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Rigorous modeling, simulation and optimization of a conventional and nonconventional batch reactive distillation column: A comparative study of dynamic optimization approaches

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ARTICLE INFO

Article history:

Received 9 February 2016

Received in revised form 31 March 2016

Accepted 5 April 2016

Available online 26 April 2016

Keywords:

Dynamic optimization

Batch distillation

discretization methods

ABSTRACT

In this paper we address the optimization of two batch distillation columns: a conventional batch distillation column (BDC) and a nonconventional dividing wall batch distillation column (DWBDC) with and without chemical reaction. The simultaneous solution of these systems of differential and algebraic equations is performed using two different approaches: pure equation oriented approach (EOA) based on orthogonal collocation over finite elements implemented in GAMS (24.2.2), and control vector parameterization (CVP) as implemented in gPROMS (3.7.1). In order to accomplish this objective, we describe and propose for the nonconventional batch configuration, two dynamic models that involve stage-by-stage calculations for the time varying column profiles. Case studies with and without reaction are presented in order to compare the two discretization approaches and to demonstrate possible benefits of dividing wall columns in batch separations.

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1. Introduction

Modeling, simulation, and optimization of batch distillation processes rely on dynamic models described by a set of differential and algebraic equations (DAEs). Over the last three decades, a number of different solution approaches have been used for the solution of Batch Distillation Columns (BDC). One of these approaches is Control Vector Parameterization (CVP) approach, proposed by Vassiliadis et al. (1994a,b). This approach relies on the iterative solution of DAEs in the space of the control variables in order to perform the optimization. Another method that has been used for the discretization of these dynamic systems is Orthogonal

Collocation over finite elements, developed by Biegler (1984). With this method, the dynamic optimal control problem is approximated by a finite dimensional nonlinear program (NLP) through the discretization of all variables. With the new discretized set of equations, the model can then be solved as an NLP problem to simultaneously perform the optimization while converging the differential-algebraic equations for the dynamic model. The use of these approximations over finite elements, the size and number of which must be specified ahead of time, allows some control over the error associated with the discretization. Even though various batch distillation models have been solved using the CVP approach, there is still a lack of information when a simultaneous

Abbreviations: BDC, batch distillation column; BRDC, batch reactive distillation column; D, distillate; DWBDC, dividing wall batch distillation column; DWBRDC, dividing wall batch reactive distillation column.

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<http://dx.doi.org/10.1016/j.cherd.2016.04.005>

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Nomenclature

1	superindex indicating the left section in the dividing wall batch distillation column
2	superindex indicating the right section in the dividing wall batch distillation column
C	molarity (mol/L)
C_{energy}	cost of energy (\$)
C_{feed}	cost of feed (\$/kmol)
$C_{product}$	sales value of distillate product (\$/kmol)
$D_{product}$	amount of distillate product (kmol)
H	vapor enthalpy (kJ/kmol)
h	liquid enthalpy (kJ/kmol)
i	number of components
j	number of stages
k	reaction rate constants (L/gmol/min)
K	vapor–liquid equilibrium constant
M	holdup (kmol)
Δn	total produced products during the reaction (kmol/h)
P	total pressure (bar)
p^{sat}	vapor pressure (bar)
Q_{cond}	Condenser heat duty (kJ/h)
Q_{reb}	reboiler heat duty (kJ/h)
r	reaction rate (gmol/s)
R	liquid flowrate (kmol/h)
RR	internal reflux ratio
T	temperature (K)
t_F	final batch time (h)
V	vapor flowrate (kmol/h)
x	liquid composition in mole fraction
y	vapor composition in mole fraction

approach like orthogonal collocation over finite elements is used.

BDC and as Continuous Distillation Columns (CDC), are characterized by high energy consumption. An innovative solution to overcome this problem in CDC is the use of Dividing Wall Distillation Columns (DWD), which have evolved from the Petlyuk configuration (two coupled distillation columns (Petlyuk et al., 1965)) by the addition of a vertical wall that splits the column into two separate sections. Thanks to this, DWC have been applied in the chemical process industry as it can separate more components in a single distillation unit thus achieving cost savings by requiring single columns instead of two columns. In fact, the use of DWC in Continuous Distillation Columns can save up to 30% in capital investment and up to 40% in operating costs (Isopescu et al., 2008). Reviews and research papers have been published covering the design, simulation, optimization, control, and applications of DWC (Hernández and Jimenez, 1999a; Hernández and Jimenez, 1999b; Rong and Turunen, 2006; Segovia-Hernández et al., 2007; Rangaiah et al., 2009; Asprión and Kaibel, 2010; Dejanović et al., 2010; Diggelen et al., 2010; Kiss and Bildea, 2011; Kiss and Rewagad, 2011; Yildirim et al., 2011). Furthermore, the DWC processes covering the design, simulation, optimization, control and applications can be used even in reactive distillation processes (Mueller and Kenig, 2007; Hernández et al., 2009; Kiss et al., 2009; Kiss and Bildea, 2011; Delgado-Delgado et al., 2012).

In this study we propose the optimal design and operation of a BDC with and without reaction for a given product

specification while comparing two different approaches: pure equation oriented approach (EOA) based on orthogonal collocation over finite elements as implemented in GAMS, and CVP approach as implemented in gPROMS. In order to study the potential impact (observed in continuous processes) of dividing walls in batch configurations, a rigorous model and solution of new nonconventional dividing wall batch distillation columns (DWBDC) with and without chemical reaction are also presented. The nonreactive case study is the separation of methanol from a quaternary mixture of light alcohols (methanol, ethanol, *n*-propanol and *n*-butanol), and will be explored by maximizing a profit function while the reflux ratio (RR) is used as the control variable. The reactive case will be explored by maximizing the limiting reactant conversion for the production of ethyl acetate via esterification of acetic acid with ethanol. This study investigates how variables, such as vapor flowrate (*V*) and RR are adjusted to maximize an objective function for a given product specification.

The paper is organized as follows. First, we provide the problem statement in Section 2 followed by the proposed mathematical model in Section 3. The discretization methods used to convert the optimal control problem into an NLP problem are presented in Section 4. The column configuration and operational conditions are presented in Section 5. The results are shown in Section 6 followed by the conclusions in Section 7.

2. Problem statement

In general, the problem addressed in this paper can be stated as follows:

Given a feed consisting of a mixture of NC components, the column configuration, and product purity specification for a key distillate component. The goal is to maximize an objective function by manipulating the column reflux ratio RR(t) and the vapor flowrate V to purify a given mixture of NC components. All the alternatives from conventional batch columns to dividing wall batch columns with and without reaction are considered.

The specific dynamic optimization problem can then be stated as follows:

Given:	Column configuration, feed mixture, vapor flowrate, product purity and batch time.
Determine:	Optimal reflux ratio profile.
To maximize:	A profit/conversion equation.
Subject to:	Equality and inequality constraints.

In this study, two of the most common optimization problems are considered, but the performance of batch distillation columns can also be studied by optimizing different objective functions, such as the amount of distillate product, operation time, energy consumption in the reboiler, etc. The selection of the optimization problem to be solved depends on the scope of the separation.

2.1. Maximum profit problem

An objective function for the maximization of a profit function *P* that combines the minimum time and the maximum distillate problem is given by

$$\text{Profit} = \frac{\text{Sales revenue} - \text{Feed cost} - \text{Operating cost}}{\text{Total batch time}} \quad (1)$$

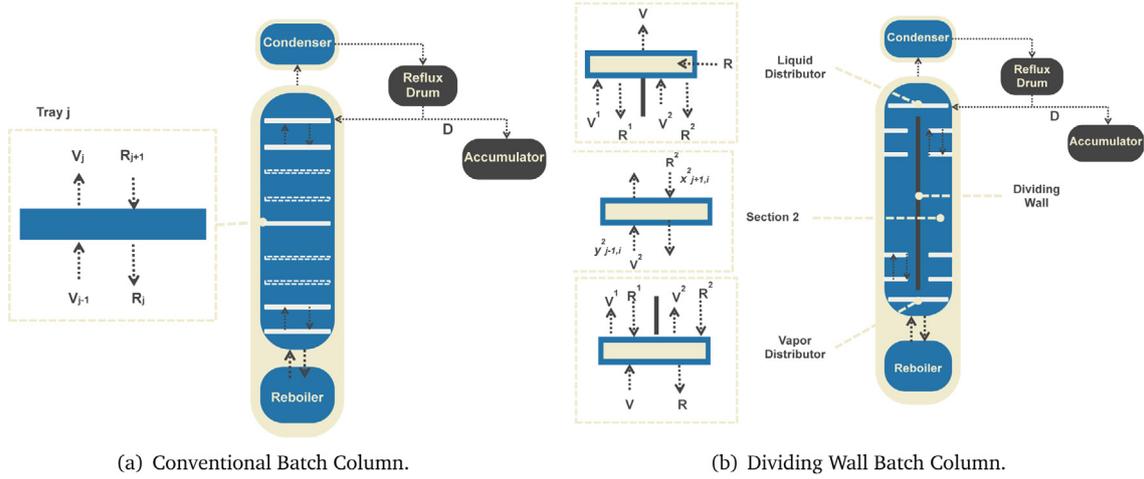


Fig. 1 – Conventional and nonconventional batch columns.

Condenser: $j = NT$

$$\frac{d(M_j h_j)}{dt} = V_{j-1} H_{j-1} - R_j h_j - Q_{cond} \quad (11)$$

Equilibrium relationship and summations

$$y_{j,i} = K_{j,i} x_{j,i} \quad \text{where} \quad \sum_{i=1}^{NC} y_{j,i} = 1 \quad \text{and} \quad \sum_{i=1}^{NC} x_{j,i} = 1 \quad (12)$$

Vapor-liquid equilibrium constant and activity coefficient

$$K_{j,i} = \alpha_{j,i} \frac{p_{j,i}^{sat}}{P_j} \quad \text{where} \quad \alpha_{j,i} = \alpha_{j,i}(x_{j,i}, T_j) \quad (13)$$

Liquid and vapor enthalpy

$$h_{j,i} = h_{j,i}(x_{j,i}, T_j, P_j) \quad \text{and} \quad H_{j,i} = H_{j,i}(y_{j,i}, T_j, P_j) \quad (14)$$

Other equations

$$D = V_{NT-1}(1 - RR) \quad (15)$$

3.2. Dividing wall batch reactive distillation column

The proposed model is given by the set of Eqs. (16)–(39), which are derived from the batch column in Fig. 1(b). Due to the formation of new products, the liquid holdups are not constant during the time of operation. The stages are also numbered from bottom to top of the column. The heat of reaction is omitted because heat of formation at the standard conditions is used as a base for enthalpy calculations. A nonreactive dividing wall batch column can be solved by ignoring the reaction terms included in the mass balances.

Total mass balances

Reboiler: $j = 1$

$$\frac{dM_j}{dt} = R_{j+1} - V_j + \Delta n_j \quad (16)$$

Vapor distributor: $j = 2$

$$\frac{dM_j}{dt} = R_{j+1}^1 + R_{j+1}^2 - R_j + V_{j-1} - V_j^1 - V_j^2 + \Delta n_j \quad (17)$$

Internal stages: $j = 3$ and $NT - 2$

$$\frac{dM_j^1}{dt} = R_{j+1}^1 - R_j^1 + V_{j-1}^1 - V_j^1 + \Delta n_j^1 \quad (18)$$

Liquid distributor: $j = NT - 1$

$$\frac{dM_j}{dt} = R_{j+1} - R_j^1 - R_j^2 + V_{j-1}^1 + V_{j-1}^2 - V_j + \Delta n_j \quad (19)$$

Component mass balances Reboiler: $j = 1$

$$\frac{d(M_j x_{j,i})}{dt} = R_{j+1} x_{j+1,i} - V_j y_{j,i} + r_{j,i} \quad (20)$$

Vapor distributor: $j = 2$

$$\begin{aligned} \frac{d(M_j x_{j,i})}{dt} &= R_{j+1}^1 x_{j+1,i}^1 + R_{j+1}^2 x_{j+1,i}^2 - R_j x_{j,i} + V_{j-1} y_{j-1,i} \\ &\quad - V_j^1 y_{j,i}^1 - V_j^2 y_{j,i}^2 + r_{j,i} \end{aligned} \quad (21)$$

Internal stages (sections 1 and 2): $j = 3, \dots, NT - 2$

$$\frac{d(M_j^1 x_{j,i}^1)}{dt} = R_{j+1}^1 x_{j+1,i}^1 - R_j^1 x_{j,i}^1 + V_{j-1}^1 y_{j-1,i}^1 - V_j^1 y_{j,i}^1 + r_{j,i}^1 \quad (22)$$

$$\frac{d(M_j^2 x_{j,i}^2)}{dt} = R_{j+1}^2 x_{j+1,i}^2 - R_j^2 x_{j,i}^2 + V_{j-1}^2 y_{j-1,i}^2 - V_j^2 y_{j,i}^2 + r_{j,i}^2 \quad (23)$$

Liquid distributor: $j = NT - 1$

$$\begin{aligned} \frac{d(M_j x_{j,i})}{dt} &= R_{j+1} x_{j+1,i} - R_j^1 x_{j,i}^1 - R_j^2 x_{j,i}^2 + V_{j-1}^1 y_{j-1,i}^1 \\ &\quad + V_{j-1}^2 y_{j-1,i}^2 - V_j y_{j,i} + r_{j,i} \end{aligned} \quad (24)$$

Condenser: $j = NT$

$$\frac{M_j dx_{j,i}}{dt} = V_{j-1}(y_{j-1,i} - x_{j,i}) + r_{j,i} \quad (25)$$

Energy balance

Reboiler: $j = 1$

$$\frac{d(M_j h_j)}{dt} = Q_{reb} + R_{j+1} h_{j+1} - V_j H_j \quad (26)$$

Vapor distributor: $j = 2$

$$\frac{d(M_j h_j)}{dt} = R_{j+1}^1 h_{j+1,i}^1 + R_{j+1}^2 h_{j+1,i}^2 - R_j h_{j,i} + V_{j-1} H_{j-1,i} - V_j^1 H_{j,i}^1 - V_j^2 H_{j,i}^2 \quad (27)$$

Internal stages (sections 1 and 2): $j = 3, \dots, NT - 2$

$$\frac{d(M_j^1 h_j^1)}{dt} = R_{j+1}^1 h_{j+1,i}^1 - R_j^1 h_j^1 + V_{j-1,i}^1 H_{j-1,i}^1 - V_j^1 H_j^1 \quad (28)$$

$$\frac{d(M_j^2 h_j^2)}{dt} = R_{j+1}^2 h_{j+1,i}^2 - R_j^2 h_j^2 + V_{j-1,i}^2 H_{j-1,i}^2 - V_j^2 H_j^2 \quad (29)$$

Equilibrium relationship and summations

$$y_{j,i} = K_{j,i} x_{j,i} \quad \text{where} \quad \sum_{i=1}^{NC} y_{j,i} = 1 \quad \text{and} \quad \sum_{i=1}^{NC} x_{j,i} = 1 \quad (30)$$

$$y_{j,i}^1 = K_{j,i}^1 x_{j,i}^1 \quad \text{where} \quad \sum_{i=1}^{NC} y_{j,i}^1 = 1 \quad \text{and} \quad \sum_{i=1}^{NC} x_{j,i}^1 = 1 \quad (31)$$

$$y_{j,i}^2 = K_{j,i}^2 x_{j,i}^2 \quad \text{where} \quad \sum_{i=1}^{NC} y_{j,i}^2 = 1 \quad \text{and} \quad \sum_{i=1}^{NC} x_{j,i}^2 = 1 \quad (32)$$

Vapor-liquid equilibrium constant and activity coefficients

$$K_{j,i} = \alpha_{j,i} \frac{p_{j,i}^{sat}}{P_j} \quad \text{where} \quad \alpha_{j,i} = \alpha_{j,i}(x_{j,i}, T_j) \quad (33)$$

$$K_{j,i}^1 = \alpha_{j,i}^1 \frac{p_{j,i}^{sat1}}{P_j} \quad \text{where} \quad \alpha_{j,i}^1 = \alpha_{j,i}^1(x_{j,i}^1, T_j^1) \quad (34)$$

$$K_{j,i}^2 = \alpha_{j,i}^2 \frac{p_{j,i}^{sat2}}{P_j} \quad \text{where} \quad \alpha_{j,i}^2 = \alpha_{j,i}^2(x_{j,i}^2, T_j^2) \quad (35)$$

Vapor and liquid enthalpy

$$h_{j,i} = h_{j,i}(x_{j,i}, T_j, P_j) \quad \text{and} \quad H_{j,i} = H_{j,i}(y_{j,i}, T_j, P_j) \quad (36)$$

$$\sum_{i=1}^{NC} \frac{R_{j+1}^1 x_{j+1,i}^1 + R_{j+1}^2 x_{j+1,i}^2 - R_j x_{j,i} + V_{j-1} y_{j-1,i} - V_{j-1}^1 y_{j-1,i}^1 - V_{j-1}^2 y_{j-1,i}^2 + r_{j,i} M_j - x_{j,i} (dM_j/dt)}{M_j} = 0 \quad (40)$$

$$h_{j,i}^1 = h_{j,i}^1(x_{j,i}^1, T_j^1, P_j) \quad \text{and} \quad H_{j,i}^1 = H_{j,i}^1(y_{j,i}^1, T_j^1, P_j) \quad (37)$$

$$h_{j,i}^2 = h_{j,i}^2(x_{j,i}^2, T_j^2, P_j) \quad \text{and} \quad H_{j,i}^2 = H_{j,i}^2(y_{j,i}^2, T_j^2, P_j) \quad (38)$$

Other equations

$$D = V_{NT-1}(1 - RR) \quad (39)$$

It should be noted that the set of DAEs for the new dividing wall column are developed by modifying the mass and energy balances on the internal stages of the column. These mass balances are then solved simultaneously with the physical, chemical and thermodynamic equilibrium models. In both

columns the desired product is collected at the top of the column as the distillate D . More details about the columns are given in Section 5.

Conventional and nonconventional batch distillation columns go through an initial startup period carried out at total reflux, with a specified pressure, temperature, and composition. The operation of these columns can be performed using three different modes, namely, constant reflux and variable product composition, variable reflux and constant product composition of the key component, and total reflux policy. Also, periodic operation (commonly known as cyclic operation) can be performed, increasing the complexity of the dynamic models. A study presented by Lopes and Song (2010) has shown that the most profitable operational mode is at constant overhead product composition (or variable reflux). Considering this, variable reflux policy is chosen for this study.

4. Solution approaches

In order to determine the optimal solution of the dynamic models presented in the previous section, we summarize below some of the issues that arise in the two approaches used in this study.

4.1. Equation oriented approach

In this approach the set of DAEs is discretized into a set of algebraic equations (AEs) by applying orthogonal collocation over finite elements, developed by Cuthrell and Biegler (1987). These equations are then used in a large-scale NLP model. The use collocation points over finite elements provides more flexibility in the modeling, but the error in the discretization cannot be easily controlled. The proposed DAE system involves a complex set of equations that leads to an index 2 problem. To be solved the index should be reduced to 1 by reformulating the equations with the following steps:

1. Consider the algebraic summation of liquid composition on the internal stages of the column: $\sum_{i=1}^{NC} x_{j,i} = 1$.
2. Differentiate the equation in step 1, leading to: $\frac{d(\sum_{i=1}^{NC} x_{j,i})}{dt} = 0$.
3. Substitute Eqs. (21)–(24) in step 2 equation. An example is given for the vapor distributor in Eq. (21).

Now Eq. (40) replaces one equation for a NC component in Eq. (21). This reformulation must be applied to the rest of the equations on the internal stages (batch reactive column) and internal stages and distributors (dividing wall batch column). The modified equations lead to an index 1 DAE model.

For the optimization, it is necessary to calculate a consistent set of initial values for all variables in the stationary state. If the composition profile is too far from the desired one, the optimization (even the simulation) leads to an infeasible solution. It should be noted that in DAEs systems only some of the variables need to be initialized, being the same number of differential variables involved in index 1 systems. The other variables can be determined using the algebraic equations. With the proper initialization and a finite number of elements in the model, now discretized, the problem can be solved using orthogonal collocation over finite elements with a NLP solver.

Table 1 – Operating conditions for the nonreactive distillation column.

Number of Stages	10	Holdup, M_i^0 , kmol	
Feed, M_{B_0} , kmol	10	Condenser	0.333
		Internal stages	0.083
Feed composition, x_i^0 , mole fraction			
Methanol	0.25		
Ethanol	0.25	Feed cost ^a , C_{feed} , \$/kmol	1
n-Propanol	0.25	Product price ^a , $C_{product}$, \$/kmol	35
n-Butanol	0.25		
Dividing wall column			
Vapor distributor, β		Liquid distributor, κ	
Section 1	0.7	Section 1	0.7
Section 2	$1 - \beta_1$	Section 2	$1 - \kappa_1$

Column pressure, P (bar). Condenser: 1.05, internal stages: 1.12–1.08, reboiler: 1.20.
^a Low and Sørensen (2003).

4.2. Control vector parameterization approach

In contrast to the above approach, the CVP developed by Pantelides (Vassiliadis et al., 1994a,b), relies on the iterative solution of DAEs in the space of the control variables in order to perform the optimization. To formulate the optimal control problem as a reduced NLP problem, the control variable $RR(t)$ is approximated by a finite dimensionally equation. The time interval is divided into a finite number of subintervals, each one involving a finite number of parameters. This new problem is subjected to the constraints of the model and can be solved using a Successive Quadratic Programming (SQP) algorithm. The difference with the method developed by Cuthrell and Biegler (1987) is that the solution of DAEs relies in the reduced space of the control variables in order to perform the optimization. By directly integrating the equations with a DAEs solver, this ensures that the DAEs are satisfied within a given tolerance at every step of the optimization procedure. In addition to the smaller size of the nonlinear programming problem, this approach has the advantage of providing a direct control of the discretization error by adjusting the size and order of the integration steps using integration techniques.

5. Case study

The different batch configurations and cases solved in this paper are presented in this section: a conventional and nonconventional nonreactive and reactive BDC. The conventional batch configuration is a 10 stage batch column with stages numbered from bottom to top, stage 1 being the reboiler and stage 10 the condenser, as the one shown in Fig. 1(a). The BRDC is a 10 stage BDC with a reactive zone that extends from stage 1 to 9. The nonconventional batch configuration is a 10 stage BDC divided by a wall that extends from stages 3 to 8, as it is shown in Fig. 1(b). This stage configuration corresponds to a real dividing wall batch reactive distillation column used for the production of ethyl acetate performed by Delgado-Delgado et al. (2012). This new nonconventional DWBDC has an upper stage that distributes the liquid into two sections in the column: β_1 represents the fraction of liquid that feeds section 1 (left side of the column) and β_2 the fraction of liquid that feeds section 2 (right side of the column). The bottom stage is a vapor distributor, being κ_1 the vapor flowrate fraction that goes up to section 1 and κ_2 the vapor flowrate fraction that goes up to section 2. The DWBRDC is a 10 stage batch column divided by a wall that extends from stage 3 to 8, with a reactive zone that

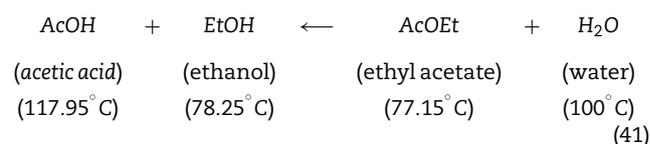
extends from stage 1 to 9. The nonreactive and reactive cases are described in Sections 5.1 and 5.2, respectively.

5.1. Nonreactive distillation: methanol, ethanol, n-propanol and n-butanol separation

The separation of a quaternary mixture (methanol, ethanol, n-propanol and n-butanol) is carried out using two different columns: a 10 stage conventional BDC and a 10 stage nonconventional DWBDC. An amount of 10 kmol is charged into the reboiler for each case at the start of the operation. The operating conditions are given in Table 1. A distillate product with a methanol purity of at least 0.90 in mole fraction is required for the optimization problem. Ideal activity coefficients are assumed for modeling the phase equilibrium.

5.2. Reactive distillation: esterification of acetic acid with ethanol

The production of ethyl acetate by esterification of acetic acid with ethanol is accomplished by the following stoichiometric equation



where acetic acid and ethanol react to produce ethyl acetate (as the main product) and water. Due to the similar boiling points of ethyl acetate and ethanol, this separation is considered difficult. The overall reaction rate of this system is

$$r = k_1 C_A C_B - k_2 C_C C_D \quad (42)$$

where the rate constants values are

$$k_1 = 4.76 \times 10^{-4} \quad \text{and} \quad k_2 = 1.63 \times 10^{-4} \quad (43)$$

and C_i denotes the molarity in mol/L of the different components A (acetic acid), B (ethanol), C (ethyl acetate), and D (water). The separation of ethyl acetate (as the desired product) is carried out using two different reactive columns: a 10 stage conventional batch reactive column (BRC) and a 10 stage dividing wall batch reactive column (DWBRDC). The operating conditions are given in Table 2. An amount of 10 kmol is fed into the reboiler at the start of the operation with the next

Table 2 – Operating conditions for the reactive distillation column.

Number of Stages	10	Holdup, M_j^0 , kmol	
Feed, M_{B_0} , kmol	10	Condenser	0.333
		Internal stages	0.083
Feed composition, x_i^0 , mole fraction			
Acetic acid	0.45		
Ethanol	0.45		
Ethyl acetate	0		
Water	0.10		
Dividing wall column			
Vapor distributor, β		Liquid distributor, κ	
Section 1	0.7	Section 1	0.7
Section 2	$1 - \beta_1$	Section 2	$1 - \kappa_1$
Column pressure, P (bar): 1.013.			

composition in mole fraction: 0.45 acetic acid, 0.45 ethanol and 0.10 water. The distillate must achieve a purity higher than 0.50 in mole fraction of ethyl acetate in the distillate. The activity coefficients are calculated using the NRTL method.

6. Results

In this section, the solution of the dynamic models presented in Section 3 for a conventional and nonconventional BDC with and without reaction is presented. In order to study any potential benefits of the new nonconventional dividing wall batch configuration, the results are compared with those of the BDC. All examples were solved on a Dell Workstation with 8 GB RAM memory and Intel® Core™i7 CPU (2.20 GHz). The nonreactive case study is solved first to be used as a point of reference for the reactive case which is more complex.

6.1. Conventional batch distillation column

The optimization problem is solved by discretizing the differential equations using the two approaches presented in Section 4 with the next specifications: CVP approach implemented in gPROMS (3.7.1) using SQP as the NLP solver, and EOA implemented in GAMS (24.2.2) using IPOPT (3.11) as the NLP solver when 10 finite elements and 3 collocation points are used. Four cases with different vapor flowrates were considered and solved first for the nonreactive and reactive case. Both set of results are taken as a reference for a further comparison with the DWBDC and DWBRDC. For all the cases presented in this work, a fixed batch time of 1 h is used.

6.1.1. Nonreactive case study

The nonreactive model for a BDC is obtained by removing the reaction terms in the dynamic model shown in Eqs. (3)–(15).

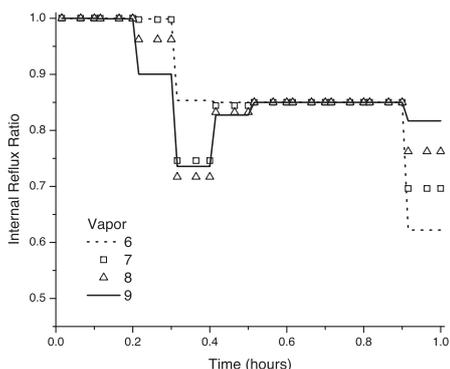
The separation is carried out in a 10 stage batch column with a 10 kmol initial feed into the reboiler of a quaternary mixture (methanol, ethanol, *n*-propanol, and *n*-butanol) with the following concentration in mole fraction: 0.25 methanol, 0.25 ethanol, 0.25 *n*-propanol, and 0.25 *n*-butanol. The objective is to maximize a profit function (given in Eq. (2)) using the reflux ratio $RR(t)$ as control variable until a concentration in mole fraction of 0.90 of methanol in the distillate is achieved. The prices used to solve the optimization problem were taken from Low and Sørensen (2003): methanol price $C_A = 35$ \$/kmol and initial feed price $C_B = 1$ \$/kmol. The energy cost was $C_E = 2.7$ \$/kWh.

The EOA results in a system of 249 equations and 319 variables. The optimization problem is solved in 13 s and the results when 10 finite elements and 3 collocation points are used are shown in Table 3(a). To determine the initial values for the algebraic and differential variables we considered that the column operates at total reflux. The CVP approach results in a system of 234 equations and 285 variables. The optimization problem is solved in 10 s and the results are presented in Table 3(b). The two approaches predict that profit and energy consumption are directly proportional to changes on the vapor flowrate, reaching a maximum value when $V = 9$ kmol/h. In terms of produced distillate, no differences were observed.

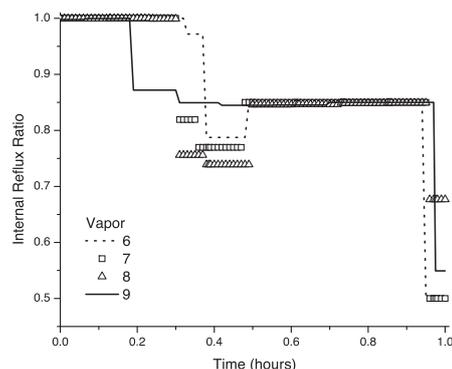
For both approaches, the duration of the startup period (total reflux) is shorter when the vapor flowrate increases, allowing the withdrawal of more distillate. This can be seen in the reflux ratio optimal profiles presented in Fig. 2. As a result, profit (directly proportional to productivity) increases when reflux ratio values are smaller. We will analyze when $V = 9$ kmol/h, the highest value of profit. For the EOA, the piecewise reflux ratio profile changes faster than CVP, leading to less liquid sent back to the top stage of the column. This allows EOA to withdraw a higher amount of distillate,

Table 3 – Maximum profit results in a batch distillation column for the EOA and CVP approach.

Vapor (kmol/h)	$Q_{REB_{total}}$ (MJ/h)	D (kmol)	Profit (\$/year)
<i>(a) EOA approach when 10 finite elements and 3 collocation points are used</i>			
6	226.73	0.76	13,685.75
7	264.75	0.92	36,481.02
8	302.85	1.06	55,448.17
9	341.02	1.19	71,130.32
<i>(b) CVP approach</i>			
6	231.78	0.77	13,630.56
7	269.92	0.93	38,360.04
8	308.03	1.05	53,392.20
9	345.95	1.19	71,472.84



(a) EOA approach when 10 finite elements and 3 collocation points are used.



(b) CVP approach.

Fig. 2 – Maximum profit reflux ratio optimal profiles in a batch distillation column for the EOA and CVP approach.

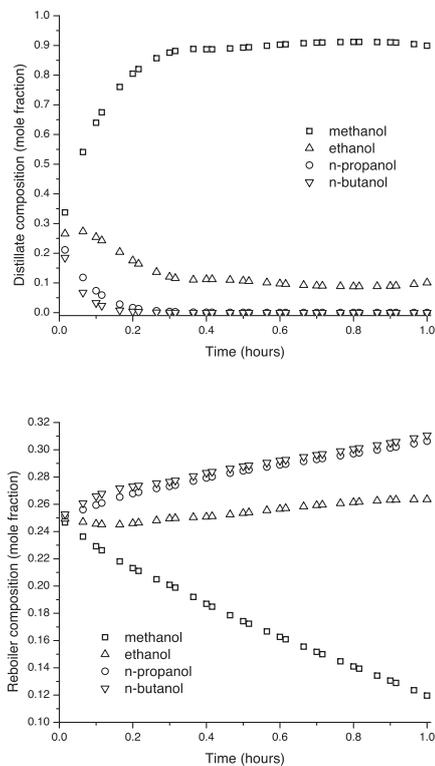
reducing the composition of methanol in the distillate to a maximum value of 0.91 in mole fraction. The composition profiles for both approaches are presented in Fig. 3. On the other hand, the CVP approach reaches a maximum methanol composition in the distillate of 0.918 in mole fraction. Because our constraint only indicates compositions higher and/or equal to 0.90, the profiles for both approaches are accepted as a solution of our problem.

But not only is the way each approach manipulates the control variable that has an influence on the optimal results, these differences can also be due to the accuracy of the methods. In order to compare the effectiveness of these approaches, a comparison analysis for the EOA was performed when the number of finite elements vary. This sensitivity analysis was performed by solving the problem with 20 and 30 finite elements with 3 collocation points. The

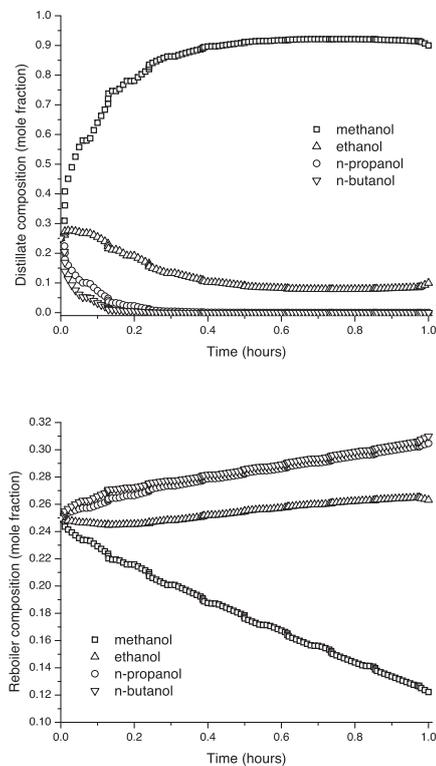
results are presented in Table 4. The optimization times vary: when 20 finite elements are used, the computational time is 23s, while 30 finite elements takes 100s. It is clear that changes on the number of finite elements affects computational times. A comparison between the reflux ratio optimal profiles for the three finite element values is presented in Fig. 4(a) for $V=9$ kmol/h. As the reflux ratio jumps from different values, it allows more withdrawn of distillate product at the expense of less smooth composition values, as shown in Fig. 4(b). By comparing these results, and considering computational time, 10 finite elements were used for further comparisons.

6.1.2. Reactive case study

The performance of a conventional batch reactive column is defined in terms of maximum conversion of the limiting



(a) EOA approach when 10 finite elements and 3 collocation points are used.



(b) CVP approach.

Fig. 3 – Distillate and reboiler composition profiles in a batch distillation column for EOA and CVP approach.

Table 4 – Maximum profit results in a batch column for different finite elements.

Vapor (kmol/h)	20 finite elements		30 finite elements	
	Q_{REB_total} (kJ/h)	Profit (\$/year)	Q_{REB_total} (kJ/h)	Profit (\$/year)
6	226.73	18,114.80	226.69	18,774.65
7	264.75	43,599.40	264.71	43,497.78
8	302.80	61,710.70	302.81	64,516.52
9	340.98	74,653.60	340.94	78,234.68

reactant (ethanol) subject to a given purity of ethyl acetate (0.5 mol fraction in distillate). The reactive system is solved for the dynamic model given in Eqs. (3)–(15). The separation is carried out in a 10 stage BRDC with a 10 kmol feed into the reboiler with the following composition in mole fraction: 0.45 acetic acid, 0.45 ethanol, and 0.10 water with piecewise reflux ratio, discretized into 10 time intervals.

The results in terms of the maximum conversion and final ethyl acetate composition in the distillate for different vapor flowrates (between 6 and 9 kmol/h) are given in Table 5 for the two approaches. The EOA results in a system of 1051 equations and 1062 variables. The optimization problem is solved in 400 s when 10 finite elements and 3 collocation points are used. To determine the initial values for the system we consider total reflux in the steady state. The CVP approach results in a system of 988 equations and 1040 variables. The optimization problem is solved in 10 s. Both approaches involve a different number of equations and variables and a significant difference in the computational times. In terms of energy consumption in the reboiler, CVP results vary in less than 5% of the EOA solution, while conversion values are not significantly different between the two approaches. This could be explained by studying the internal piecewise reflux ratio profiles in Fig. 5.

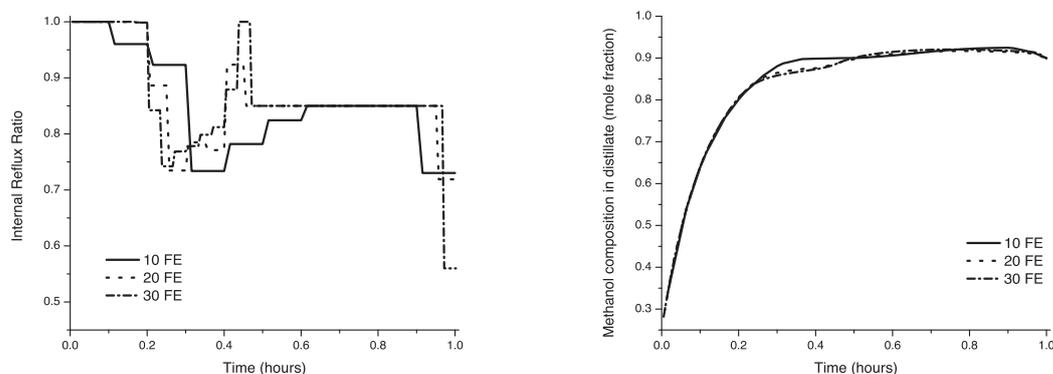
We observe that the first 0.4 h of the batch processing time corresponds to the startup period (total reflux operation). This time is needed to concentrate the distillate product before any product is withdrawn from the column. Thanks to this, the constraint of the ethyl acetate final composition (higher than 0.5 in mole fraction) is achieved. After the startup period ends, the CVP approach achieves a constant internal reflux ratio value of 0.45, which means that distillate is withdrawn as product into the accumulator. On the other hand, the EOA solves a different set of profiles, higher than 0.45 for almost all vapor flowrates (lower values of 0.61). This will reduce the composition of the ethyl acetate in the product.

When EOA is used, the dimension of the dynamic model increases with the number of finite elements leading to longer computational times. In order to estimate the impact of the discretization error and the suitable number of finite elements, the optimization problem is solved for different number of finite elements. For the batch reactive column, the optimization results for 5 and 15 finite elements are presented in Table 10. The computational time when 15 finite elements are used is 2400 s, while 5 finite elements takes 280 s. It is clear that cpu-time increases when the number of finite elements increases. By comparing the results, we see that the number of finite elements will have an influence on the ethanol conversion, reducing its value (59.48% with 10 finite elements). Considering the computational time and for further comparison with other columns, 10 finite elements were used.

In terms of design operation conditions, in Table 5 we observe that the conversion is directly proportional to increases on the vapor flowrate. In this column (and for both approaches) the conversion increases by 3% when working with the maximum vapor flowrate. This happens in both approaches. This will also increase the energy consumption in the reboiler. At the beginning of the operation, the column is filled with acetic acid and ethanol. As soon as the operation starts, ethanol is consumed by the reaction in the reboiler yielding a low concentration at the final time. The composition profiles in the distillate and reboiler are shown in Fig. 6. Since there is very little (almost nothing) acetic acid at the top of the column, no forward reaction is possible (no ethyl acetate production). It can also be seen that there is some unreacted acetic acid and ethanol in the reboiler, being available for further reaction if more time in the process were available. The composition profiles along the column can be seen in Fig. 7.

Table 6

Changes of the concentration profiles are also reflected in the temperature profiles in Fig. 8(a) for the two approaches.



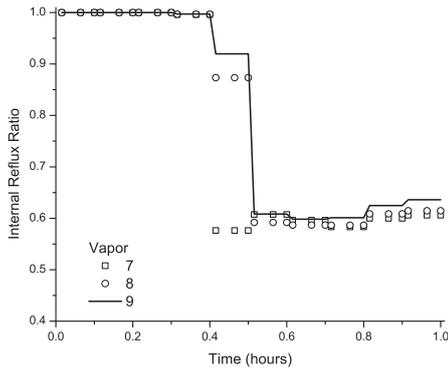
(a) Reflux ratio optimal profiles when 20 and 30 finite elements are used for the EOA.

(b) Methanol composition profiles in the distillate when 20 and 30 finite elements are used for the EOA.

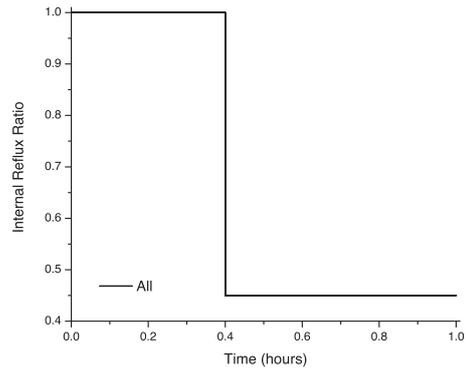
Fig. 4 – Maximum profit reflux ratio and methanol composition profiles in a batch column for 20 and 30 finite elements for the EOA.

Table 5 – Maximum conversion optimal results in a batch reactive column for the production of ethyl acetate for the EOA and CVP approach.

Vapor (kmol/h)	$Q_{REB_{total}}$ (MJ/h)	X_{EtOH} (conversion in %)	x_{AcOEt}^D (mole fraction)
<i>(a) EOA approach when 10 finite elements and 3 collocation points are used</i>			
6	235.25	58.60	0.500
7	274.65	60.07	0.501
8	313.18	59.33	0.507
9	351.86	59.48	0.510
<i>(b) CVP approach</i>			
6	233.58	57.00	0.518
7	271.87	57.61	0.523
8	310.21	58.27	0.526
9	348.46	58.99	0.527

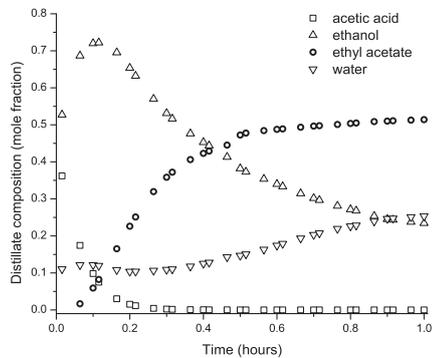


(a) EOA approach when 10 finite elements and 3 collocation points are used.

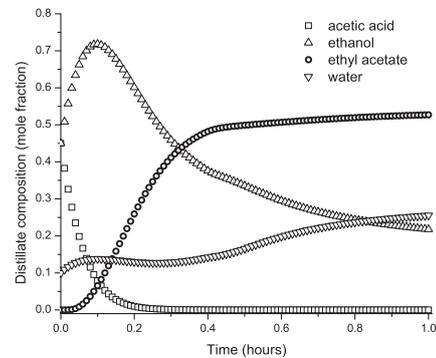


(b) CVP approach.

Fig. 5 – Maximum conversion optimal reflux ratio optimal profiles in a batch reactive distillation column for the production of ethyl acetate for the EOA and CVP approach.



(a) EOA approach when 10 finite elements and 3 collocation points are used.



(b) CVP approach.

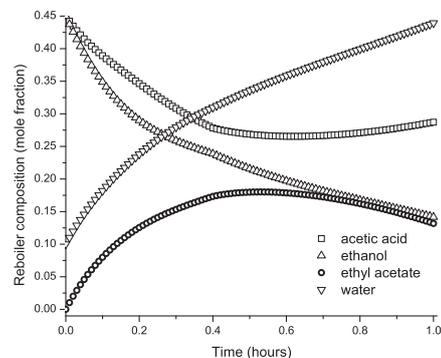
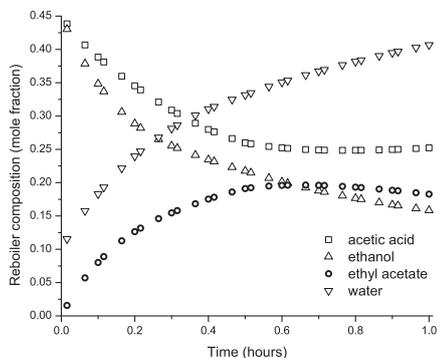


Fig. 6 – Maximum conversion distillate and reboiler composition profiles in a batch reactive distillation column for the production ethyl acetate for the EOA and CVP approach.

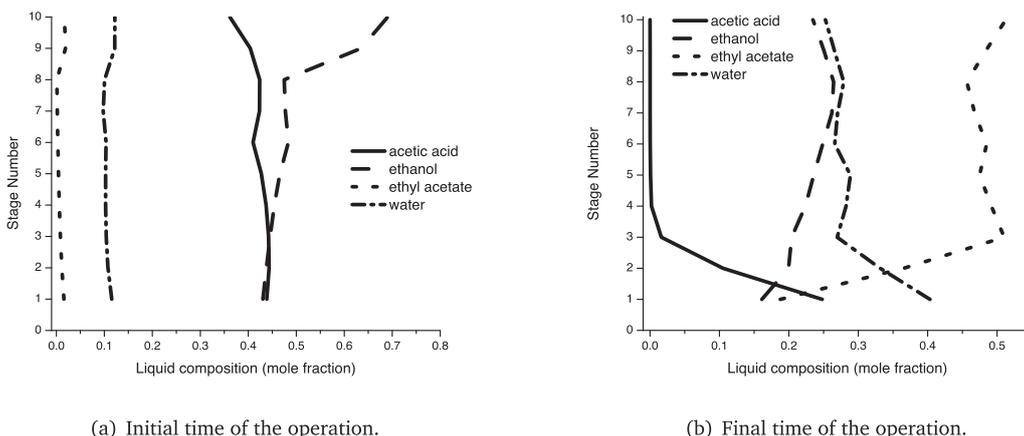


Fig. 7 – Maximum conversion liquid composition along the column in a batch reactive distillation column for the production of ethyl acetate for the EOA approach.

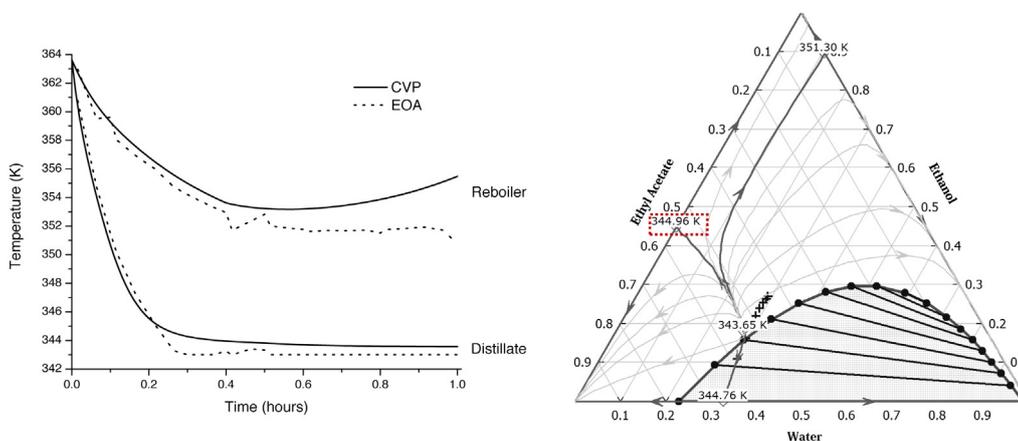
Table 6 – Maximum conversion results in a batch reactive column when 5 and 10 finite elements are used in the EOA.

Vapor (kmol/h)	5 finite elements		15 finite elements	
	$Q_{REB_{total}}$ (kJ/h)	Profit (\$/year)	$Q_{REB_{total}}$ (kJ/h)	Profit (\$/year)
6	235.18	58.70		Infeasible
7	273.22	58.42	273.26	56.44
8	312.73	58.46	312.58	58.41
9	351.34	58.51	351.26	58.60

The reboiler and distillate temperatures start at a high temperature, and then decrease until both reach a constant value (reboiler EOA/CVP: 352/355 K, and condenser EOA/CVP: 343/344 K). The initial decrease in temperature is due to the presence of ethyl acetate (minimum boiling point) produced by reaction. However, as the separation of ethyl acetate continues, CVP reboiler temperature starts increasing (due to the evaporation/separation of ethyl acetate and the increasing amount of water formed by reaction) while EOA temperature decreases due to a higher amount of ethyl acetate in the reboiler. Also, a temperature change was observed for the EOA, caused by a sudden change on the reflux ratio. Since there is not enough water and acetic acid, the temperature on the distillate starts decreasing until it reaches a constant value. The boiling point of ethanol is reached around 0.1h, reason why the highest ethanol composition in the distillate is observed in Fig. 6. After this temperature is reached,

the separation of ethyl acetate starts and the temperature decreases until a constant value below ethyl acetate boiling point is achieved. Due to the similar boiling points of ethyl acetate and ethanol, this separation is difficult: multiple azeotropes are found that may prevent obtaining high purity ethyl acetate. The phase equilibria diagram in Fig. 8(b) reveals that this quaternary reactive system presents three minimum boiling azeotropes and one minimum boiling ternary azeotrope:

- (1) Homogeneous azeotrope EtOH/EtAc/H₂O: 343.65 K (0.1812/0.5371/0.2818)
- (2) Heterogeneous azeotrope EtAc/H₂O: 344.14 K (0.5982/0.4018)
- (3) Homogeneous azeotrope EtOH/EtAc: 344.96 K (0.4467/0.5533)



(a) Maximum conversion reboiler and distillate temperature profiles for the EOA and CVP approach. (b) Azeotropes in the quaternary system for the production of ethyl acetate.

Fig. 8 – Maximum conversion reboiler and distillate temperature profiles for the EOA and azeotropes in the quaternary system for the production of ethyl acetate.

Table 7 – Maximum profit results in a dividing wall batch column for EOA and CVP approach.

Vapor (kmol/h)	$Q_{\text{REB, total}}$ (MJ/h)	D (kmol)	Profit (\$/year)
<i>(a) EOA approach when 10 finite elements and 3 collocation points are used</i>			
6	225.89	0.73	14,371.66
7	263.83	0.92	37,212.48
8	301.41	1.06	57,008.33
9	337.17	1.17	73,617.29
<i>(b) CVP approach</i>			
6	231.74	0.75	10,883.42
7	269.92	0.92	35,710.14
8	308.06	1.05	53,365.92
9	346.03	1.19	71,429.92

(4) Heterogeneous azeotrope EtOH/H₂O: 351.30 K (0.8952/0.1048)

From the list of azeotropes we observe that the ternary azeotrope 1 has the lowest temperature (343.65 K). When most of the acid is consumed in the reactive stages of the column, the separation ends when the EtOH/EtAc azeotrope (3) is present at the top of the column (344.96 K). Due to this, the final composition in the distillate of ethyl acetate is not higher than the azeotrope composition (0.598 of ethyl acetate in mole fraction).

6.2. Nonconventional dividing wall batch distillation column

In order to compare the two discretization approaches for the solution of large systems of equations and to demonstrate possible benefits of dividing wall columns in batch separations, the solution of a nonconventional dividing wall batch column with and without reaction is presented in this section. The optimization problem is solved by discretizing the differential equations using the two approaches presented in Section 4 with the next specifications: CVP approach implemented in gPROMS (3.7.1) using SQP as the NLP solver, and EOA implemented in GAMS (24.2.2) using IPOPT as the NLP solver using 10 finite elements and 3 collocation points. To study potential benefits on the use of dividing walls in distillation processes, the two conventional batch distillation columns in Section 6.1 are taken as a reference for a comparison with this new nonconventional batch configuration. For all the cases, a fixed batch time of 1 h is used.

6.2.1. Nonreactive case study

The nonreactive model is obtained by removing the reaction terms in the dynamic model in Eqs. (16)–(39). The separation is carried out in a 10 stage DWBDC with a feed of 10 kmol of a quaternary mixture (methanol, ethanol, *n*-propanol, and *n*-butanol) to the reboiler with the following concentration in mole fraction: 0.25 methanol, 0.25 ethanol, 0.25 *n*-propanol, and 0.25 *n*-butanol. The objective is to maximize a profit function (given in Eq. (2)) using the reflux ratio $RR(t)$ as control variable until a concentration of at least 0.90 in mole fraction of methanol is achieved in the distillate. The prices used to solve the optimization problem were given in Section 6.1.1. The EOA results in a system of 394 equations and 434 variables. The optimization problem is solved in 27 s and the results are presented in Table 7(a) when 10 finite elements and 3 collocation points are used. The CVP approach results in a system of 354 equations and 427 variables. The optimization problem is solved in 12 s and the results are presented in Table 7(b). As in

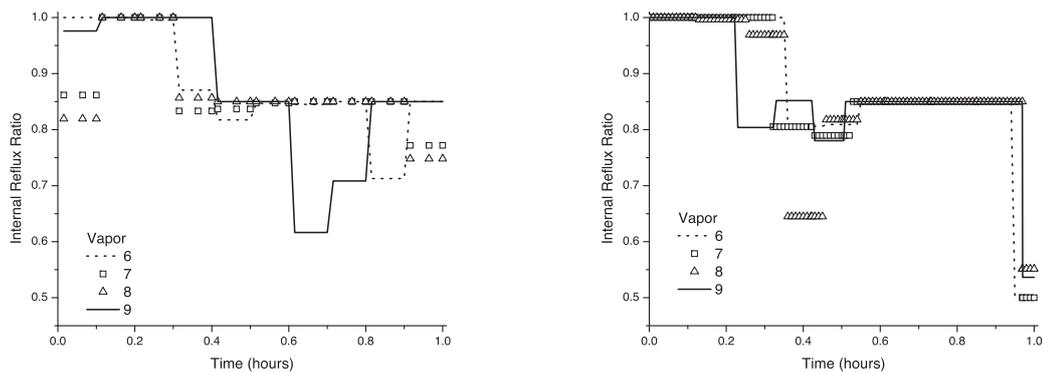
the conventional BDC, both approaches show that the maximum profit is achieved when $V = 9$ kmol/h, increasing also the energy consumption.

Notice in Table 7(b) that CVP results for the DWBDC are not different from the results in Table 3(b) for a BDC. By comparing CVP reflux ratio and distillate composition profiles in Figs. 9(b) and 10(b) with BDC results in Figs. 2b and 3b we observe that the profiles have no significant differences. On the other hand, EOA results in Table 7(a) vary around 3% in terms of profit when compared to BDC results in Table 3(a). To explain this difference, we will compare the reflux ratio and distillate composition profiles in Figs. 9(a) and 10(a) with the BDC profiles in Figs. 2(a) and 3(a). We observe that, even though some of the reflux ratio values are not the same, they follow the same trend. In a DWBDC, EOA startup period is extended to 0.4 h (BDC startup time was 0.2 h), allowing the higher concentration of methanol in the distillate, increasing the profit. This is clear in the composition profiles in Fig. 10(a). In the distillate, we observe methanol compositions higher than 0.9 in mole fraction, while methanol profile in Fig. 3(a) for a BDC shows a constant value of 0.9 in mole fraction. After the startup period, the DWBDC reflux ratio decreases, reducing methanol composition (around 0.6 h). In order to increase and meet the methanol final specification, the reflux ratio is increased, concentrating the methanol product at the end of the operation. In terms of energy consumption in the reboiler, a final comparison between the two batch configurations shows that no savings are achieved when a dividing wall is added to the column.

When using the EOA for a larger system of equations we observe differences on the optimal control variable profiles. In order to compare the effectiveness of the EOA, a comparison analysis was also performed when 20 and 30 finite elements with 3 collocation points are used. The results are presented in Table 8. The computational time when 20 finite elements are used is 65 s, while 30 finite elements take 87 s. The piecewise optimal reflux ratio profiles when $V = 9$ kmol/h are shown in Fig. 11(a) for the three different used finite elements. By studying these profiles we observe that sudden changes are observed which results in less smooth composition profiles in the distillate, as observed in the methanol composition profiles in Fig. 11(b). It is clear that an increase on the number of finite elements will reduce the concentration of methanol in the distillate, with sudden changes after the startup period is over. Due to this, and considering the computational time, 10 finite elements were considered.

6.2.2. Reactive case study

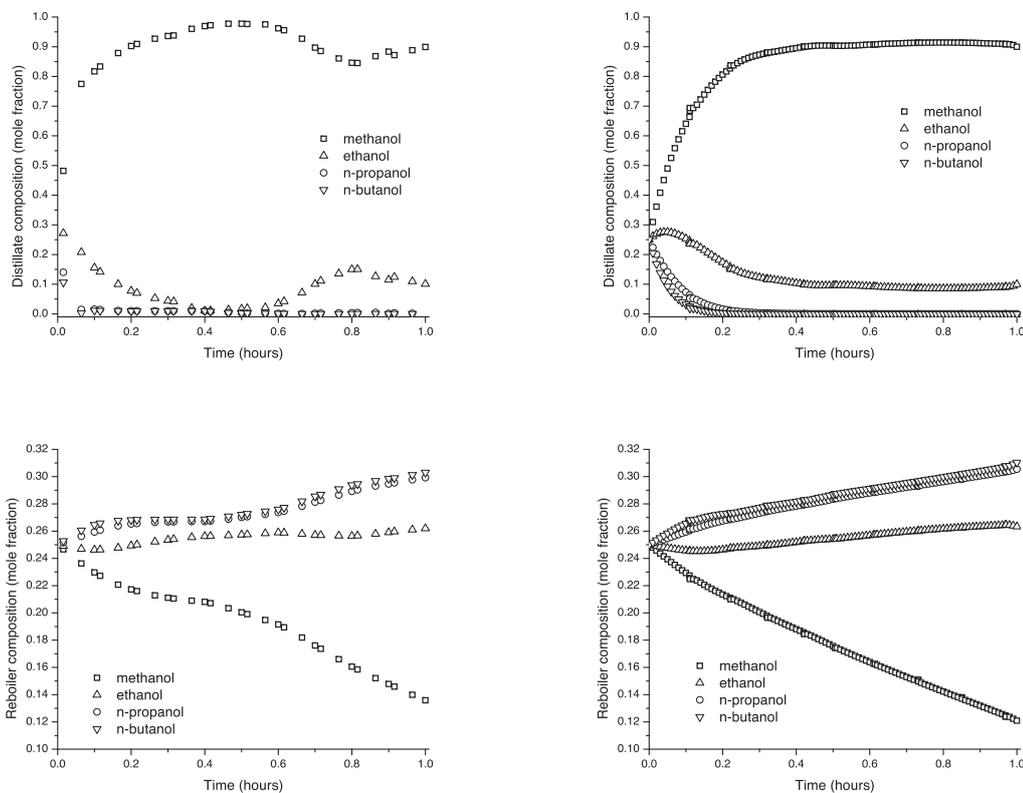
The performance of a nonconventional DWBRDC is defined in terms of maximum conversion of the limiting reactant



(a) EOA approach for 10 finite elements and 3 collocation points.

(b) CVP approach.

Fig. 9 – Maximum profit reflux ratio optimal profiles in a dividing wall column for EOA and CVP approach.



(a) EOA approach when 10 finite elements and 3 collocation points are used.

(b) CVP approach.

Fig. 10 – Maximum profit distillate and reboiler composition profiles in a dividing wall batch column for the EOA and CVP approach.

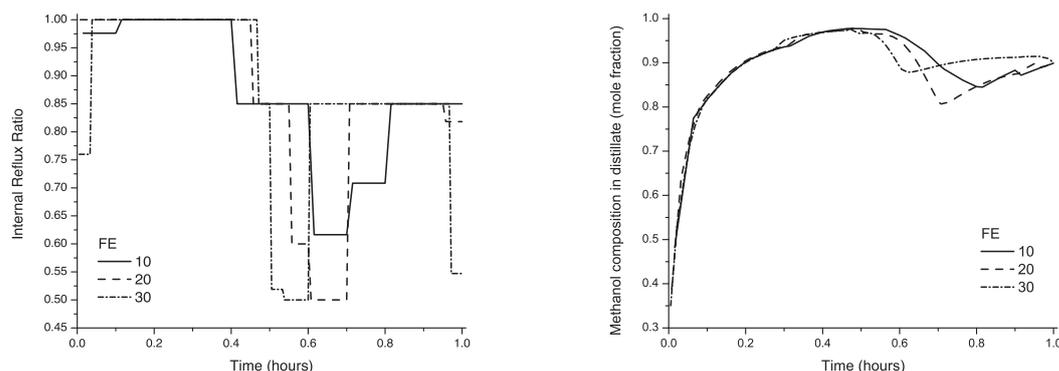
(ethanol) subject to a given purity of ethyl acetate (0.5 mole fraction in distillate). The reactive system is solved for the dynamic model given in Eqs. (16)–(39). The separation is carried out in a 10 stage DWBRDC with a 10kmol feed into the reboiler with the following composition in mole fraction: 0.45 acetic acid, 0.45 ethanol, and 0.10 water

with piecewise reflux ratio, discretized into 10 time intervals.

The results in terms of the maximum conversion of ethanol and final composition of ethyl acetate in the distillate for different vapor flowrates (between 6 and 9 kmol/h) are given in Table 9 for the EOA and CVP approaches. The EOA results in

Table 8 – Maximum profit results in a dividing wall batch column for different finite elements for the EOA.

Vapor (kmol/h)	20 finite elements		30 finite elements	
	$Q_{REB_{total}}$ (kJ/h)	Profit (\$/year)	$Q_{REB_{total}}$ (kJ/h)	Profit (\$/year)
6	225.81	14,394.43	225.81	14,402.32
7	263.63	37,288.70	263.59	37,297.45
8	301.18	57,121.33	301.14	57,137.98
9	337.13	73,644.44	337.09	73,658.46



(a) Reflux ratio optimal profiles when 20 and 30 finite elements are used for the EOA. (b) Methanol composition in distillate profiles when 20 and 30 finite elements are used for the EOA.

Fig. 11 – Maximum profit reflux ratio and methanol optimal profiles in a dividing wall batch column when 20 and 30 finite elements are used for the EOA.

a system of 1682 equations and 1726 variables. The optimization problem is solved in 300 s when 10 finite elements and 3 collocation points are used. To determine the initial values for the system variables we consider total reflux operation. The CVP approach results in a system of 1480 equations and 1570 variables. The optimization problem is solved in 10 s. It is clear that both approaches involve a significant difference in the computational time. This difference is due to the control variable considerations: CVP only discretizes the control variable, while EOA discretizes control and state variables. In terms of the system variables, CVP results vary in less than 1% of the EOA solution in terms of conversion and around 1.2% in terms of energy.

In Table 9 we observe that ethanol conversion is directly proportional to increases on the vapor flowrate. Also, for the two approaches, ethanol conversion increases by 3% when the maximum vapor flowrate is used, also increasing the reboiler energy consumption. As in the BRDC, the DWBRDC is filled with acetic acid and ethanol at the beginning of the operation and, as soon as the operation starts, ethanol is consumed by the reaction decreasing its concentration in the reboiler. The composition profiles in the distillate and reboiler for a DWBRDC are shown in Fig. 13. Since there is very little (almost nothing) acetic acid at the top of the column no forward reaction is possible (no ethyl acetate production). The EOA results in Table 9(a) show that ethyl acetate final compositions in the distillate have smaller values when compared to CVP results in Table 9(b). This is explained by studying the piecewise reflux ratio profiles in Fig. 12. If we observe the reflux ratio profiles when $V=9$ kmol/h we notice that both approaches have a startup period of 0.4 h (total reflux operation). This time was needed to concentrate the distillate product before any

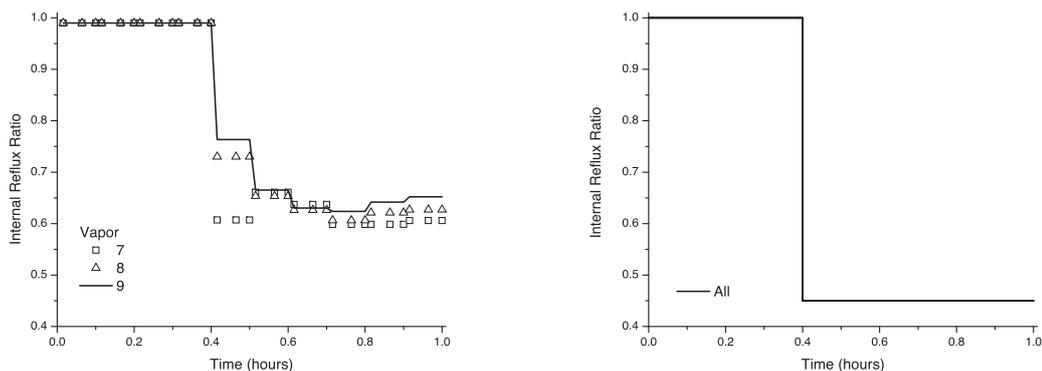
product is withdrawn out the column. As soon as CVP achieves a composition of ethyl acetate of at least 0.5 in mole fraction, the reflux ratio reaches a constant value of 0.45, withdrawing a total amount of 2.97 kmol of distillate product. On the other hand, after the startup period ends, the EOA approach reaches ethyl acetate desired composition of 0.5 in mole fraction. Since this constraint is satisfied, the distillate withdrawn starts, separating a total amount of 1.87 kmol. This reduction on the amount of accumulated distillate is consistent with the reflux ratio differences between the two approaches.

Notice in Table 9 that CVP and EOA values for the DWBRDC are not different from the results in Table 5. This is explained by comparing the reflux ratio and distillate composition profiles in Figs. 12 and 13 with BDC profiles in Figs. 5 and 6. For the CVP approach no differences were observed, while EOA approach reflux ratio profiles for a DWBRDC in Fig. 12(a) show small differences when compared to the BRDC reflux ratio profiles in Fig. 5(a). These differences are not significant since they both follow the same trend. The duration of the startup period is the same for all the batch reactive configurations, 0.4 h, allowing higher methanol concentrations in the distillate. Finally, in terms of energy consumption in the reboiler, a final comparison between the two batch reactive configurations shows that no savings are achieved when a dividing wall is added to the column.

When EOA is used, the dimension of the dynamic model increases with the number of finite elements leading to longer computational times. In order to estimate the impact of the discretization error and the suitable number of finite elements, the optimization problem is solved for different number of finite elements. The optimization results for 5 and 15 finite elements are presented in Table 10. The

Table 9 – Maximum conversion results in a dividing wall batch column for ethyl acetate for the EOA and CVP approach.

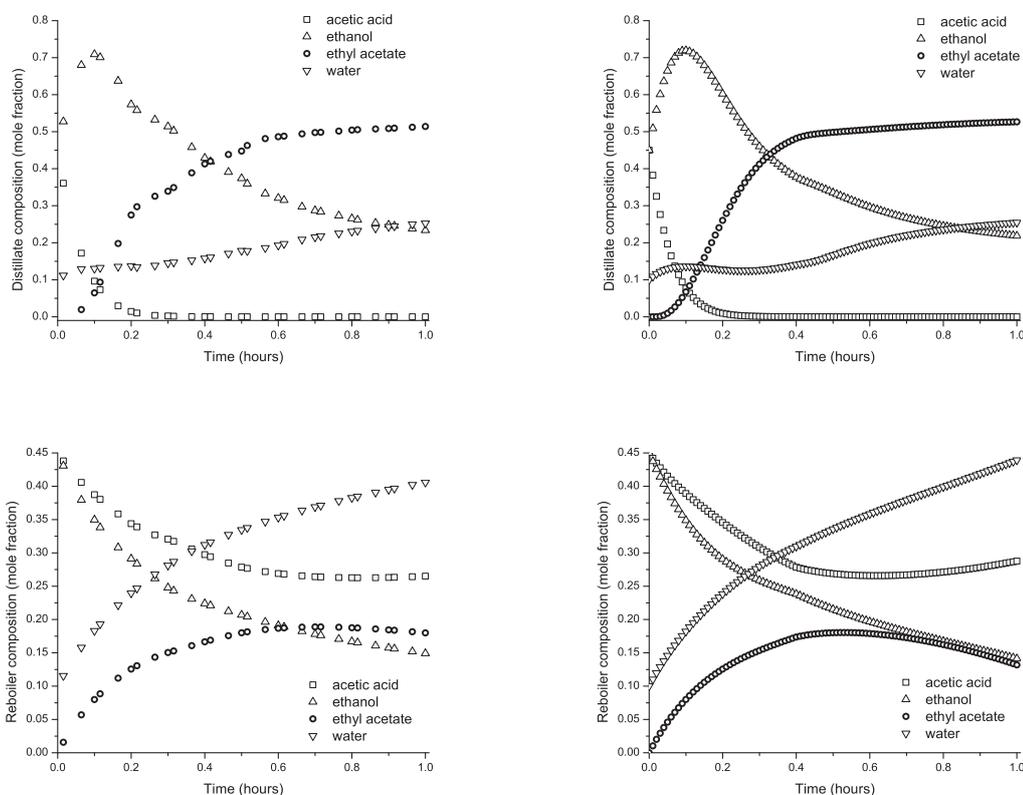
Vapor (kmol/h)	Q_{REB_total} (MJ/h)	X_{EtOH} (conversion in %)	x_{AcOEt}^D (conversion in %)
<i>(a) EOA approach when 10 finite elements and 3 collocation points are used</i>			
6		Infeasible	
7	274.68	59.08	0.506
8	313.48	59.16	0.510
9	352.24	59.40	0.513
<i>(b) CVP approach</i>			
6	233.78	57.83	0.518
7	271.90	57.65	0.523
8	310.21	58.30	0.525
9	348.44	59.00	0.527



(a) EOA approach when 10 finite elements and 3 collocation points are used.

(b) CVP approach.

Fig. 12 – Maximum conversion optimal reflux ratio optimal profiles in a dividing wall batch reactive distillation column for the production of ethyl acetate for the EOA and CVP approach.



(a) EOA approach when 10 finite elements and 3 collocation points are used.

(b) CVP approach.

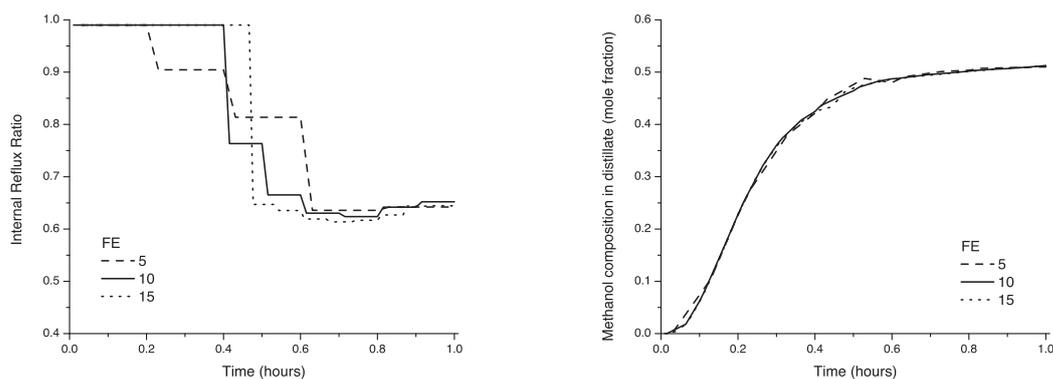
Fig. 13 – Maximum conversion distillate and reboiler composition profiles in a dividing wall batch reactive distillation column for the production ethyl acetate for the EOA and CVP approach.

computational time when 15 finite elements are used is 1400 s, while 5 finite elements take 400 s. By studying the final composition of ethyl acetate in the distillate in Fig. 14, it is clear that an increase on the number of finite elements will

not have a significant influence on ethyl acetate composition in the distillate. This is due to the different piecewise reflux ratio profiles for the three cases. The use of less than 10 finite elements reduces ethanol conversion while and

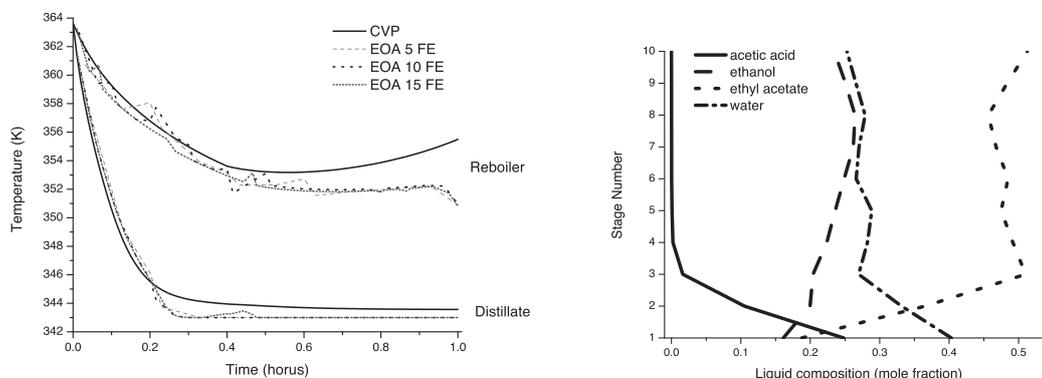
Table 10 – Maximum conversion results in a dividing wall batch reactive column when 5 and 10 finite elements are used in the EOA.

Vapor (kmol/h)	5 finite elements		15 finite elements	
	$Q_{REB_{total}}$ (kJ/h)	Profit (\$/year)	$Q_{REB_{total}}$ (kJ/h)	Profit (\$/year)
6	235.47	59.01	235.66	57.98
7	274.35	60.25	274.68	58.50
8	313.25	60.74	313.44	58.73
9	352.16	59.85	352.20	59.00



(a) Reflux ratio optimal profiles when 5 and 15 finite elements are used for the EOA. (b) Ethyl acetate composition in distillate profiles when 5 and 15 finite elements are used for the EOA.

Fig. 14 – Maximum profit reflux ratio and methanol optimal profiles in a dividing wall batch reactive column when 5 and 15 finite elements are used for the EOA.



(a) Maximum conversion reboiler and distillate temperature profiles in a dividing wall batch reactive column for the EOA and CVP approach.

(b) Final time of the operation.

Fig. 15 – Maximum conversion reboiler and distillate temperature profiles and liquid composition along the column in a dividing wall batch reactive distillation column for the production of ethyl acetate for the EOA approach.

increase in the number of finite elements reduces the discretization error, achieving smaller conversion values. Since the values are similar and also considering cpu-time, the number of finite elements used for a comparison was fixed to 10.

Changes in the column temperatures are also reflected on the composition profiles in Fig. 15. As it can be seen in the temperature profiles in Fig. 15(a), the temperature in the reboiler and distillate start at a high value and starts decreasing until both reach a constant value. The initial decrease in temperature is due to presence of ethyl acetate. However, as the separation of ethyl acetate continues, CVP reboiler temperature starts increasing (due to the evaporation/separation of ethyl acetate and the increasing amount of water formed by reaction), while the EOA temperatures present some sudden changes that are due to a poor temperature initial point. An increase on the number of finite elements can reduce these sudden changes, as it is shown in Fig. 15(a). At the end of the operation, since there is not enough water and acetic acid in the reboiler, the temperature on the distillate starts decreasing and remains constant when a minimum value of 343 K is achieved.

7. Conclusion

In this work, two models for the optimization of nonreactive and reactive conventional and nonconventional batch distillation columns have been presented. The optimization problem is solved using two different approaches: equation oriented approach based on orthogonal collocation over finite elements implemented in GAMS (24.2.2), and control vector parametrization implemented in gPROMS (3.7.1). The following conclusions are drawn based only on the nonreactive and reactive cases studied in this paper. For the nonreactive case, a quaternary mixture (methanol, ethanol, n-propanol and n-butanol) is separated in order to obtain methanol with a final composition of at least 0.9 mol fraction in the distillate, while a profit function is optimized for a fixed time of 1 h. The results for this nonreactive case show that the separation can be performed using a BDC and a nonconventional DWBDC with no significant differences. The addition of a dividing wall in a BDC shows no benefits in terms of energy savings. When the two approaches are compared, we observe that CVP and EOA have similar optimal profiles for the control variable. A comparison between the CVP and EOA optimization cpu-time required to solve the optimization problem shows no

significant differences for the solution of these nonreactive batch columns. For the reactive case, the production of ethyl acetate via esterification of acetic acid with ethanol is studied. A maximum conversion problem is solved under fixed product purity (ethyl acetate concentration of at least 0.50 in mole fraction in the distillate) and fixed batch time of 1 h. The results show that the production and purification of ethyl acetate can be carried out using a conventional BRDC and a nonconventional DWBRDC with no significant differences: the addition of a dividing wall in a BRDC shows no benefits in terms of energy savings and optimal conversion values. The optimization problem is solved by using the CVP and EOA approaches with a difference on the results of around 1% in terms of conversion and reboiler energy consumption. A comparison between the CVP and EOA computational time required to solve the conversion problem shows that CVP approach reduces the CPU solution time significantly for all the batch configurations, while EOA requires longer cpu-time. This solution time is influenced by the NLP solver used for each approach: EOA solver IPOPT simultaneously optimizes the objective function while enforcing the constraints of the model, while CVP solver SQP optimizes the problem in the reduced space of the control variables. In order to reduce EOA computational times, better initial points must be given.

Acknowledgements

The authors wish to acknowledge financial support from CONACyT for the development of this project, and Universidad de Guanajuato and Carnegie Mellon University for all the support.

References

- Asprion, N., Kaibel, G., 2010. *Dividing wall columns: fundamentals and recent advances*. *Chem. Eng. Process.* 49, 139–146.
- Biegler, L.T., 1984. *Solution of dynamic optimization problems by successive quadratic programming and orthogonal collocation*. *Comput. Chem. Eng.* 8, 243–248.
- Cuthrell, J.E., Biegler, L.T., 1987. *On the optimization of differential-algebraic process systems*. *AIChE J.* 33, 257.
- Dejanović, I., Matijašević, L., Olujić, Ž., 2010. *Dividing wall column – a breakthrough towards sustainable distilling*. *Chem. Eng. Process.* 49, 559–580.
- Delgado-Delgado, R., Hernández, S., Barroso-Muñoz, F.O., Segovia-Hernández, J.G., Castro-Montoya, A.J., 2012. *From simulations studies to experimental tests in a reactive dividing wall distillation column*. *Chem. Eng. Res. Des.* 90, 855–862.
- Diggelen, R.C., van Kiss, A.A., Heemink, A.W., 2010. *Comparison of control strategies for dividing-wall columns*. *Ind. Eng. Chem. Res.* 49, 288–307.
- Górak, A., Sørensen, E., 2014. *Distillation: Fundamentals and Principles*. Elsevier.
- Hernández, S., Jimenez, A., 1999a. *Design of energy-efficient Petlyuk systems*. *Comput. Chem. Eng.* 23, 1005–1010.
- Hernández, S., Jimenez, A., 1999b. *Design of optimal thermally-coupled distillation systems using a dynamic model*. *Comput. Chem. Eng.* 23, 1005–1010.
- Hernández, S., Segovia-Hernández, J.G., Rico-Ramírez, V., 2009. *Reactive dividing wall distillation columns: simulation and implementation in a pilot plant*. *Chem. Eng. Process.* 48, 250–258.
- Isopescu, R., Woinaroschy, A., Draghiciu, L., 2008. *Energy reduction in a divided wall distillation*. *Rev. Chim.* 59, 812–815.
- Kiss, A.A., Bildea, C.S., 2011. *A control perspective on process intensification in dividing-wall columns*. *Chem. Eng. Process.* 50, 281–292.
- Kiss, A.A., Bildea, C.S., 2011. *A control perspective on process intensification in dividing-wall columns*. *Chem. Eng. Process.* 50, 281–292.
- Kiss, A.A., Rewagad, R.R., 2011. *Energy efficient control of a BTX dividing-wall column*. *Comput. Chem. Eng.* 35, 2896–2904.
- Kiss, A.A., Pragt, H., van Strien, C., 2009. *Reactive dividing-wall columns – how to get more with less resources?* *Chem. Eng. Commun.* 196, 1366–1374.
- Lopes, M.M., Song, T.W., 2010. *Batch distillation: better at constant or variable reflux*. *Chem. Eng. Process.* 49, 1298–1304.
- Low, K.H., Sørensen, E., 2003. *Simultaneous optimal design and operation of multi-vessel batch distillation*. *AIChE J.* 49, 2564–2576.
- Mueller, I., Kenig, E.Y., 2007. *Reactive distillation in a dividing wall column-rate-based modeling and simulation*. *Ind. Eng. Chem. Res.* 46, 3709–3719.
- Mujtaba, I.M., 2004. *Batch Distillation Design and Operation. Series in Chemical Engineering, vol. 3*.
- Petlyuk, F.B., Platonov, V.M., Slavinskii, D.M., 1965. *Thermodynamically optimal method for separating multi-component mixtures*. *Int. Chem. Eng.* 55, 5–561.
- Rangaiyah, G.P., Ooi, E.L., Premkumar, R., 2009. *A simplified procedure for quick design of dividing-wall columns for industrial applications*. *Chem. Prod. Process Model.* 4, Article 7.
- Rong, B.G., Turunen, I., 2006. *A new method for synthesis of thermodynamically equivalent structures for Petlyuk arrangements*. *Chem. Eng. Res. Des.* 84, 1095–1116.
- Segovia-Hernández, J.G., Hernández-Vargas, E.A., Marquez-Muñoz, J.A., 2007. *Control properties of thermally coupled distillation sequences for different operating conditions*. *Comput. Chem. Eng.* 31, 867–874.
- Vassiliadis, V.S., Sargent, R.W.H., Pantelides, C.C., 1994a. *Solution of a class of multistage dynamic optimization problems. Part I: Algorithmic framework*. *Ind. Eng. Chem. Res.* 33, 2115–2123.
- Vassiliadis, V.S., Sargent, R.W.H., Pantelides, C.C., 1994b. *Solution of a class of multistage dynamic optimization problems. Part II: Problems with path constraints*. *Ind. Eng. Chem. Res.* 33, 2123–2133.
- Yildirim, O., Kiss, A.A., Kenig, E.Y., 2011. *Dividing wall columns in chemical process industry: a review on current activities*. *Sep. Purif. Technol.* 80, 403–417.