r$[a] |
|---|---|---|---|
| $\bar{v}_R$ | ✓ | | ✓ |
| $\bar{v}_D$ | ✓ | | ✓ |
| $x_F$ | ✓ | ✓ | ✓ |
| $\psi_L$ | ✓ | ✓ | ✓ |
| $\psi_V$ | ✓ | ✓ | ✓ |
| $\psi_R$ | ✓ | ✓ | ✓ |
| $\psi_D$ | ✓ | ✓ | ✓ |
| $C_h$ | ✓ | | ✓ |
| $C_{\Delta P}$ | | | |
| $C_{k^L}$ | ✓ | ✓ | ✓ |
| $C_{k^V}$ | ✓ | ✓ | ✓ |
| $M_T^V$ | ✓ | | ✓ |
| $\tau_R$ | ✓ | | |
| $\tau_{L_r}$ | ✓ | | |
| $\tau_F$ | ✓ | | |
| $\tau_{T^F}$ | ✓ | | |

[a] $p_r$ groups all the parameters that are selected to be estimated from the available measurements.

Based on the sensitivities it is possible to reduce the search space for the parameter estimation problem. In this case the original vector $p \in \mathbb{R}^{16}$ is reduced to $p_r \in \mathbb{R}^{11}$ as shown in Table 5. Although not presented here, for simplicity, the dynamic sensitivity analysis helps to determine which parameters present influence on the dynamic and static parts of the model response. This knowledge can be used to set up steady state experiments to determine values for those parameters.

## 7. Discussion

The model presented here is developed for a particular binary mixture of methanol–isopropanol. However, due to the properly referenced correlations other binary mixtures can be easily adapted. In the case of multicomponent separation, the model presented in Section 2 has to be adapted. Particularly the mass and energy transfer coefficients are represented by a matrix whose components model the transfer from element $i$ to $j$ (Taylor and Krishna, 1993). Moreover, the structure can be exploited in the same form presented in Section 4. The index problem arises in that model formulation but it can be analyzed using the same procedure proposed here and the proper assumptions need to be performed in order to reduce the index of the DAEs (Peng et al., 2003). Note the sparse form in the RORBM allows for the use of the model in more advance numerical tasks such as online estimation and control. Despite the considerable number of states, the presented sparse and non-stiff form allows for efficient numerical solutions. This combines the advantages of rigorous first principles models with the computational tractability of highly structured reduced order models. On the other hand, the sensitivity analysis of model parameters reduces the space of parameters to tune for parameter estimation tasks. The procedure introduced here, considers a reduced set of measurements, this lack of information allows for the estimation of a reduced set of parameters only, i.e., the ones that exhibit the highest influence in the trajectories to fit. This identifiability analysis provides the necessary information to formulate the parameter estimation problems with a reduced set of parameters, those that are more likely to be identified. However, in the case of highly correlated parameters this study does not guarantee identifiability of true values for those parameters. On the other hand, in the case of parameter estimation with multiple experiments, the structure exploitation does not lead to computationally heavier problems as it can be the case if the model Jacobian would be treated in a dense form.

## 8. Conclusions

A reduced order rate based model has been presented. It is shown that despite the large number of variables involved in this complex model, structure can be exploited so that the computational effort required to solve the system of equations is alleviated. Moreover, the differentiation index problem for the proposed reduced rate based model is studied from the numerical point of view and an index reduction procedure based on physical and numerical properties is proposed. The common assumption of a constant vapor holdup is justified numerically showing that it not only leads to a less stiff differential-algebraic system but also to a model Jacobian that is structurally non-singularity. The resulting model can be solved with off-the-shelf solvers to find the solution to the dynamic system in an efficient form by exploiting the sparse structure of the model Jacobian. In addition the identifiability of model parameters is studied showing that with a reduced set of state measurement only a subset of model parameters can be estimated. Particularly it is presented that heat loss coefficient exhibits the highest sensitivity with respect to the

measured trajectories. Hence the tuning of the model to a particular setup can be performed on a reduced search space exploiting the sparsity and making the use of the model computational attractive for more advance applications.

## Nomenclature

| | |
|---|---|
| $a$ | specific interface area, $m^{-1}$ |
| $a^I$ | net interfacial area, $m^2$ |
| $B$ | bottom flow, mol/s |
| $c_t$ | molar density, $mol/m^3$ |
| $C$ | condenser |
| $d$ | column internal diameter in $m$ |
| $D$ | distillate flow, mol/s |
| $\Delta P$ | pressure drop, Pa |
| $F$ | feed flow, mol/s |
| $h$ | heat transfer coefficient, kJ/mol |
| $h_t$ | specific liquid holdup |
| $H$ | molar enthalpy, kJ/mol |
| $\overline{H}$ | partial molar enthalpy, kJ/mol |
| $k$ | mass transfer coefficient, m/s |
| $K$ | vapor–liquid distribution ratio |
| $L$ | liquid flow, mol/s |
| $M_t$ | total molar holdup, mol |
| $\mathcal{N}$ | mass transfer flux, mol/s |
| $P$ | total pressure, Pa |
| $P^s$ | component vapor pressure, Pa |
| $Q$ | heat added or removed, kW |
| $T$ | temperature, K |
| $V$ | vapor flow, mol/s |
| $x$ | liquid composition, mol/mol |
| $y$ | vapor composition, mol/mol |

*Greek letters*

| | |
|---|---|
| $\epsilon$ | packing void fraction % |
| $\gamma$ | activity coefficient |

*Subscripts*

| | |
|---|---|
| $i$ | component index |
| $j$ | stage index |
| $R$ | reboiler |
| $D$ | reflux drum |
| $C$ | condenser |

*Superscripts*

| | |
|---|---|
| $L$ | liquid related |
| $V$ | vapor related |
| $I$ | interface related |
| $T$ | vector transpose |

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