Numerical methods and initial estimates for the simulation of steady-state reactive distillation columns with an algorithm based on tearing equations methodology

V. Steffen[a,*], E.A. Silva[b]

[a] Academic Departament of Chemical Engineering, Federal University of Technology – Parana, Linha Santa Bárbara, w/o No., 85601-971 Francisco Beltrão, Paraná, Brazil
[b] Center for Engineering and Exact Sciences, State University of Paraná, Rua da Faculdade, 645, 85903-000 Toledo, Paraná, Brazil

A R T I C L E   I N F O

A B S T R A C T

The solution of phenomenological models for steady-state reactive distillation columns involves the solution of a set of nonlinear algebraic equations. In this work was employed a method for generating initial estimates and an algorithm that uses the "tearing equations" methodology on the steady-state reactive distillation mathematical model, i.e., the large and sparse nonlinear system of equations were tired into several subsets of equations, wherein each subset of equations is solved in sequential steps to obtain model unknowns (temperatures, flow rates, extents of reaction, mole fractions, etc.). Among these steps, the most complex step is, the only nonlinear subset of equations, that is solved for obtaining the extents of reaction by using a method for the solution of a set of nonlinear algebraic equations. For this step were tested the Newton-Raphson and homotopy continuation methods. This methodology was used in two cases of study, one case with a less complex solution, the production of ethylene glycol, and another case with a little more difficult solution (metathesis of 2-pentene). In the simpler case of study, the methodology presented convergence using both Newton-Raphson and homotopy continuation methods. In the metathesis of 2-pentene case, convergence was obtained only when the homotopy continuation method was used.

1. Introduction

Reactive distillation is a process in which the chemical reaction and distillation take place continuously in a single unit operation [1]. This is a process with great potential of application in substitution to conventional processes of chemical reaction in liquid phase, mainly in the systems that exhibit one or more of the following characteristics: equilibrium limited reactions, exothermic reactions, bad use of the raw material due to low selectivity or excessive complexity of the flowchart production process [2,3].

The most important industrial applications of reactive distillation are in the field of etherification and esterification processes, an example is the synthesis of methyl acetate. This process combines reactive and non-reactive sections in a single reactive distillation column and thereby replaces a complex production process consisting of eleven steps. With this technology the investment and the energy costs were reduced by a factor of five, and with a conversion of approximately 100%. Another processes that have great attractiveness to reactive distillation began in the 80's by the use of this technology for the

obtainment of MTBE (Methyl t-butyl ether), TAME (t-Amyl methyl ether), and ETBE (Ethyl t-butyl ether), which are produced in large quantities as fuel additives because of their excellent antidetonating properties. It was only at this time that the reactive distillation process received the status of a multifunctional, promising and independent unit operation [4].

The mathematical models of steady-state chemical processes are usually composed by non-linear algebraic equations, which must be solved iteratively. The Newton-Raphson method and like ones are the most popular to solve these kind of problems, but these methods can fail when no good initial estimates are available or there are several solutions. These problems can be overcome by applying the homotopy continuation method [5].

There are several papers in the literature that have investigated the simulation [6,7] and optimization [8,9] of reactive distillation processes, however, many of these studies do not present a consistent methodology to generate the initial estimates for the solution algorithm. Some studies use homotopy continuation as a method that do not need good initial estimates for reactive distillation [10,11]. In the work

---

Nomenclature		
		(kJ h^{-1})
		r_B reboil ratio
a	activity	r_D reflux ratio
B	bottoms molar flow rate (kmol h^{-1})	R_j total rate of generation on stage j (kmol h^{-1})
D	Distillate molar flow rate (kmol h^{-1})	T temperature (K)
Da	Damköler number	tol tolerance
F_j	feed molar flow rate on stage j (kmol h^{-1})	V_j vapor molar flow rate leaving from stage j (kmol h^{-1})
k	rate contante of reaction (h^{-1})	V_{hj} liquid molar holdup in stage j (kmol)
K	thermodynamic reaction equilibrium constant	x_{ij} liquid mole fraction of component i in stage j
L_j	liquid molar flow rate leaving from stage j (kmol h^{-1})	y_{ij} vapor mole fraction of component i in stage j
P	pressure (atm)	z_{ij} feed mole fraction of component i in stage j
Q_C	heat flow transferred from condenser to the surroundings (kJ h^{-1})	γ_{ij} activity coefficient of component i in stage j
Q_R	heat flow transferred from surroundings to the reboiler	ξ_{ij} extent of reaction i on stage j.

of Steffen and da Silva [12] was proposed an algorithm that splits the model equations in several smaller subsets of equations by tearing equations methodology, obtaining some linear algebraic equations systems and just one set of nonlinear equations (equations that model the chemical reaction). This makes the algorithm simpler, but becomes even more important the availability of good initial estimates due to the increase in the difficulty of achieving convergence. Therefore, it is necessary to use a methodology to generate good initial estimates and also robust numerical methods for solving chemical reaction rates equations (the step responsible by most convergence problems for the task in question).

In this way, the idea of this work is to use the same methodology of initial estimates generation and solution algorithm, that uses tearing equations methodology, proposed by Steffen and Silva [32] (Appendix A) and a robust method for solving the set of nonlinear equations used to obtain que extent of reaction values. In an attempt to solve this set of nonlinear equation the Newton-Raphson and homotopy continuation methods were used.

2. Modeling

In the work of Steffen and da Silva [12] was proposed a method to generate initial estimates (Appendix C) and the system of equations were tered in subsets of equations. The susbsets of equations are solved in sequential iterative steps (Appendix B). The only step in which the equations are nonlinear, is that one where is calculated the extent of chemical reaction. For the solution of this step the mentioned authors used the method of Broyden [13].

The model considered for solution, is obtained from steady-state mass and energy balances, phase equilibrium and reaction rate equation (Appendix D). In an attempt to solve the equations that model the extent of chemical reaction, in this work were used the Newton-Raphson and homotopy continuation, considering for this last the Newton-homotopy type.

The algorithm consider that properties of all input streams are specified (temperature, pressure, mole fractions and quality) and the column has no pressure drop with pressure equal to input streams. So, considering n stages and m components, there is the following number of unknowns: $n \times m$ for liquid mole fractions (m for each stage), $n \times m$ for vapor mole fractions (m for each stage), n for stages temperatures, $n-1$ for liquid flow rates outputing each stage, $n-1$ for vapor flow rates outputing each stage, 2 for bottoms and distillate flow rates, n_r for extent of reaction and 2 for heat duties at reboiler and condenser. That gives a total of $(2m + 3)n + n_r + 2$ unknowns.

The number of available equations are: $n \times m$ for components mass balances (m for each stage), $n \times m$ for phase equilibria (m for each stage), n energy balances, n_r for reactions, n for the sum of liquid mole fractions and n for the sum of vapor mole fractions. So it give us $(2m + 3)n + n_r$, i.e., the degrees of freedom is equal to 2, and for this

algorithm was chosen condenser and reboiler reflux ratios to be specified. If would necessary to specify another conditions, the algorithm would need some modifications.

The model equations of steady-state reactive distillation columns is a system of strongly non-linear equations, normally solved by Newton-Raphson and like ones methods. The solution of these equations is very difficult and the convergence depends strongly on the goodness of initial guesses. The greaters non-linearities are in the phase equilibrium, energy balances (because of enthalpies) and chemical reaction equations (mainly if it is considered chemical equilibrium). In the algorithm here used, all equations are put in a linear form but chemical reaction, using tearing equations methodology, what makes the convergence more difficult to be reached, the convergence process is very slow not quadratic as when Newton-Raphson and like ones methods are used. The advantage of this algorithm is that it is simpler and very easy to implement.

Due to the importance of initial guesses goodness, was used the an approach based on simpler cases. For temperatures is used a linear profile considering the bubble points of components, a maximum value with quadratic decay for extent of reaction and for flow rates is considered a non-heat effects (similar to McCabe-Thiele algorithm, but for multicomponent). After the generation of these values, the iterative calculation process can start. The algorithm is described in details in Appendices A–D.

The end of the iterative process occurs when the condition in the Eq. (1) is satisfied

$$\sum_j \left[\frac{T_j^{(k)} - T_j^{(k-1)}}{T_j^{(k)}} \right]^2 + \sum_j \left[\frac{V_j^{(k)} - V_j^{(k-1)}}{V_j^{(k)}} \right]^2 + \sum_i \sum_j \left[\frac{\xi_{ij}^{(k)} - \xi_{ij}^{(k-1)}}{\xi_{ij}^{(k)}} \right]^2 \leqslant tol \tag{1}$$

Table 1
Operational conditions for the reactive distillation column of Example 1.

Variables	Specifications	
Pressure	All stages	15 atm
Reflux ratio	Condenser (r_D)	1000
	Reboiler (r_B)	65.5
Condenser type	Partial	Stage 1
Reboiler type	Partial	Stage 7
Feed	Saturated liquid	Stage 3
	Flow rate	50 kmol/h
	Temperature	400.4 K
	Pressure	15 atm
	Mole Fractions	EO (0.4878)
		W (0.5122)
		EG (0.0000)
		DEG (0.0000)
Holdup*	Reactive stage ($j = 2$)	111.2 kmol

* Calculated for $Da = 7.9$.