

Dynamics of Reactive Distillation Processes with Potential Liquid Phase Splitting

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Abstract

A dynamic reactive distillation (RD) column model is developed for highly nonideal systems with potential phase splitting. Dynamic simulations and non-linear dynamic analysis are performed for recovery of acetic acid from waste waters by esterification with n-butanol, which is an interesting alternative to nonreactive separation processes. Two alternative RD column designs were tested with respect to their open loop transient responses to process disturbances. One parameter continuation with eigenvalue calculations reveals existence of multiple steady states with stable and unstable branches. These steady states were found to have totally different phase splitting behavior of the original liquid phase inside the column. Conclusions are drawn for process operation.

Keywords phase splitting, continuation, dynamic simulation, reactive distillation, butyl acetate, esterification, acetic acid recovery

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1. Introduction

Reactive distillation (RD) processes with a single liquid phase can be easily simulated in steady state as well as in dynamic mode. The models and the numerical methods are well understood. An extension to the steady state simulation of RD processes with a potential phase splitting of the liquid phase is also fairly standard [1, 2]. However, no standard simulation tools are available for the dynamic simulation of these processes. Typical process examples are C3 and higher esters synthesis, cyclohexanol production, recovery of acetic acid and lactic acid via RD route etc.

This contribution proposes a dynamic reactive distillation column model taking into account the potential liquid phase splitting, very useful in practical studies on the intricate nonlinear process dynamic behavior (including steady state multiplicities, bistability and self sustained nonlinear oscillations). The algorithm is successfully tested on a benchmark example for acetic acid (AcH) recovery [3].

2. Dynamic RD model with potential liquid phase splitting

The mathematical model of a RD column with phase splitting calculations has been written in two parts. The first part contains the classical MESH equations of a reactive distillation column model [4]. However, slight modifications are required in the main column model. Extra component and total material

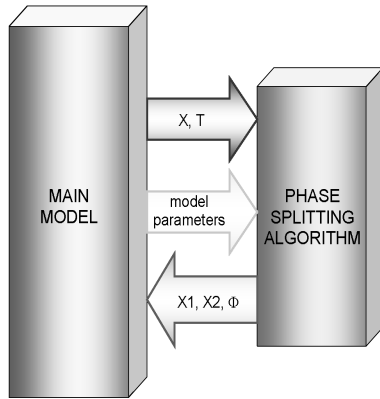


Figure 1: Components of a dynamic RD model with potential liquid phase splitting.

balances are required to describe the “connection” between original liquid phase and the two potential liquid phases. These balances are general and even valid when no splitting happens to occur, because the first liquid phase will have the molar flow and the compositions equal to those of the original liquid phase and the second liquid phase can have then absolute molar flow of zero. The liquid-liquid equilibrium equation $x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II}$ with the vapor-liquid equilibrium equation $y_i P = x_i^I \gamma_i^I P_i^{sat}$ or $y_i P = x_i^{II} \gamma_i^{II} P_i^{sat}$ will determine the compositions of vapor and both liquid phases. The overall reaction rate for the global liquid phase in case of heterogeneously catalyzed reactive trays is easier to calculate as both potential liquid phases possess iso-activities, i.e. $r_i^{overall} = Mcat_{st}^{overall} f(a_i^I) = Mcat_{st}^I f(a_i^I) + Mcat_{st}^{II} f(a_i^{II})$. In case of

homogeneously catalyzed reactive trays, one may assume a uniform catalyst distribution among the potential liquid phases, i.e. $r_i^{overall} = \varphi r_i^I + (1 - \varphi) r_i^{II}$.

The second part is the phase splitting routine which precisely identifies the phase splitting existence on a considered tray. This routine is based on the *quick and reliable VLE flash* algorithm proposed by Bausa and Marquardt [5] and subsequently modified by Steyer et al. [6]. When phase splitting is reported to occur on a particular tray, this routine returns to the main model a state vector $\{x^I, x^{II}, \varphi\}$ for further calculations.

Figure 1 shows the phase splitting routine and its interaction with the main column model. The combined model equations were solved in the process simulator DIVA [7]. The external phase splitting routine was written in Fortran77 language. For the purpose of this work, we have developed only a stand alone reactive distillation column model, however, it can readily be coupled anywhere in a plant wide framework.

3. Process example – treatment of waste waters polluted with AcH

The treatment of waste waters polluted with AcH is a major concern for many petrochemical and fine chemical industries. Conventional distillation processes to complete this separation are highly uneconomic. On the other hand, RD not only significantly reduces the capital and the operating costs but also offers a clean operation. Here, AcH present in the waste water stream is converted to n-butyl acetate (BuAc) by esterification with n-butanol (BuOH) in a reactive

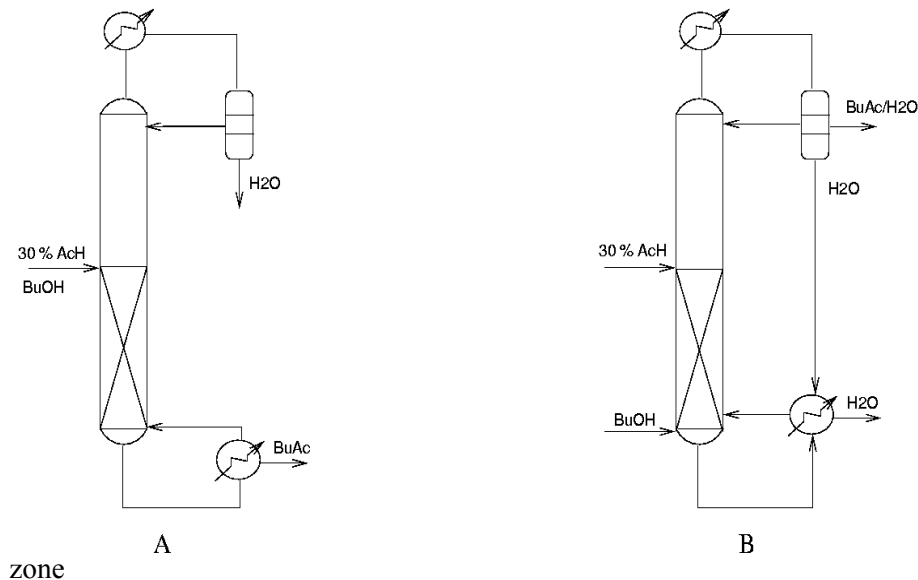


Figure 2: RD columns with potential liquid phase splitting.

of the column. BuAc, BuOH and water form a minimum boiling azeotrope near the column top, which upon condensation forms a water rich aqueous phase and a BuAc-BuOH rich organic phase. With a suitable column design, it is possible to obtain high purity end products water and BuAc.

Figure 2 shows two alternative RD column designs, configurations A and B, for the waste water treatment. It can be seen that, depending upon the reflux policy, water (BuAc) is obtained as distillate (bottoms) or as bottoms (distillate). The configurational details for both designs are presented in Table 1.

Table 1: Configurational details

		configuration A	configuration B
feed	BuOH feed flow rate (kmol/hr)	—	0.00062534
	AcH feed flow rate (kmol/hr)	0.00615	0.0055
	x_{AcH}	0.1017	0.1137
	x_{BuOH}	0.1057	—
	x_{H_2O}	0.7926	0.8863
bottoms	flow rate (kmol/hr)	0.000608	0.005421
	x_{BuAc}	> 0.9940	0.0
	x_{H_2O}	0.0	> 0.9960
distillate	flow rate (kmol/hr)	0.005542	0.0007
	x_{BuAc}	0.0020	0.8604
	x_{H_2O}	> 0.99	0.1106
configurational details	AcH conversion	98.5	96.91
	reboiler duty (kW)	0.1004	0.3497
	$M_{cat, st}$ (kg/tray)	0.004	0.5289
	Rf_{org}	—	0.9288
	Reactive trays location	from 22 to 26	from 16 to 29
	Number of stages	27	30
	Feed tray location	4	10 and 29
	Trays with phase splitting	from 4 to 19	from 10 to 13

4. Non linear dynamic analysis and dynamic simulations

Besides steady state design, the process sensitivity with regards to disturbances and the process stability are important for operability. For this purpose, dynamic responses to disturbances in the feed flow rate and disturbances in the feed composition are evaluated. Moreover, a one-parameter continuation with eigenvalue calculations is performed in order to determine regions of instability and multiple steady states.

Figure 3(a) shows the dynamic simulation results for configuration A when a 5% increase of feed flow rate is applied. The conversion of AcH reduces from

99% at the initial steady state to 40% at the new steady state. The three-phase region extends in the column as it can be seen from the ϕ profiles evolution.

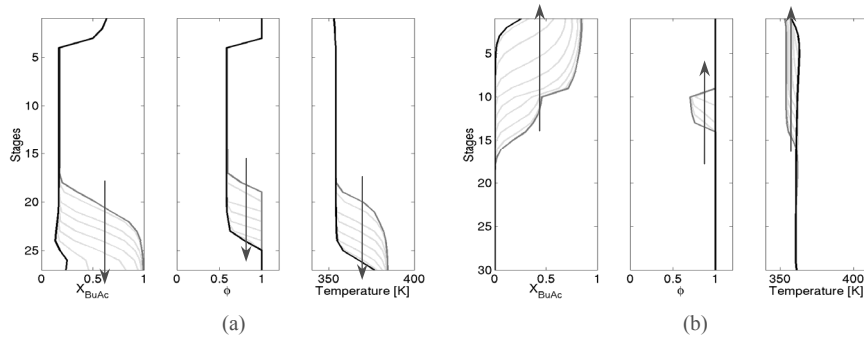


Figure 3: (a) Transient response of configuration A to a 5% increase in the feed flow rate; (b) Transient response of configuration B to a 5% decrease in both feed flow rates. Arrows indicate transition from initial steady state (gray line) to final steady state (dark line).

When a 5% decrease in the feed flow is applied to configuration B, here too the column profiles significantly change as it can be seen from figure 3(b). The conversion of AcH reduces to 64% at the new steady state and the three-phase region vanishes.

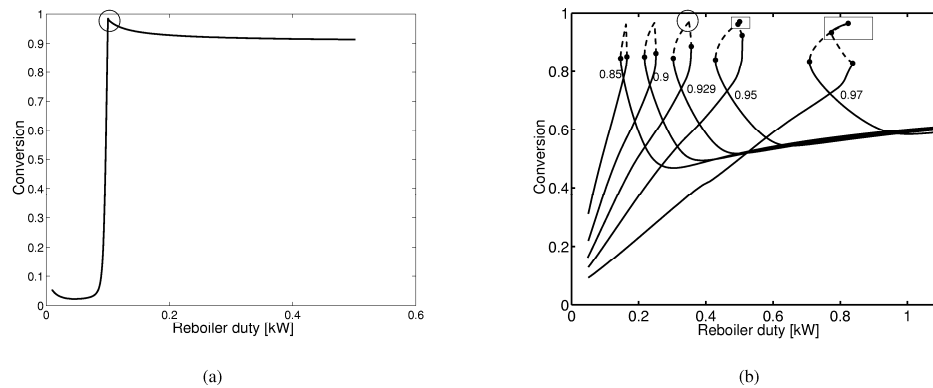


Figure 4: Continuation diagram for (a) configuration A and (b) configuration B.

Figure 4 shows one-parameter continuation diagrams for both process candidates as the reboiler duty is varied from its nominal values (represented by an open circle on these curves). In Figure 4 AcH conversion is plotted against the reboiler duty. Configuration A possesses a single stable steady state over the entire range of the reboiler duty. In contrast to this, configuration B shows multiple steady states in form of a hysteresis loop. In particular, the nominal

operating point lies within the multiplicity region. The nominal point is lying on a very small stable branch, which is hardly visible in figure 4(b). Similar stable branches can be seen, however, for continuation curves calculated at higher values Rf_{org} , shown by open rectangles. It is clear from figure 4 that the desired nominal operating points are located at the steep hill position. It is expected that a slight process disturbance will significantly deteriorate the process performance.

5. Conclusions

A dynamic reactive distillation column model with liquid phase splitting calculations is successfully applied for the recovery of acetic acid from waste waters. A one-parameter continuation with eigenvalue calculations shows the presence of multiple steady states with unstable branches in case of configuration B. However, dynamic simulation shows both configurations A and B are difficult to operate at their desired set point. Hence, suitable control strategy is required to nominally operate these processes.

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Nomenclature

a_i^I or a_i^{II}	activity of i^{th} component in liquid phase I or II
φ	phase fraction
$Mcat_{st}^{overall/I/II}$	mass of catalyst per stage – overall, in liquid phase I and II
$Rf_{org}^{overall/I/II}$	organic reflux ratio, i.e. (reflux)/(total organic inflow)
$r_i^{overall/I/II}$	reaction rate due to component i – overall, in phase I and II
P	pressure
P_i^{sat}	saturation pressure of i^{th} component in the vapor phase
x_i, y_i	mole fraction of i^{th} component in liquid/vapor phase
$\gamma_i^I, \gamma_i^{II}$	activity coefficient of i^{th} component in liquid phase I and II

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