Novel Control Structures for Heterogeneous Reactive Distillation

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An important class of reaction systems which can be efficiently performed by catalytic distillation comprises two reactants (A, B) and two products (C, D). Often, one product is the high-boiling species and is obtained as bottom stream, while the other is involved in a low-boiling heterogeneous azeotrope and is obtained as distillate. The heterogeneity of the azeotrope makes possible a liquid–liquid split, where the product-rich phase is on the side of the distillation boundary which allows obtaining the top-product with a relatively high-purity. Integration of reaction and separation in a single unit reduces the investment and operating costs. However, the controllability of the process is as important as the economics. In this contribution, a novel class of control structures with one-point temperature control is presented. The flow rate of one fresh reactant sets the production rate. The product purity is achieved by temperature control manipulating the reboiler duty, while monitoring the phase ratio organic/aqueous and adjusting the second reactant feed ensures the correct stoichiometric ratio. This control philosophy can be implemented in different ways. Moreover, design modifications with the purpose of increasing the control flexibility are suggested. Overall, given the range of disturbances applied to the esterification system studied in this work, the performance of the new one-point temperature control structures is comparable with that of the different schemes present in the literature.

1. Introduction

Reactive distillation offers significant advantages such as reduced investment and operating costs. An important class of reaction systems which can be efficiently performed by reactive distillation (RD) comprises two reactants (A, B) and two products (C, D). Often, one product is the high-boiling species and is obtained as bottom stream, while the other is involved in a low-boiling azeotrope and is obtained as distillate. This azeotrope has the beneficial effect of displacing the chemical equilibrium, but also the disadvantage of an impure distillate. However, when heterogeneity of the azeotrope makes possible a liquid–liquid split of the condensed distillate, the reactant-rich phase can be returned to the column as reflux, while the product-rich phase on the side of the distillation boundary allows obtaining the top-product with a relatively high-purity. Typical systems of industrial importance are esterification and etherification processes such as *n*-propyl propionate (Xu et al., 2014), *n*-butyl acrylate (Moraru and Bildea, 2017), *2*-ethylhexyl acrylate, triacetin (Hung et al., 2014), fatty acid esters (Dimian et al., 2009, Kiss and Bildea, 2011), glycerol *tert*-butyl ethers (Vlad and Bildea, 2012) - to name just a few. Figure 1 shows a typical example. The heavy reactant B (*2*-ethylhexanol, *2*-EH) is fed as liquid at the top of the reactive zone of the RD column. The light reactant A (acrylic acid, AA) is fed as vapour at the bottom of the reactive zone. The reactants flow in counter-current and reaction takes place in the liquid phase. The heavy product C (*2*-ethylhexyl acrylate, *2*-EHA) is recovered in the stripping zone of the column, being obtained as high purity bottom stream. The light product D (water) forms several binary and ternary low-boiling heterogeneous azeotropes. Thus, water is removed from the liquid mixture with the result of increased reaction rate due to equilibrium displacement. The distillate is condensed, cooled, and sent to liquid–liquid separation. The organic phase is refluxed. The aqueous phase is the top product. If required, a simple flash can remove the small amounts of organics that are still dissolved. In this way, integrating reaction and separation in a single unit greatly reduces the energy requirements (by 70%,

compared to the conventional reaction–separation–recycle process for 2-EHA production, not shown in this paper).
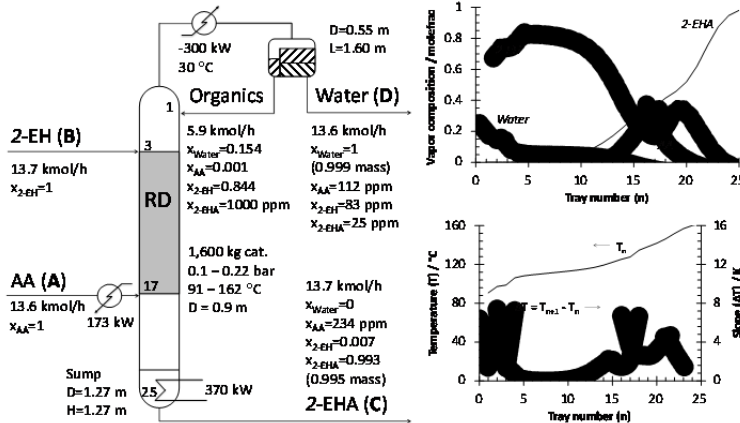

Figure 1. Process flow diagram, mass balance and main sizes (left), vapour phase composition (top-right), and temperature profile (bottom-right) of the reactive-distillation process for 2-ethylhexyl acrylate production

2. Problem formulation

Integration of reaction and separation in a single unit it is perceived as a source of control problems, compared to that of the conventional reactor-separation-recycle system. Firstly, the reactants must be fed in the stoichiometric ratio. This cannot be achieved by simple ratio control or other feed-forward techniques due to unavoidable measurement and control implementation errors (Al-Arfaj and Luyben, 2000). Therefore, the control structure shown in Figure 2 - left might work in a process simulation but will never work in practice. One workable solution (Figure 2 - middle), derived from plantwide control principles (Dimian et al., 2014), measures the inventory of reactants at appropriate location in the column and adjusts the flow rates of fresh reactants. Since the use of concentration control loops are preferred to be avoided due to significant time lags, reduced reliability and costs associated with laboratory analyses, the inventory measurements are usually indirect. Thus, species accumulation or depletion is inferred from temperature measurements. To achieve production rate changes, one internal variable – for example the reboiler duty – is used as throughput manipulator. Note that for the reactive distillation systems involving a heterogeneous azeotrope, both decanter-outlet flow rates must be used for decanter level control. Thus, degrees of freedom (reflux or distillate rate, reboiler duty) which in conventional distillation are normally used for controlling the product purity are no longer available.
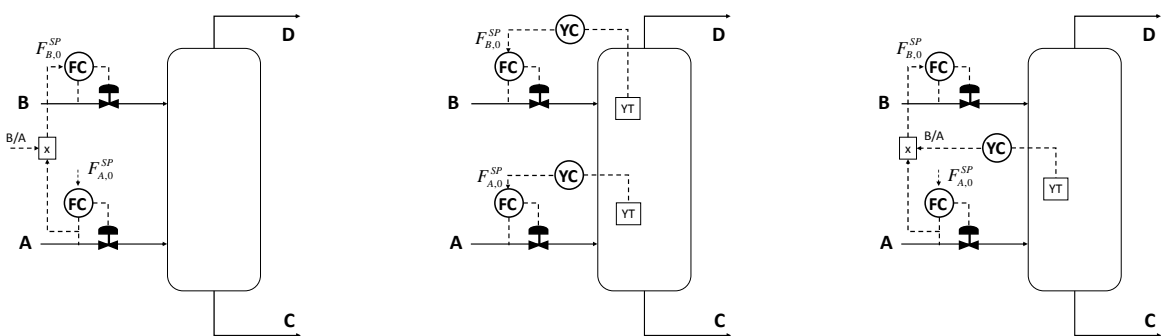

Figure 2. Different inventory-control strategies. Left: reactants fed according to their stoichiometric ratio. Middle: for each reactant, the inventory is measured and controlled by adjusting the fresh feeds. Right: the feed rate of one reactant is fixed, while the inventory of the other reactant is measured and controlled by adjusting its fresh feed.

One solution (Figure 2 - right) is to use the flow rate of the one fresh reactant for setting the production rate. Then, the flow rate of the other reactant is used to control its inventory, therefore ensuring that the fresh feed rates satisfy the reaction stoichiometry. Often, the interaction between the temperature control loops, and the

nonlinearity of the system requires de-tuning of the control loops. As a result, some disturbances are rejected with large settling times and significant deviation of the purity from the setpoint during the transition period between steady states.

In this contribution, we present a novel class of control structures with one-point temperature control applicable to heterogeneous reactive distillation. The basic idea comes from the inventory of the reactant involved in the heterogeneous azeotrope, which can be inferred from measuring the reflux rate (or reflux ratio). Thus, when this reactant is not fed in the correct stoichiometric ratio, it will either accumulate in the system (case in which the reflux increases) or get depleted (reflux decreases). This simple solution reduces the number of temperature control loops, therefore minimizing interaction. Moreover, the reboiler duty becomes available to be used as manipulated variable in the quality-control loop. Several control strategies are possible based on this idea. The efficiency of these novel control structures is illustrated using the production of *2-ethylhexyl acrylate* by reactive distillation. Overall, the efficiency of the new control structures is compared with that of the different control schemes suggested in the literature.

3. Process and equipment design

The equilibrium esterification reaction between *2*-EH and AA with formation of water and *2*-EHA is described by Equation (1), and assumed to be the only reaction taking place in the system due to operation at relatively low temperatures and low residence times. Komon et al. (2013) studied this liquid phase reaction, taking place in the presence of Amberlyst 70, an acidic ion-exchange resin acting as solid catalyst. We used the experimental data provided in that reference to determine the kinetic parameters (Moraru and Bildea, 2017):

$$AA \; + \; 2\text{-}EH \; \xrightleftharpoons{catalyst} \; 2\text{-}EHA \; + \; water \tag{1}$$

The UNIQUAC model is used to describe the liquid phase, while the Hayden-O'Connell equation of state describes the vapor phase behavior. This four-component system shows minimum boiling heterogeneous azeotropy and complex phase equilibria. Based on this kinetic and thermodynamic basis, a pragmatic approach is adopted for the steady-state design of the reactive distillation process (Figure 1 - left). Some preliminary process simulations show that a catalyst amount of 1,600 kg is sufficient to produce about 20,000 t/a of *2*-ethylhexyl acrylate. Given the total amount of catalyst, the number of reactive trays was determined using a simple iterative procedure: (1) select the number of trays, (2) calculate the mass of catalyst per tray, (3) calculate the column diameter, (4) calculate the maximum allowed amount of catalyst per tray, and (5) if the mass of catalyst is higher than the maximum, then increase the number of trays and re-iterate from step-2; if not, then stop. Dividing the total amount of catalyst to the number of reactive trays (15 trays), results the mass of catalyst (107 kg/tray). Based on the selected structured catalytic packing (Katapak™-SP11) and catalyst characteristics, the maximum amount of catalyst per tray (108 kg) is determined. A brief sensitivity analysis shows that the selected number of rectifying (2 trays) and stripping trays (8 trays, including the reboiler) is sufficient to obtain a mixture containing mostly water and alcohol in the top vapors, and high-purity ester as bottom liquid, respectively.

The material balance of the steady-state simulation provides the basis for equipment sizing, basically the holdup required in dynamic simulations. The column diameter is calculated by Aspen Plus. The sump is sized considering 10 min residence time and liquid inlet, while the decanter and the acrylic-acid evaporator are based on 20 min residence time and liquid inlet. The condenser is considered instantaneous in the dynamic simulations. The main dimensions, the mass balance and selected profiles are shown in Figure 1.

4. Control structures

Figure 3 presents several control structures which can be applied to reactive distillation systems involving a heterogeneous azeotrope. Control structures S-1, S-2 and S-3 are taken from literature (Luyben and Yu, 2008). S-1 uses two temperature measurements for inferential control of reactants inventory, similarly to Figure 2 - middle. Note the rather unusual arrangement: the top feed controls a temperature in the stripping section while the bottom feed controls a temperature on the top of the reactive zone. The production rate is indirectly set by the reboiler duty. Control structure S-2 sets the production rate directly, by changing the feed rate of the light reactant. The second reactant and the reboiler duty are used to control two temperatures in the stripping and reactive sections, respectively. Control structure S-3 attempts to reduce interaction by eliminating one temperature control loop and setting the ratio between the reboiler duty and the flow rates of fresh reactants.

The novel control structures S-4, S-5 and S-6 are based on the idea previously explained. In all cases, the reboiler duty is used to control the temperature in the stripping section, therefore providing an indirect control

of the bottom product purity. The flow rate of the limiting reactant is used to set the production rate. The other reactant is brought to the process at a rate that ensures that reaction stoichiometry is satisfied. Its accumulation / depletion is inferred from changes in the reflux ratio (S-4) or the reflux rate (S-5). Control structure S-6 takes a slightly different approach: the reflux ratio is fixed. The non-limiting reactant is fed at two different locations: at the top of the reactive section, and directly in the decanter. This second feed provides an additional degree of freedom which is used to control the level of the organic phase.

In all cases, the slope criteria (see the bottom-right diagram of Figure 1 for temperature profiles) indicates trays 4, 17 or 21 as suitable for temperature control. For control structures S-1 and S-2 (which require two temperature measurements), various combinations were tested. Dynamic simulations confirmed that the unusual configuration provides indeed the best control performance. For the other control structures, one temperature in the stripping section (tray 21) is selected, as it provides the tightest control of the bottom purity. For all temperature measurements, a deadtime of 1 minute was considered. PI control was used in all cases. The temperature control loops were tuned by finding the ultimate gain and period of oscillations at stability limit by the ATV technique and using the Tyreus-Luyben settings. For the pressure and level controllers the gain was set to 1 %/%, while the integral time was set to 12 min. and 60 min., respectively.
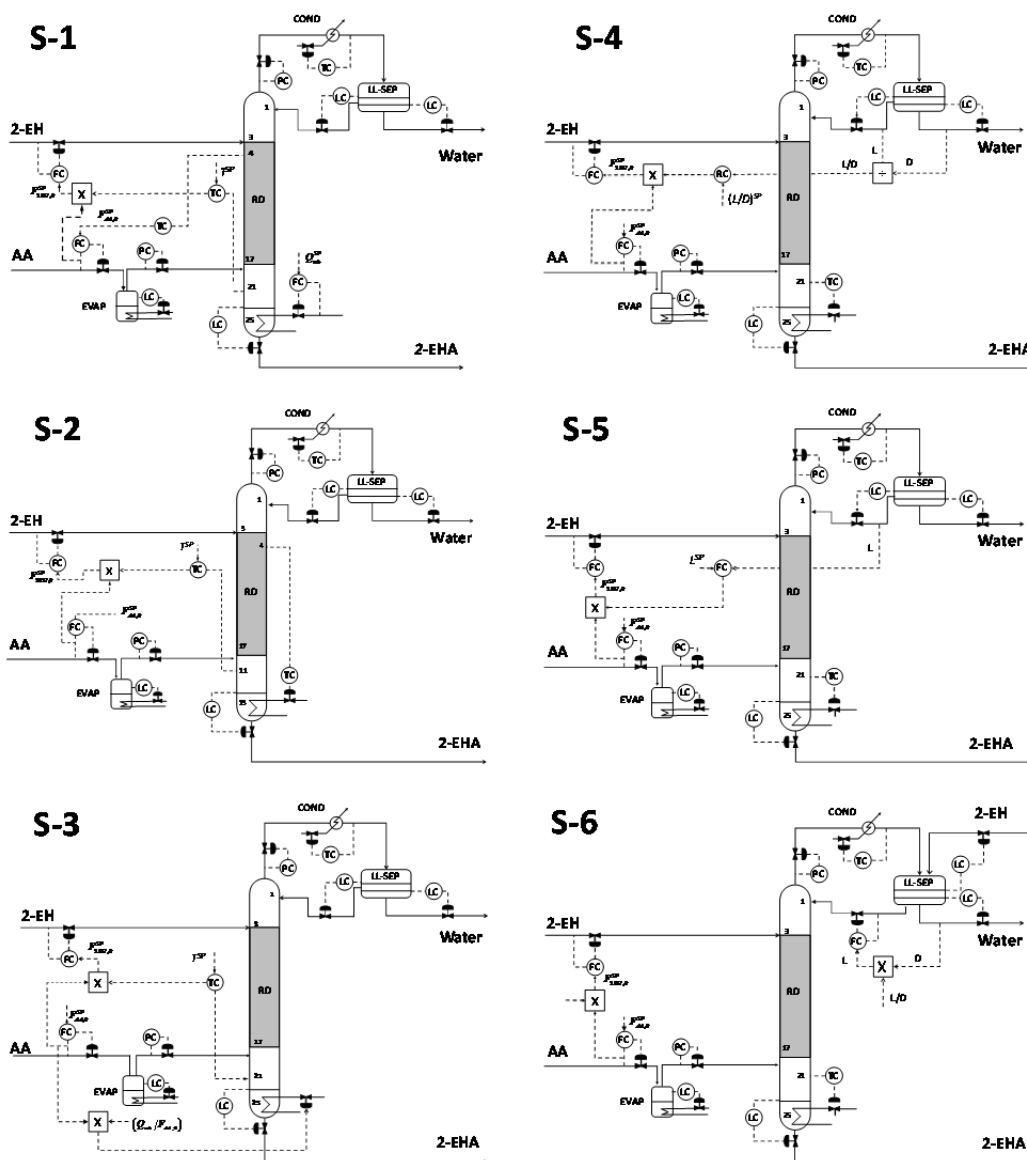

Figure 3. Control of reactive distillation processes involving a heterogeneous azeotrope. Left – control structures presented in the literature. Right – new control structures proposed by this work.

5. Dynamic behavior

Figure 4 presents dynamic simulation results, comparing the performance of the literature control structures (left column) and of the new control structures proposed in this work (right column). All simulations start from steady state, which is maintained for 2 hours. Then, several disturbances are introduced: production rate changes (top and middle-top rows), and raw materials contamination with water (middle-bottom and bottom rows). For all control structures, the production rate increase is the most difficult disturbance. A new stationary regime is reached in about five hours. Among the literature control structures, S-1 is the best performing. Among the new control structures, S-5 is the best, showing comparable performance with S-1 in terms of speed of disturbance rejection and offset in product purity.
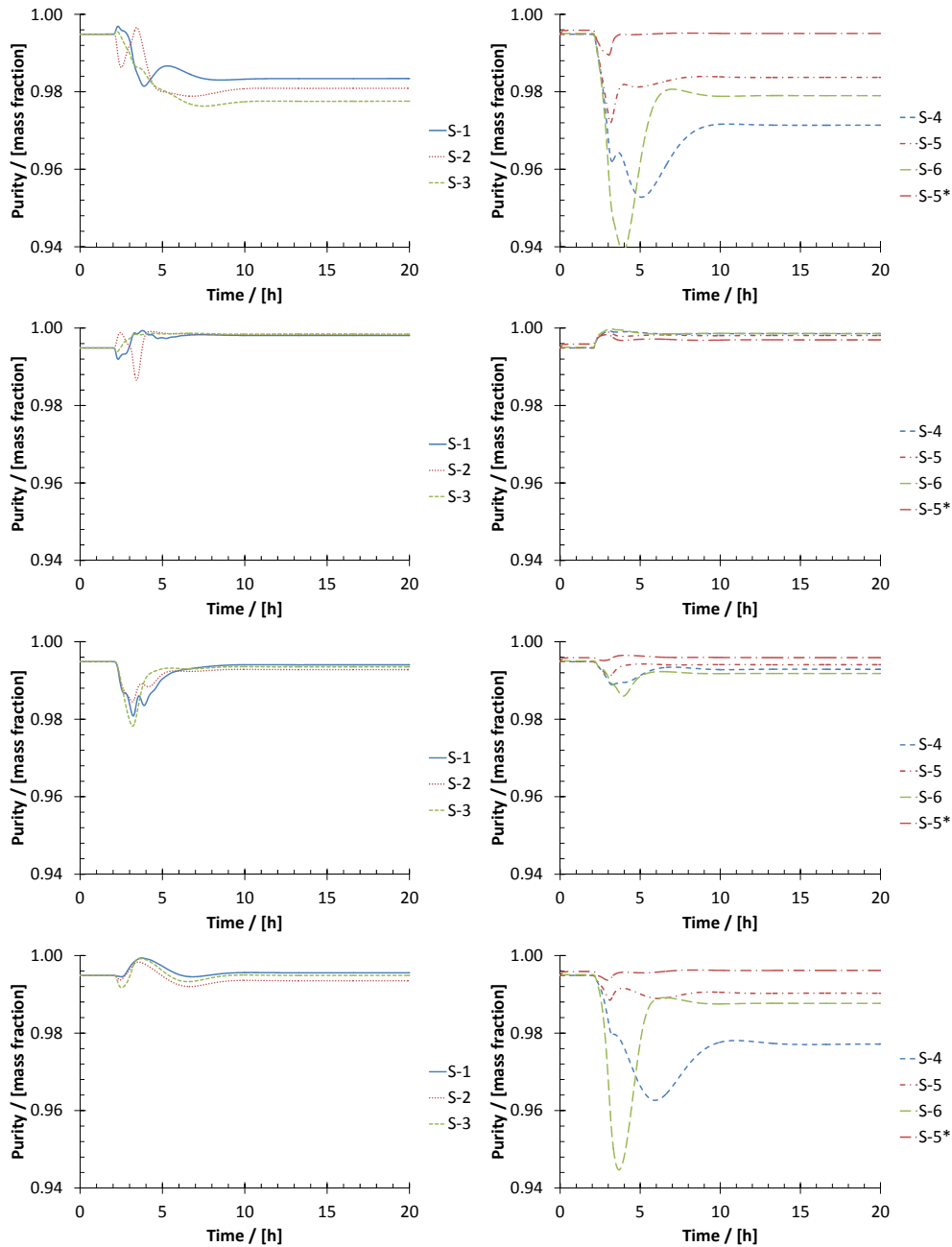

Figure 4. Process dynamics associated with each control structure (left column: literature structures S-1, S-2, S-3; right column: novel structures S-4, S-5, S-6) at various perturbations: top diagrams: +25% production; middle-top diagrams: -25% production; middle-bottom diagrams: 5 %mass water in fresh acid; bottom diagrams: 5 %mass water in fresh alcohol

The vapor–liquid traffic in the column increases when more reactants are fed to the process (e.g. at production increase and contamination of fresh alcohol). This results in a higher pressure at the bottom of the column, and even if the temperature set-point is maintained, the product purity is no longer ensured. For this reason, the set-point of the temperature controller was compensated according to a linear pressure-temperature relationship. The performance of this extended controls structure (S-5*) is excellent, all disturbances being rejected with small overshoots, low settling time and almost no composition offset. This extension is applicable to all control structures.

6. Conclusions

A novel class of control structures with one-point temperature control applicable to heterogeneous reactive distillation process is presented. The flow rate of one fresh reactant sets the production rate. Monitoring the phase ratio organic/aqueous and adjusting the second reactant feed ensures the correct stoichiometric ratio.
The product purity is achieved by temperature control manipulating the reboiler duty. This control philosophy can be implemented in different ways. Overall, the new control structures are resilient to a wide range of disturbances, and can represent a good alternative to two-point temperature control schemes when strong control loop interactions require de-tuning.

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