

Nonlinear Behavior of Reactor-Separator and Reactor-Distillation Networks: Influence of the Energy Balance Formulation

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Abstract

In previous work the influence of different formulations of the energy balance equation on a single heated flash and on a simple reactor-flash (single tray) system was investigated. In the present work this study is extended to reactor-distillation systems with recycle, i.e. the separator is now a multi tray column. Focus is on the influence of the energy balance formulation on uniqueness, stability, and dynamics of the system.

Keywords: flash, reactor-separator system, recycle, nonlinear dynamics, distillation, chaos

1. Introduction

Modeling of evaporative separators with mass and energy balances, only, often leads to differential algebraic systems (DAE) with differential index 2. To overcome the problems which are associated with the numerical solution of index 2 DAEs either a formal index reduction can be applied or the model can

be reformulated by modifying the underlying assumptions. Typical modifications leading to index 1 problems are either the assumption of a quasistatic energy balance or the inclusion of some simple fluid dynamics.

In previous work [1] the dynamic behavior predicted by these different model formulations were analyzed and compared with each other. First, focus was on an isolated single stage flash process with given heat input. It was shown that the dynamic behavior of the different model formulations for a stand alone flash are rather close. In particular, in all cases a stable steady state was predicted. Second, a simple reactor-separator system with recycle was considered. The reactor was a CSTR, whereas the separator was again a constantly heated flash. It was shown, that the recycle in such a system can induce instability and multiplicity of steady states [2]. In this case the energy balance has significant influence on the behavior of the system [1].

In the present paper these investigations are extended to reactor-distillation column models. In such models complex bifurcation structures consisting of periodic, complex-periodic, and even deterministic chaotic oscillations have been found. It is shown that the observed bifurcation scenario critically depends on the formulation of the energy balance equation of the distillation column.

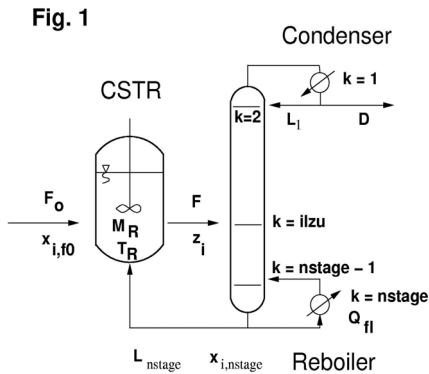
2. Model equations

2.1 CSTR

Assuming isothermal operation of the reactor, the model equations follow from the corresponding material balances. Material balance of component z_i

$$M_R \frac{dz_i}{dt} = F_0 x_{i,f0} + L_{nstage} x_{i,nstage} - F z_i + v_i r(\underline{z}) \quad (1),$$

where z_i is the mole fraction of component i and M_R is the molar hold-up of the reactor which is kept constant. F_0 is the molar feed of the reactor and $x_{i,f0}$ are the



mole fractions of components i in the feed. L_{nstage} is the molar liquid outflow of the bottom tray (reboiler) of the column which is recycled to the CSTR. $x_{i,nstage}$ characterizes the mole fractions of components i on the bottom tray and therefore also in the recycle. F is the molar outflow of the CSTR. r is a reaction rate and v_i is a stoichiometric coefficient.

The total material balance is

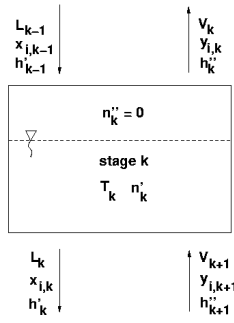
$$0 = F_0 + L_{nstage} - F + \sum v_i r(\underline{z}) \quad (2).$$

In the remainder emphasis is first on the limit of vanishing reaction. Afterwards also finite reaction rates are briefly discussed.

2.2 Distillation column

Inner trays of the distillation column ($k = 2$ to $nstage-1$)

Fig. 2



A schematic view of the liquid and vapor flows between neighboring column trays is depicted in Fig. 2. A standard equilibrium model is used and fluid dynamics are neglected. Each liquid phase of tray k has a liquid inflow from the tray above (L_{k-1}) and a liquid outflow to the tray below (L_k). A vapor stream from the tray below (V_{k+1}) enters tray k and another vapor stream (V_k) is leaving tray k to tray $k-1$ above. The investigated column should have one liquid feed on tray $ilzu$. Therefore, for $k = ilzu$ the liquid feed flow F which has the composition z_i must also be balanced. The molar

liquid hold-up n_k' of all trays is assumed to be equal and constant. The molar vapor hold-up n_k'' of all trays is neglected.

The following component material balance holds for $x_{i,k}$ which is the mole fraction of the liquid component x_i on tray k

$$n_k' \frac{dx_{i,k}}{dt} = L_{k-1}x_{i,k-1} + V_{k+1}y_{i,k+1} - V_k y_{i,k} - L_k x_{i,k} + \delta_{k,ilzu} z_i F \quad (3),$$

$$i = 1, \dots, nc-1, k = 2, \dots, nstage-1,$$

$$\sum_{i=1}^{nc} x_{i,k} = 1 \quad (4),$$

where $y_{i,k}$ signifies the mole fraction of component i in the vapor phase on tray k . δ is the Kronecker symbol which is equal to 1 if $k = ilzu$ otherwise it is equal to 0. nc is the number of components which is 2 in this work.

The total material balance for tray k is

$$0 = L_{k-1} + V_{k+1} - V_k - L_k + \delta_{k,ilzu} F \quad (5).$$

For each tray thermodynamic equilibrium is assumed between the liquid and the vapor phase. Since both phases are considered to be ideal Dalton's and Raoult's law are used for the vapor-liquid equilibrium. The Clausius-Clapeyron law is used to describe the dependence of the vapor pressure as a function of the temperature T_k on tray k as described in [1] ($p_{fl} = 101325.0$ Pa).

For each inner tray an energy balance equation is considered. The energy balances contain the molar enthalpies h of the inflows and outflows. h_f is the enthalpy of the feed flow. The molar enthalpies of the liquid and the vapor

phase on tray k are h'_k and h''_k , respectively. The energy balance of a tray assuming equal heat capacities of the components $c_{p,1} = c_{p,2} = c_p$ reads

$$n'_k c_p \frac{dT_{fl}}{dt} = L_{k-1} h'_{k-1} + V_{k+1} h''_{k+1} - V_k h''_k - L_k h'_k + \delta_{k,ilzu} F h_f \quad (6).$$

In case of a quasistatic energy balance the left hand side is set to zero. In case of a dynamic energy balance the equation is used as given above.

The molar enthalpies of the liquid and the vapor phase of a given tray are calculated from the enthalpies of the pure liquid and vapor components and the respective mole fractions

$$h'_k = \sum_{i=1}^{nc} h'_{i,k} x_{i,k} \quad (7) \text{ and } h''_k = \sum_{i=1}^{nc} h''_{i,k} y_{i,k} \quad (8).$$

The temperature dependence of the enthalpies of the pure liquid components is calculated according to

$$h'_{i,k} = c_{p,i} (T_k - T_0) \quad (9),$$

where $c_{p,i}$ is the heat capacity of component i at constant pressure and $T_0 = 273.15$ K is a reference temperature. The temperature dependency of $c_{p,i}$ is neglected. The evaporation enthalpies Δh_i are added to the enthalpies of the pure liquid components to calculate the enthalpies of the pure vapor components. The molar enthalpy of the liquid feed flow is calculated accordingly. The enthalpies of the pure liquid feed components $h'_{i,f}$ are calculated as described above but are related to the temperature T_R of the column feed.

Condenser tray of the column ($k = 1$)

For the condenser total and instantaneous condensation is assumed. For this tray only three material flows must be considered (Fig. 1). The material and energy balances are formulated analogously as described above. Note that in this case V_1 is a liquid flow (distillate D) which has the same composition $x_{i,1}$ as the recycle L_1 .

Reboiler tray of the column ($k = nstage$)

As in the case of the condenser only three material streams have to be considered for the reboiler (Fig. 1) except for the case of $ilzu = nstage$ where the reboiler is chosen as the feed-tray. Material and energy balances are formulated analogously to the inner trays. To account for the external heating of the reboiler the heating power Q_{fl} has to be considered as an additional term on the right hand side of the energy balance.

In all cases the feed to the CSTR F_0 , the heating power Q_{fl} , and the recycle at the column top L_1 are used as parameters. Integration and continuation of the model system is performed by our numerical tool DIVA [3]. The parameter set given in [1] Tab. 1 for Fig. 9 is used. $L_1 = 0.7$ mol/s and x_f, M_{fl} in [1] correspond to $x_{1,0}, n_k$.

3. Results

3.1 Quasistatic energy balance

First a 3-tray column is studied (condenser: $k = 1$, reboiler: $k = 3$). Choosing $k = 2$ as the feed-tray ($ilzu = 2$) exclusively stable stationary solutions are found. In sharp contrast to that, one gets surprisingly complex behavior if $ilzu = 3$. In this case two Hopf bifurcation points (squares) are found at $F_0 = 3.11$ mol/s and $F_0 = 15.51$ mol/s (Fig. 3a) similar to the reactor-separator system (Fig. 9a in [1]).

Fig. 3a

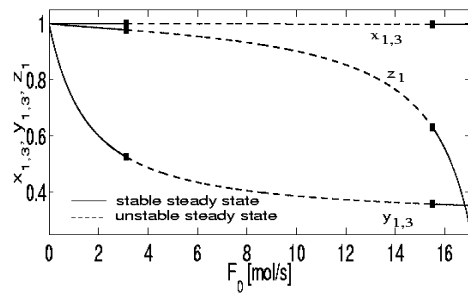
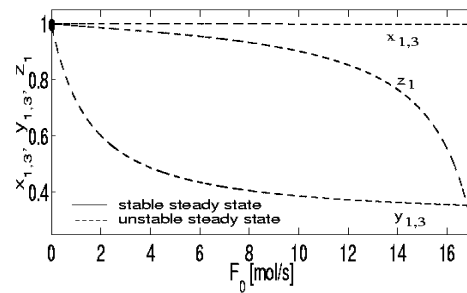


Fig. 3b



At the Hopf points stable oscillations of period-1 emerge. If F_0 is increased period-2 oscillations consisting of alternating large and small oscillations can be found ($F_0 = 3.7$ mol/s). A period-doubling cascade manifests for higher F_0 -values (period-4 at $F_0 = 3.85$ mol/s). The period-doubling sequence finally leads to a region of chaos ($F_0 = 4.0$ mol/s)(Fig. 4a). The occurrence of a period-doubling cascade and the existence of a positive Lyapunov exponent are evidence for the deterministic origin of the observed aperiodicity. From the spectrum of Lyapunov exponents the Lyapunov dimension D_L of the attractor is calculated using the Kaplan-Yorke conjecture [4]. $D_L = 3.01$ has been found.

Fig. 4a

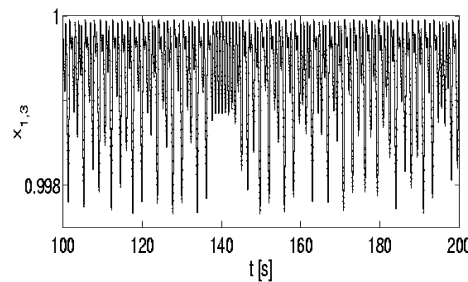
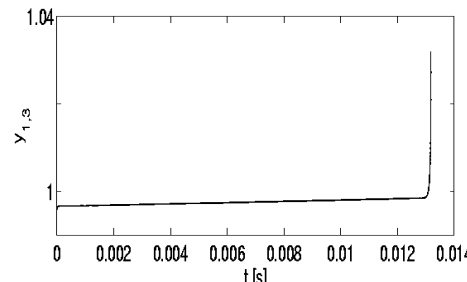


Fig. 4b



If one increases F_0 beyond the region of chaos, a surprisingly large number of different complex periodic and chaotic regions follow. For a 4-tray column using the same conditions (reboiler $k = 4$ as feed tray) Farey-ordered mixed-mode oscillations [5] and a period-adding sequence leading to chaos, where the

individual elements of this sequence show themselves period-doubling, can be found (not shown). This bifurcation sequence shows interesting analogies to scenarios in isothermal autocatalytic oscillators, like the Belousov-Zhabotinsky reaction [6] or the peroxidase-oxidase reaction [7].

3.2 Dynamic energy balance

For the same parameters totally different behaviour emerges if the dynamic energy balance is used (Fig. 3b). No Hopf bifurcation is found, but a stability change occurs at $F_0 = 0.013$ mol/s (dots) where a branch of stable steady states is getting unstable. This is related to a pole of eigenvalues with sign change. For $F_0 > 0.013$ mol/s monotonic instability is observed (Fig. 4b, $F_0 = 4.0$ mol/s).

4. Conclusion

In the present work a multi-tray distillation column with liquid recycle has been studied. Whereas the corresponding system which consists of a single-tray column (flash) can display periodic oscillations, a multitude of periodic, complex periodic, and chaotic oscillation patterns can occur in the case of a multi-tray column with quasistatic energy balance. A period-doubling cascade leading to chaos has been characterized. In sharp contrast to that, a stability change connected with a pole of eigenvalues is observed in case of a dynamic energy balance. For a stand alone column no qualitative difference for models with dynamic or quasistatic energy balance has been found so far. This is different for recycle systems as shown in this paper. Similar patterns of behaviour have also been found for finite reaction rates. Hence, correct energy balance formulation is crucial for dynamic flowsheet simulation.

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