

Thermal flux use for optimal control of a semi-continuous batch reactive rectifier

Cristian CIORNEI and Vasile LAVRIC

University Politehnica of Bucharest

RO-011061, 1-7, Polizu Street, Building S, Bucharest, Romania

Phone: +40-21-4023808, email: c_ciornei@chim.upb.ro

Reactive distillation (RD) has become an important way to increase valuable product formation overcoming both chemical equilibrium and non-ideal thermodynamic behaviour (physical azeotropes) limitations. Integration of the two processes generates important advantages, among which better utilization of the reaction heat and a significant increase in the chemical driving force are the most important. The present paper addresses the issue of computing an optimal control policy of a semi-continuous batch reactive rectifier (SCBR) using the thermal flux as control variable.

Modelling SCBRD is not a trivial task as the mathematical model is of DAE type. The equations correspond to the MESH model: heat and component mass balance as differential equations and total mass balance, thermodynamic equilibrium and mole fractions summation as algebraic equations. The chemical process is lumped in the mass balance equations and is computed using the reaction kinetics. The heterogeneous catalytic chemical process is confined to the rectifying section trays, the reboiler being free of catalyst. VLE is assumed on each reactive tray, no mass transfer resistance being accounted for. The phases' nonideality is described through thermodynamic models; for the test system under study (methyl acetate) Nothnagel and UNIQUAC are suitable.

The mathematical model is solved using genetic algorithms (GA). The process time is divided into a suitable number of intervals characterized by constant heat fluxes, seen as genes, the step-wise profile defining a chromosome. The restrictions are coped with during the birth of each individual, permitted only inside the feasible domain. One-point crossover method is used for breeding of individuals with appropriate frequencies of selection. Then mutation is applied to randomly selected ones. A composite objective function was used, maximizing the ester and minimizing the water molar fractions in the distillate, searching for an optimal thermal flux profile. The starting point for the simulation was the steady state initial solution, considering the column filled with the lightest reactant. The results showed a significant improvement in both the quantity of the valuable product obtained and the energetic yield.

1. Introduction

Batch reactive distillation (BRD) is more versatile and suited for production of small amounts of high valuable substances than continuous processes. Features like ease of handling and flexibility offer a higher degree of freedom to adapt to customer changing demands. Aside capital and energy savings RD can produce further benefits switching to semi-continuous (SC) operating policies. Industries like pharmaceuticals, fine and

specialty chemicals use BRD to overcome thermodynamic equilibrium removing a product, to prevent further sequential reactions or to increase the overall process rate in the case of irreversible reactions. The main drawback is that SC columns should have a tight control capability, due to the removal of some degrees of freedom; this cannot be guaranteed based only on regulatory/tracking control of certain variables. The control actions have to be continuously adjusted according to the state of the process and the desired objectives, trading off different criteria, such as costs and energy consumption.

Despite numerous studies aimed to understand the thermodynamics and kinetics of RD, few papers approached the control and optimization issues and even fewer addressed the DC/SC processes. Venimadhavan et al. (1999) used reflux ratio as command variable for equimolar reactions with the aim of increasing not only the conversion but also the purity of butyl acetate at the end of the run. Nougues et al. (2002) used the feeding profile as command variable searching, with GA, for the minimum operating time under a supplemental constraint (the vessel temperature could not exceed a certain threshold). Balasubramhanya and Doyle (2000) used a very simple model based on travelling wave phenomena to design a model predictive control methodology for which the objective was to obtain the final product as pure as possible using the temperature of the feeding tray as control variable.

The presence of azeotropes could make a BRD infeasible in certain conditions. Incorrect quantification of phase thermodynamics or simplifications like balancing the energy through algebraic equations may produce inaccurate results. Giessler et al. (2001) investigated optimization aspects of BRD and identified different optimal operating policies using diverse objective functions, emphasizing the importance of appropriate description of phase non-ideal behaviour. Furlonge et al. (1999) showed that, although fed-batch RD typically consumes more energy than the continuous process, this operating technique avoids azeotropes formation easing the separation while taking advantage of the benefits of RD. Due to the ever increasing use of RD in chemical production, identification of a flexible operating policy is of primary importance. Still, this is not a trivial task due to the mathematical difficulties of finding the time-optimal policy. Rigorous models that offer the process dynamics and correct description of liquid vapour thermodynamics are essential for obtaining appropriate results.

In the present paper, we seek for an optimal operating strategy (in terms of a piece-wise step profile for the reboiler heat flux) for a SCBRR which maximizes the ester and minimizes the water molar fractions in the distillate. As a result of the ever changing composition along the reactive column and in the reboiler, the SCBRR cannot be trapped in an azeotrope state. Due to the continuous feeding of the heavier reactant, even if an azeotrope appears in the reboiler, it will be drain out towards the condenser.

2. Semi-Batch Reactive Distillation Rigorous Model

The mathematical model of the SCBRR is of MESH type, under the usual constraints written for the designated envelopes of the column. VLE without mass transfer limitations and ideal trays, in terms of liquid and vapour flows, are assumed. The tray's liquid phase is perfectly mixed, whereas the tray's gas phase hold-up is neglected.

The overall molar balance for a tray k inside the column is given by equation (1), which can have an arbitrary feed F_k .

$$\frac{dM_k}{dt} = F_k + V_{k+1} - V_k + L_{k-1} - L_k + \frac{M_k}{\rho_M} \left[\sum_{i=1}^R (\Delta V_i \cdot r_i^k) \right] \quad (1)$$

The total mole balance equations are completed with component j mole balance equations written for each tray k .

$$\begin{aligned} \frac{dx_j^k}{dt} = & \frac{F_k}{M_k} (x_j^{F_k} - x_j^k) + \frac{L_{k-1}}{M_k} (x_j^{k-1} - x_j^k) - \frac{V_k}{M_k} (y_j^k - x_j^k) + \frac{V_{k+1}}{M_k} (y_j^{k+1} - x_j^k) + \\ & + \frac{\sum_{i=1}^R [(v_{i,j} - x_j^k \cdot \Delta V_i) \cdot r_i^k]}{\rho_M^k} \end{aligned} \quad (2)$$

The overall heat balance equation considers two external heat streams: the heat added to the reboiler, \dot{Q}_W , and the heat removed from the condenser, \dot{Q}_C . The heat of reaction is implicitly taken into consideration, due to the way the enthalpies are computed. The heat balance equation for a tray k reads:

$$\frac{dT_k}{dt} = \left(M_k \frac{dH_L^k}{dT} \right)^{-1} \left[F_k (H_L^{F_k} - H_L^k) + V_{k+1} (H_V^{k+1} - H_L^k) - V_k (H_V^k - H_L^k) - L_{k-1} (H_L^{k-1} - H_L^k) \right] \quad (4)$$

The mathematical model of the SCBRR is completed with the equations representing the main constraints due to the thermodynamics (5) and mole-fractions summation (6).

$$\mu^L(T, P, x_{j=1..S}^{k=0..N+1}) = \mu^V(T, P, y_{j=1..S}^{k=0..N+1}) \quad (5)$$

$$\sum_{j=1}^S y_j^{k=0..N+1} = 1, \quad \sum_{j=1}^S x_j^{k=0..N+1} = 1 \quad (6)$$

The objective function that maximizes the ester and minimizes the water molar fractions in the distillate is:

$$F_{obj} = x_{Water} + e^{-x_{Methyl\ Acetate}} \quad (7)$$

3. Solving strategy

The resulted DAE system is solved using a strategy based upon two numerical methods coded in C language and implemented in MATLAB: the stiff integration routine for the differential equations (mass and heat balances) and Newton-Raphson non-linear solver routines for the algebraic equations (the summation equations and liquid vapour equilibrium). The solving strategy has an iterative nature: for a given vapour flow rate profile, the differential system is integrated for temperature and mole fractions (Ciornei et al., 2006). The sums of the mole fractions and VLE equations are checked. In case of violation, a new vapour flow rate profile is used to integrate again the differential equations. Different liquid flow rate profiles are used until the constrains are fulfilled. This solution is the new starting point for continuing the integration one time step ahead.

The starting values for the dynamic simulation correspond to a column (trays, total condenser and reboiler) filled with the lightest reactant. The initial temperature on each tray corresponds to the boiling temperature of the liquid.

The problem of finding the optimal control of a SCBRR using a specific piece-wise step heat flux for the still pot is analyzed in the present paper. The main objective is to obtain at the end of the operating time the largest distillate quantity containing methyl acetate (the valuable product) as pure as possible. This goal was coded into the fitness function (7) which was minimized with the GA implemented in MATLAB.

4. Case Study

The SCBRR under study is used to produce methyl acetate by esterification of methanol with acetic acid. The chemical transformation has a slow reaction rate and the conversion is thermodynamically limited. The column has a still pot, four trays, and a total condenser. All four trays are filled with acidic ion exchange resin (Lewatit K2621) used as catalyst. The condenser and column trays hold-ups were assumed constant during the whole operation, and such was the reflux ratio. Before starting the RD process, the still pot was filled with the lightest reactant (methanol) and column was brought at thermodynamic equilibrium. During the RD, the acetic acid is continuously fed onto the first tray, its actual flow being the ratio between the stoichiometric quantity needed to react with the initial loaded methanol and the operating time. Methyl acetate (the lightest component) is removed from the top of the column and collected as liquid distillate. The reaction kinetics was modelled through a LHHW expression (Noeres, 2004).

5. Results and Discussions

In order to compare the optimal control policy results with, a reference case was firstly investigated, using a constant heat flux for the still pot, in the amount of 90 kW. The main results are condensed in Table 1, while some typical profiles are depicted in Figures 1 to 3. The main observation, analysing the figures from Table 1 corresponding to the base case, is the high concentration of the methanol in the distillate. This is the result of the way the SCBRR starts working, filled with boiling methanol. As can be seen from Figures 2 and 3, the methanol instantaneous molar fraction drops continuously, due to the chemical process, but the molar flow of acetic acid is too small, in the beginning, to consume the methanol significantly. The molar fraction of water in distillate is quite large, an improvement of the process being its diminution.

Table 1. Performance comparison of the investigated cases

Components	Reference Case		Optimal Case		Energy yield, kmole / kW · 10 ²	
	Mass, kmole	Molar fractions	Mass, kmole	Molar fractions	Reference Case	Optimal Case
Methanol	0.9741	0.6407	0.9582	0.6965	1.082	1.158
Acetic acid	0.0988	0.0650	0.0312	0.0227	0.110	0.038
Methyl acetate	0.2901	0.1908	0.2959	0.2151	0.322	0.358
Water	0.1575	0.1036	0.0905	0.0658	0.175	0.109

The results obtained for the optimally controlled SCBRR using as command variable the still pot duty, are presented in Table 1 and in the aforementioned figures. The piece-wise step profile for the optimal heat duty (Figure 1) shows an oscillatory evolution.

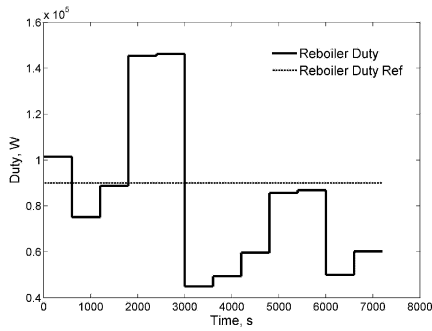


Figure 1. Still pot duty profile

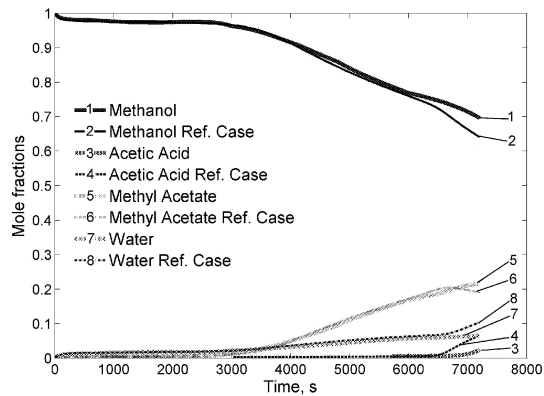


Figure 2. Cumulative distillate composition

has a lower mean value than the reference case. This results in an increase of the energetic yield, from 3.22 to 3.58 mole/kW.

Examining the profiles presented in Figures 2 and 3, we observed that the behaviour of

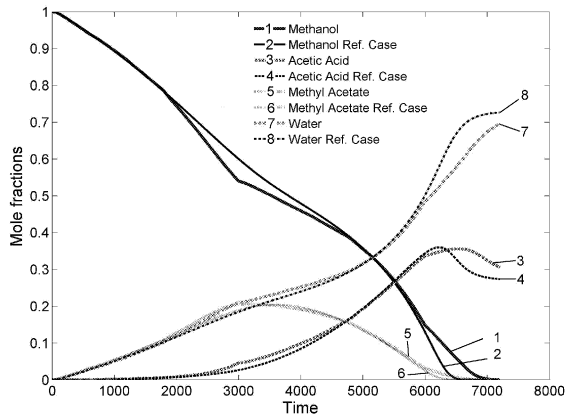


Figure 3. Still pot composition profile

At the beginning of operation, the duty is decreased since the distillate contains small concentrations of methyl acetate; this diminishes the contribution of this period in the output of the whole process. As the second reactant is added onto the first reactive tray and accumulates in the column, the valuable product concentration increases and a higher heat flow rate in the still pot favours methyl acetate rejection at the top of the column (see the profiles from Figure 3). Removing a higher amount of liquid as distillate causes

an increase of the lightest reactant in the reaction zone, as it is pushed up from the still pot. A lower heat flow rate is necessary to decrease the vapour flow rates in the column in order to retain the reactants in the reactive zone (profiles not presented, due to the lack of space). After a while, the still pot duty is increased again to remove the valuable product which accumulated in the reboiler, creating an oscillatory profile. Analysing the optimal still pot duty profile (Figure 1), we noticed that during the first half of the operating time, its mean value is higher than that of the reference case, while in the second half, the optimal control

has a lower mean value than the reference case. This results in an increase of the energetic yield, from 3.22 to 3.58 mole/kW. Examining the profiles presented in Figures 2 and 3, we observed that the behaviour of the SCBRR is dramatically changed by the optimal duty policy with respect to the reference case at two distinct moments: when the ester concentration reaches a maximum in the reboiler, when the duty is sharply decreased to favour its preferential removal in the vapour phase, and towards the end, when water and the other heav-

ier components are prevented from being withdrawn preferentially. Compared with the reference case, water is not accumulating faster at the end of the process, nor does the acetic acid in the distillate (Figure 2). On the other hand, the methanol is retained a little bit longer in the reboiler, thus diminishing the quantity of the water formed towards the end, preventing, this way, its increase in the vapour phase (Figure 3).

The constant reflux ratio policy used in the reference case has as consequence the removal of a distillate with a low concentration in methyl acetate at the beginning of operation. At the end, the main cut composition profile shows a high concentration of methanol; approximately 70% of that can be lowered if a suitable reflux ratio policy is used in conjunction with the heating policy. Cumulative distillate composition profile shows a rapid increase at the end of main cut in water and acetic acid for the reference case. Employing the optimal control policy for the still pot duty will produce a more concentrated distillate in methyl acetate, but with less water (Table 1) and heavier reactant (acetic acid).

6. Conclusions

In the present paper we present an optimal control strategy for a SCBRR. Still pot duty was used as control variable to generate a richer distillate cut in methyl acetate. The results obtained with the optimal control duty profile proved that a more concentrated cut with less water is possible to be obtained by properly adjusting the heat flow rate in the still pot. Also, the energy yield, seen as the component mass in the final cut with respect to the consumed heat, shows more that 10% reduction (Table 1). Considering the oscillatory profile of the still pot duty and the rapid decrease of methanol concentration profile in the still pot (Figure 3), an optimal reflux ratio policy should be investigated in future studies. Through this we expect a higher conversion of the light reactant and a better quality of the main cut in the methyl acetate.

Also, an optimal feeding policy is to be investigated since the reactants' concentration in the reactive zone is decisive to the process performance. The feed flow rate needs to be higher at the beginning in order to balance the methanol and lower at the end as the second reactant is depleted.

6. References

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