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Chapter 7

7 Process design and control of reactive distillation in recycle systems

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Abstract

This chapter focuses on the design and control of reactive distillation (RD) columns which are seen as an integral part of an intensified chemical process. While most of the published literature presents analyses of the RD columns as standalone process units, this work frames the RD columns within a process where recycle streams (to these columns) are present, as typical to industrial practice. These recycle streams originate from the incomplete conversion of reactants or their conversion to undesired by-products. Therefore, the unreacted reactants need to be recovered and recycled, while the by-products need to be recovered and reconverted into reactants followed by their recycle to the RD columns.

A case study of industrial importance is used to illustrate key aspects of design and control of such reactive distillation systems with recycles. The design is focused on developing the topology of the entire process and solving the mass and energy balance based on which key process performance indicators (e.g., reactants utilization, energy efficiency, material and energy intensity, carbon dioxide emissions) can be analyzed. The control is focused on developing a plantwide strategy to achieve the material inventory (in other words, balancing the reactions stoichiometry), alongside with achieving the desired production rate and product purities. Several key process changes (e.g. flowrate and composition changes) are implemented to test the proposed control structure of the plant. All this work makes use of both steady-state and dynamic rigorous process simulations.

Keywords: Acrylate; Esterification; Reactions; Separations; Recycles; Process Simulation

7.1 Introduction

Reactive distillation (RD) is an important process intensification technique that can be used as a promising alternative to classical reaction-separation sequences. The RD technology has been already applied productively in the chemical process industry, particularly to overcome the challenges of chemical-equilibrium limited reactions. The main drivers for RD applications are *economical* (20-80% lower variable cost, CAPEX and energy usage), *environmental* (low GHG emissions, avoidance or reduction of solvent use or salt waste) and *social* (enhanced safety due to smaller reactive holdup and lower run away sensitivity). [Kiss \(2022\)](#) provides a general overview of RD processes, covering fundamentals, modeling and design, as well as industrial applications.

This work centers on the design and control of RD columns that are an integral part of a larger chemical process, where recycle streams (to these columns) are present, as typical to industrial practice. These recycle streams originate from the incomplete conversion of reactants or their conversion to undesired by-products. Therefore, the unreacted reactants need to be recovered and recycled, while the by-products need to be recovered and if

possible reconverted into reactants followed by their recycle to the RD columns. These aspects have a major impact on achieving the component inventory in the process, as well as achieving the desired capacity and maintaining the required products purity.

The previous work by [Baki and Kaymak \(2014\)](#) found that a limited number of studies on this topic is available in the open literature, such as the studies of [Luyben et al. \(2004\)](#) and [Wang et al. \(2011\)](#) on synthesis of butyl acetate and methanol by the trans-esterification of methyl acetate with butanol, [Lin et al. \(2008\)](#) on methyl acetate hydrolysis, [Wang et al. \(2010\)](#) on making dimethyl carbonate (DMC) and ethylene glycol by trans-esterification of ethylene carbonate (EC) and methanol, and [Pathak et al. \(2011\)](#) on cumene synthesis from benzene and propylene. More recent studies are those of [Lee et al. \(2019\)](#) on diphenyl carbonate and [Patrascu et al. \(2022\)](#) on DMC production by the indirect alcoholysis of urea.

This work presents a case study of industrial importance, in which the RD column is an integral part of a larger chemical process, namely the production of 4-hydroxybutyl acrylate by esterification of acrylic acid with 1,4-butanediol. This process is used to illustrate key aspects of design and control of reactive distillation systems with recycles. The design is focused on developing the topology of the entire process and solving the mass and energy balance. The control is focused on developing a plantwide strategy to achieve the material inventory (or differently said, balancing the reactions stoichiometry), alongside with achieving the desired production rate and product purities. Several key perturbations and process changes (e.g. throughput and reactants composition) are implemented to test the control structure of the plant. All this work makes use of both steady-state and dynamic rigorous process simulations.

7.2 Design of reactive distillation processes

Reactive distillation can be classified into homogeneous processes (either auto-catalyzed or homogeneously catalyzed) and heterogeneous processes (catalyzed by a solid catalyst) also known as catalytic distillation. Another classification commonly made is based on the phase characteristics of the component mixture, which can be *homogeneous* (i.e. a single liquid phase) or *heterogeneous* (i.e. two liquid phases; in particular, the mixture presents minimum boiling heterogeneous azeotrope that allows a relatively easy liquid-liquid split after condensing the distilled vapor). The following discussion refers to the former classification, as the equipment design and internals required are different for each class of RD.

Equipment and internals. In case of autocatalytic reactions, the rate can be affected only by pressure or temperature. In addition, homogeneous catalysis can influence the reaction rate by changing the catalyst concentration, such that the reaction rate can be properly adjusted to the needs of the RD equipment. Homogeneous catalysis is more flexible, but it

needs difficult separation steps for catalyst recovery, or it leads to salt waste formation (due to the downstream neutralization of cheap acid / base catalysts). Heterogeneous catalysis is simpler in principle, but it needs more equipment volume and it suffers from increased operating temperature and limited catalyst life time ([Schoenmakers and Bessling, 2003](#)). When using solid catalysts, a special construction is needed in practice – such as catalyst packed in ‘tea bags’ on trays, or sandwiched in structured packing (Sulzer Katapak) – in order to fix the solid catalyst particles in the reactive zone. Such constructions put a limit on the catalyst concentration that can be attained, as the reaction rate can be increased only up to the limit set by the attainable concentration range in an RD column.

The choice of internals for RD distillation is much more limited as compared to classical distillation. [Kiss \(2022\)](#) provides an overview of the specific internals used in RD processes and their performance in terms of separation and reaction. Conventional internals can be used for non-catalyzed or homogeneously catalyzed RD processes, as no development of new internals is required. The homogeneous catalyst is usually fed together with the heavy liquid feed stream (or added to the reflux), and the liquid holdup of the column internals has to be maximized towards obtaining high or full conversion. The choice of internals depends on the reaction rate. Slow reactions require large liquid holdups and long residence times in a RD column. Tray columns are typically used for such cases, applying a bubbly flow regime to ensure a larger liquid holdup and a higher residence time. In the case of fast reactions, the separation efficiency is a more important selection criterion for internals than the liquid holdup. Random or structured packing can be used as internals to provide a higher specific surface area and great separation efficiency, as the chemical equilibrium can be reached within relatively short residence times ([Schoenmakers and Bessling, 2003](#)).

Heterogeneously catalyzed RD processes require specific internals to immobilize the solid catalyst in the desired region. Moreover, it is important to ensure an adequate reaction rate by allowing sufficient contact between the liquid phase and the active sites of the catalyst. The most used catalysts for RD processes are acidic ion-exchange (IEX) resins, such as the Amberlyst or Lewatit. Various technologies for immobilizing solid catalysts have been developed, and reported elsewhere ([Kiss, 2022](#)).

Equipment design. RD sets clear specifications on the reaction conversion and the product compositions. Accordingly, the degrees of freedom (DoF) in a RD column have to be tuned accordingly to achieve these specifications, while also optimizing an objective function (e.g. total annual cost). Several specifications are typically required ([Luyben and Yu, 2008](#)):

- RD column pressure and the pressure drop along the stage or the full column. Note that setting the pressure fixes both the top and bottoms column temperatures, being constrained by the cold/hot utilities available on-site. If the bottom temperature is too

high, one could use dilution with a reactant that is recovered afterwards. Working at the highest acceptable temperature is better, as it leads to faster reaction rates.

- Total number of stages, the reactants feed locations, and the exit points of the product streams. This sets the RD configuration in term of the rectification, reaction and stripping sections.
- Top distillate (liquid, vapor, mixed) or bottoms product, as ratio or absolute values.
- Type of the condenser (partial or total) and reboiler (kettle or thermosyphon).
- Reflux ratio or the vapor boilup ratio.
- Liquid holdup distribution on the reactive stages.

The usual design specifications in classical distillation are the concentrations of heavy key component (HKC) in the distillate and light key component (LKC) in the bottom product. The liquid holdup has no effect on the steady-state design of a simple distillation column, only on the dynamic behavior. The diameter of the column can be estimated using vapor-loading correlations, after determining the vapor rates (reflux ratio) needed to achieve a desired separation. Conversely, in case of RD processes, the reaction rates strongly depend on the liquid holdup and the amount of catalyst on each stage, so these parameters are crucial. An iterative design procedure is required for RD columns, as the liquid holdup must be known prior to designing the column. A reasonable liquid holdup per tray is assumed initially and the RD column is designed to reach the desired conversion and product purities. Afterwards, the column diameter is determined, along with the liquid height on the reactive trays that is required for the assumed holdup. Liquid heights of up to 10-15 cm are common, to avoid hydraulic pressure-drop limitations. If the determined liquid height is too high, then a smaller liquid holdup is assumed and all calculations are repeated ([Luyben and Yu, 2008](#)). For the hydraulic designing of a RD column, a shortcut method can be used ([Dimian et al., 2014](#)):

1. Estimate an average volumetric liquid flow rate for the operation.
2. Assume a value for the liquid velocity at the 'load point' (U_{LP}): e.g. $10 \text{ m}^3/\text{m}^2\text{h}$
3. Assume a value for the number of theoretical stages per meter (NSTM), e.g. 2
4. Calculate the column diameter. Considering the specifications of the internals used, estimate the packing volume, the liquid and catalyst holdup per reactive stage.
5. Introduce the above values in a process simulation, expressing the reaction rate in units that are compatible with the liquid holdup (mass, molar or volumetric).
6. Determine the total number of reactive stages required to achieve a target conversion. Check the temperatures, concentrations, and reaction rate profiles. Get from the simulation the liquid and gas flows, as well as fluid properties.
7. Recalculate the load point velocity and liquid holdup by using specific correlations and diagrams. Check the hydraulic design by selecting packing with similar characteristics.
8. Verify if the gas (vapor) load and the pressure drop are within the optimal region.

9. Check all values and repeat the points 4 to 8 until acceptable values are achieved.

Other design and feasibility check methods for RD systems are available in literature. They can be classified into three groups: 1) graphical and topological methods, 2) optimization techniques, and 3) heuristic and evolutionary approaches. [Kiss \(2022\)](#) summarizes all these methods, including their principle, assumptions and a brief pro/con analysis.

RD process design. When the RD column is an integral part of a larger process involving recycles, the column design guidelines presented above are no different. What is different is that, in processes with recycles, the component mass balance around the column has to be solved first: in most of the cases, in a single-column RD process the feed streams to and product streams from the column are well known, while in recycle systems, the recycle streams – which may implicitly be part of the feeds or fed individually to the RD column – are unknown. Roughly speaking, the *process design* (i.e., process topology) activity becomes important and, next to the *equipment design* activity, adds another layer of complexity to the overall design. However, one observation is that in processes with recycles, the *process* and *equipment* design activities are to some extent influencing each other due to their iterative nature. At first, the iterative calculations are simple, based on simplifying assumptions, and describe key characteristics of both design activities. Later, the calculations become rigorous, based on physico-chemical principles, and describe a wider range of characteristics of these two design activities. This is in line and closely follows the steps of the initial conceptual design methodology proposed by [Douglas \(1988\)](#) and of that revised by [Dimian and Bildea \(2008\)](#). Simply put, the philosophy – not necessarily a methodology – adopted here starts simple and adds complexity in a progressive manner. In practical steps, this is one way to put together a process and equipment design of such a process:

1) *Initial-level calculations* (spreadsheet or hand calculations are doable):

- Understand the chemical components present in the process, the physical properties of pure components and mixtures, and in particular the azeotropy and phase equilibria of the system; and the stoichiometry of the main and secondary reactions.
- Answer the question: Is it likely that reactive distillation can be employed in this process? – if the answer is *no*, then stop; else, proceed investigating its technical feasibility ([Shah et al., 2012](#)).
- Make an overall component mass balance, say at the input / output (black-box) level, based on the feeds and stoichiometries, in order to have a feel of the magnitude of component flows / concentrations.
- Consider that inside the black-box there is a reactive distillation column, and make a mass balance based on the most likely behavior of the column, in terms of overhead

and bottoms components, considering fresh feeds and stoichiometry.

- Add additional black-box separation steps to recover reactants (for recycling) and eliminate products (from the process) that are present in the outlet streams of the column, but keep the splits at high-level.
- Other additional black-box reactive or reactive-separation steps should also be implemented if deemed necessary.
- Close the recycles, adjust the inputs and re-iterate the calculations.

2) *Intermediate-level calculations* (the use of a process simulator is highly advised):

- Use rigorous thermodynamic calculations for physical properties, especially when calculating the phase equilibria.
- Implement chemical equilibrium-based reactions, preferable kinetic-based reactions, and phase equilibrium-based separations inside the reactive distillation column. Specify feasible recoveries and product purities. Determine and implement key column characteristics like the number of stages, amount of catalyst or hold-up volume for reaction, stage pressure drop. Other calculations (such as rigorous hydraulics) can be postponed. Note that analogous to the classical Reaction-Separation-Recycle systems where the reactor is central and needs to be solved first, here, the design of the reactive distillation is in focus. This is because its product streams represent the starting point in developing the additional separation steps that are required. Of course, if multiple reactive(-separation) steps are foreseen / necessary, then one needs to decide which comes first.
- Implement equilibrium-based calculations for other separations, reaction or reactive-separation steps for reactants recycle and products elimination from the process.
- Close the recycles, adjust inputs and re-iterate the calculations accordingly.

3) *Complex-level calculations* (the use of a process simulator is unavoidable at this stage):

- Add the required level of complexity deemed to be necessary for answering all questions when determining the techno-economic feasibility of the overall process.
- Always re-iterate the calculations until convergence is achieved.

Based on our experience, achieving the mass and energy balance of the overall plant using kinetic-based rate equations, thermodynamic-based phase equilibria separations, and closing the recycles, is the most challenging task of the process design activity. The use of steady state process simulators is unavoidable, while in some instances the use of the dynamic process simulators is necessary for achieving the steady-state mass and energy balance. This has to do with the approach to solve and the numerical solvers used to find the

solution of the system of equations. [Luyben \(2004\)](#) describes in detail how Aspen Dynamics is used to find a steady state solution of a process; and several case studies are presented.

7.3 Control of reactive distillation processes

Reactive distillation is a great example of the subtle interaction between design and control. The steady-state and dynamic aspects of a process should be considered at all R&D stages and commercialization: from laboratory to pilot plant, and full scale production ([Luyben and Yu, 2008](#); [Sharma and Singh, 2010](#)). Typically, the controllability of a RD column is improved by adding more reactive trays, while taking into account the trade-off between the steady-state design and dynamic controllability. The neat operation mode requires that the reactants are fed according to the stoichiometric ratio. For this reason, the control system must be able to detect any imbalance that leads to a gradual accumulation of a reactant, lower conversion and product purities. Another option is to operate an RD column with an excess of reactant to make the control easier, but this requires the recovery and recycle of the (unreacted) excess reactant. Note that, even in the latter case, the stoichiometry still needs to be balanced out at the plant level. The control of an RD column is a rather challenging task in practice due to process nonlinearities and complex interactions between the VLE and chemical reactions. Various control methods can be used for RD processes, ranging from simple PID controllers ([Moraru and Bildea 2017](#); [Moraru et al., 2022b](#)) to advanced model predictive controllers (MPC) – including dynamic matrix control (DMC), quadratic dynamic matrix control (QDMC), robust multivariable predictive control technology (RMPCT), generalized predictive control (GPC), and others ([Sharma and Singh, 2010](#)).

Independent of the type of the control methodology adopted, the basic control structure has to achieve three main objectives: production rate, product purity, and reaction stoichiometry. There are only few process control structures that are applied to the neat operation of both homo- and heterogeneous RD processes. These process control structures use inferential temperature control (or concentration analyzers) at some location in the RD column to balance the stoichiometry.

Figure 7.1 (left column) illustrates three control structures, reported in the literature, which aim to fulfill the main control objectives, albeit in different ways. Notably, these process control structures apply to both homogeneous and heterogeneous RD processes.

- 1) *Control structure S-1* ([Roat et al., 1986](#)) manipulates the reboiler duty (or the vapor boilup) to set the production rate. The flow rates of both fresh reactants are used (either directly or involving ratio control) to control two temperatures in the column. These two control loops work jointly to achieve the specified product purity and to feed the reactants in the correct stoichiometric ratio. [Luyben and Yu \(2008\)](#) applied this control structure to several processes for acetic acid esterification.

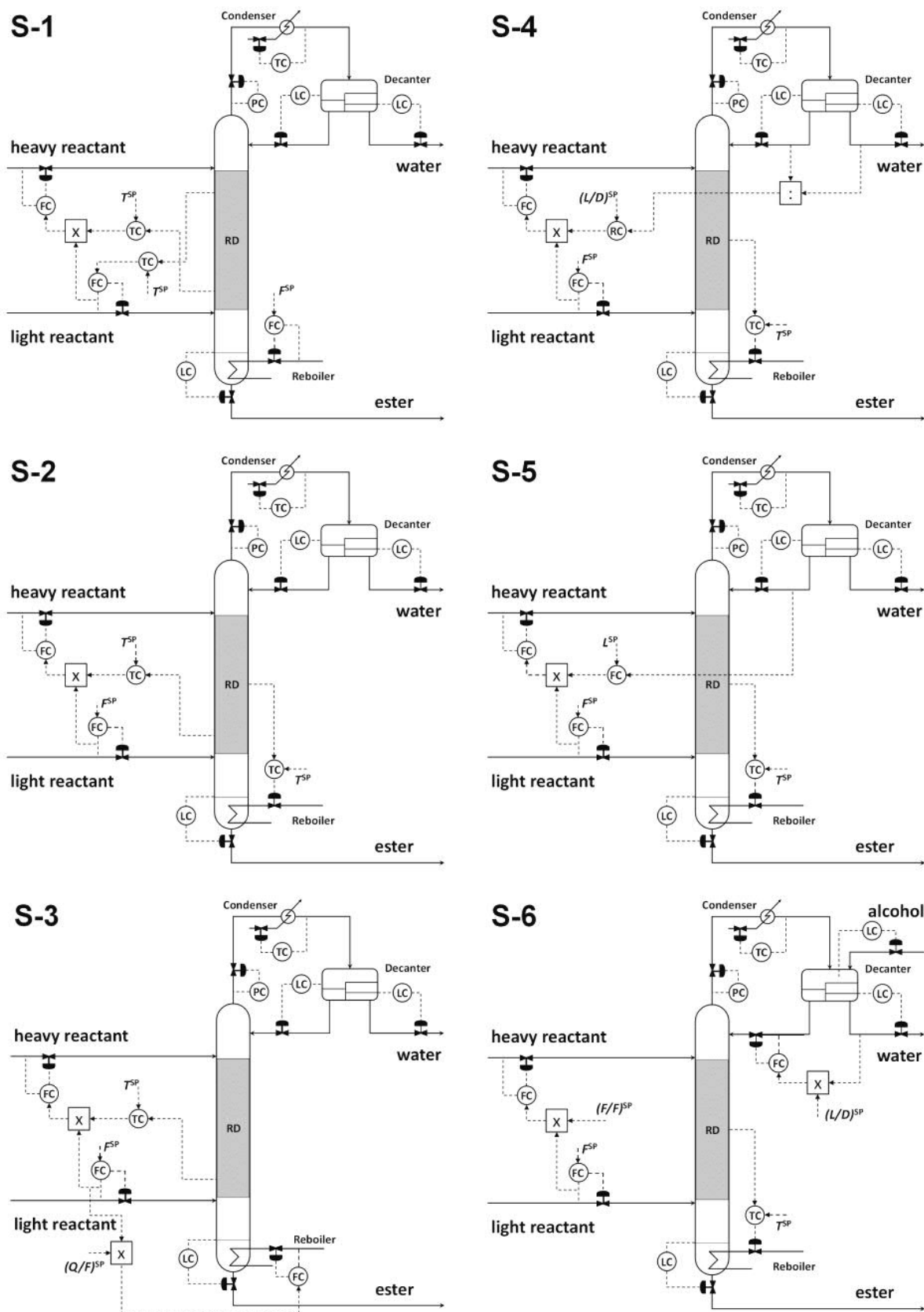


Figure 7.1 Control of reactive distillation processes involving a heterogeneous azeotrope. Left – classic control structures from literature. Right – newly proposed control structures

- 2) *Control structure S-2* (Huang et al., 2004) fixes the flow rate of one reactant (throughput manipulator) and manipulates the flowrate of the other reactant (directly or involving ratio control) and the reboiler duty to control two temperatures in the column. This was applied to RD processes for synthesis of butyl propionate and butyl acetate (Huang et al., 2004). Control structures based on the same idea were also applied to RD processes for the production of amyl acetate (Hung W.J. et al., 2006), triacetin (Hung et al., 2014), butyl and amyl acetates (Hung S.B et al., 2006), n-propyl propionate (Xu et al., 2014), butyl levulinate (Chung et al., 2015), dimethyl carbonate (Wang et al., 2010), 1,3-dioxolane (Pan et al., 2020), various esters of acetic acid (Luyben and Yu, 2008), and diphenyl carbonate (Lee et al., 2021).
- 3) *Control structure S-3* manipulates the flow rate of one reactant to set the production rate, while the ratio between the reboiler duty and limiting reactant flow rate is kept constant. The flowrate of the other reactant (or reactants ratio) is used to control one temperature in the column. Similar control structures were applied to RD processes for making butyl acrylate (Zeng et al., 2006) and butyl levulinate (Chung et al., 2015).

Figure 7.1 (right column) shows three novel control structures proposed recently by Moraru et al., (2022b), which can be applied to heterogeneous RD processes only (such as some esterifications). In all these new process control structures, the light reactant flowrate is used to set the production rate. The quality of the bottom product is controlled by the reboiler duty of the RD column. The feedback required to set the correct stoichiometric ratio between the fresh reactants is obtained from the measured reflux ratio (S-4) or reflux rate (S-5). In case of control structure S-6, a part of the heavy reactant (the alcohol, immiscible with water) is fed to the decanter. The reflux ratio (or the reflux rate) is set, and the level of the organic phase is controlled by the alcohol flowrate.

Plantwide control. Independent of the individual steps comprising a chemical process, the plantwide control (PWC) system must achieve its basic goals: setting the production rate, keeping the product purities at the required values, and maintaining the component inventory (or in other words, balancing the reaction stoichiometry when chemical transformations are involved). Therefore, no matter how complex the individual step may or may not be, these objectives are valid also for processes with recycles in which reactive-distillation columns are present. Hence, the well-known principles and methodologies described in the literature can be used to develop the plantwide control system (e.g., Luyben et al., 1999; Skogestad and Postlethwaite, 2005; Dimian et al., 2014), including those pertaining to reactive-distillation columns and other unit operations.

However, it is worth mentioning that for such processes, special attention has to be given to the control system of the reactive-distillation column. This is because, due to its fundamental

tasks, the column has to achieve simultaneously a certain conversion of reactant(s) and a certain level of separation. If the control system of the column fails to achieve these two goals, it will most likely lead to a failure of the plantwide control system in achieving the overall control objectives. We find that maintaining the component inventory is not an easy task, especially in processes with recycles and when chemical reactions are present. In most of the situations, the reason is the accumulation of one of the components: either the reaction section has insufficient capacity to achieve the conversion of reactants, or the separation section is not able to remove one of the components, while the recycle “helps” to build-up components within the process.

The typical control design problem is to obtain a controller that follows certain specifications for a given system described by a certain model. This could be relatively simple for small systems such as standalone unit operations. Nonetheless, when addressing a full chemical plant including intensified units (such as RD columns), several key issues may arise. For example, the complete process model may be unavailable, the controlled or manipulated variables may still have to be chosen, and the control specifications may be incomplete or unclear. Consequently, most traditional process control design techniques are not able to cope with large processes. From a mathematical viewpoint, the plantwide control is actually a complex combinatorial problem involving a large number of decision variables. The plantwide control involves the following tasks ([Correa de Godoy and Garcia, 2017](#)):

1. Decision on the control objectives;
2. Choice of the manipulated variables (MVs);
3. Choice of the controlled variables (CVs);
4. Selection of any extra measurements;
5. Choice of the process control configuration (i.e., structure of the overall controller that interconnects all variables that are measured, manipulated, and controlled);
6. Choice of the type of controller.

The plantwide control design implies the selection of controlled and manipulated variables, extra measurements, control configuration, and controller type. Typically, it includes all of the structural decisions of the control systems but not the actual design of the system. The major plantwide control design techniques proposed in literature are addressed in a review paper ([Correa de Godoy and Garcia, 2017](#)). An integrated framework of simulation and heuristics is recommended to be used as a hybrid plantwide control technique, aided by computer simulations at each step ([Konda et al., 2005](#)). The steps of this integrated framework are:

1. Define the plantwide control objectives;
2. Determine the degrees of freedom usable for process control;
3. Identify and analyze the plantwide disturbances;

4. Set the performance and controller tuning criteria;
5. Select the production rate manipulator;
6. Select the product quality manipulator;
7. Select manipulators for more severe controlled variables;
8. Select manipulators for less severe controlled variables;
9. Design the control for the unit operations;
10. Check the component material balances;
11. Analyze and address the effects due to integration and recycles;
12. Enhance the control system performance (if possible).

7.4 Case study: RD coupled with a distillation–reactor system and recycle

7.4.1 Basis of design and basic data

This industrially relevant case study refers to the synthesis of 4-hydroxybutyl acrylate (HBA). This reaction has been performed at lab-scale using a solid-base catalyst, as reported by [Yang et al. \(2008a,b\)](#). However, the possibility of applying this reaction at large scale using a new RD-based process was not yet investigated; although a preliminary conceptual design was reported in a conference paper ([Moraru et al., 2020](#)), and a detailed study of three RSR processes ([Moraru et al., 2022](#)). In this respect, we present here the design and control of a process comprised of a RD column coupled with an additional separation step (say for example, a distillation column) for the recovery of HBA product and a reactor for the hydrolysis of by-product 1,4-butanediol diacrylate (BDA) back to acrylic acid (AA) and HBA. The plant capacity considered is ~23 kt/a of HBA at a purity of 99.4 % HBA.

Notably, HBA is used industrially to obtain homo-/co-polymers employed in many products, such as coatings, pressure sensitive additives, or photosensitive resins. HBA is also used industrially in chemical syntheses, as it undergoes addition reactions with a large variety of inorganic and organic components ([BASF brochure, 2016a](#) & [BASF brochure 2016b](#)). The usual product specifications for HBA are min. 97 % purity, max. 0.3 % acrylic acid, max. 0.5 % diacrylate and max. 0.1 % water content (all by mass).

The chemistry routes to make HBA at industrial scale are: 1) direct esterification of acrylic acid (AA) with 1,4-butanediol (BD), leading to HBA and water as by-product, and 2) transesterification of methyl acrylate with BD, leading to HBA and methanol as by-product. Another undesired by-product that is formed in both routes is 1,4-butanediol diacrylate (BDA), due to the reaction between the HBA product and the AA reactant present in the system (while water by-product is also obtained in this esterification reaction). The paper of [Ostrowski et al. \(2011\)](#) provides more information on the possible secondary reactions. The authors employ a computational quantum mechanical modeling method (density-functional theory) to calculate the activation energy of the side reactions in a number of esterification

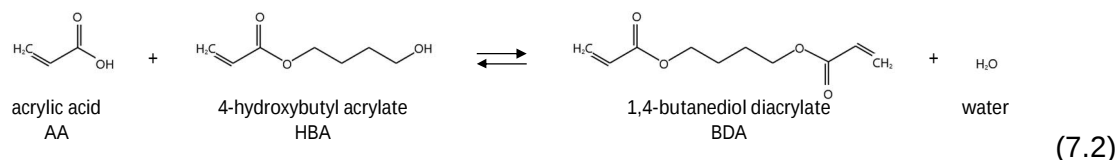
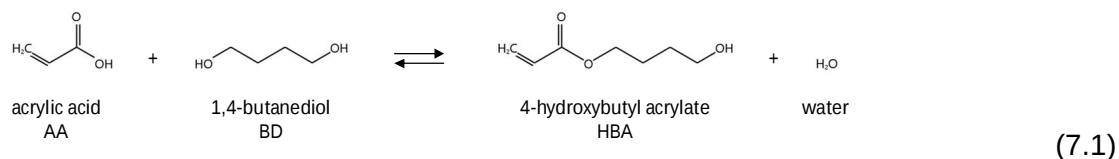
systems. These secondary reactions are the following (in order of increasing activation energy): (1) addition of acrylic acid to the double bond in acrylates, (2) additions of alcohols and water to acrylates, (3) dimerization of acrylic acid, and (4) addition of alcohol to the acid dimmer (leading to the same product as the addition of AA to an acrylate). It is worth noting that the lower the activation energy, relative to one another, the easier that chemical reaction occurs, thus favoring the by-product formation in the lower activation energy-reactions.

Most data about these chemical routes and the HBA manufacturing are available in the patent literature. A BASF patent ([Dockner et al., 1995](#)) describes the synthesis of 1,4-butanediol mono-acrylate via esterification of AA with BD in a process that leads to an aqueous solution of unreacted BD that is converted to tetrahydrofuran (THF) in the presence of a strong acid as catalyst, and eventually the THF is removed from the aqueous solution. Rohm and Haas Co ([Curtis, 2008](#)) claim an enhanced process that yields high purity hydroxyalkyl acrylates (HAA) prepared from acrylic acid and alkylene oxides. Mitsubishi Chemical ([Tokuda et al., 2009](#)) and Nippon Shokubai ([Jinno et al., 2015](#)) disclosed similar methods for the synthesis of HAA from acrylic acid and an alkylene oxide. Osaka Organic Chemical Industry Co Ltd ([Sugiura et al., 2013](#)) described a process for preparing HBA by the trans-esterification of an alkyl acrylate with BD in the presence of a dialkyltin oxide. A later patent from the same company ([Tanaka et al., 2017](#)) claims that HBA can be produced by the trans-esterification of MA with BD, in the presence of a dialkyltin oxide catalyst (such as: dioctyltin / dilauryltin / dibutyltin oxide), which can be recovered and reused. This reaction is carried out in a solvent (e.g. cyclohexane or methylcyclohexane) in the presence of an inhibitor (e.g. phenothiazine) that is needed to minimize polymerization. The same patent ([Tanaka et al., 2017](#)) also provides some details about the direct esterification reaction, particularly that by-products formation is significant, the process has a complex neutralization step due to the homogeneous acid used as catalyst (sulfonic acid or para-toluene sulfonic acid) leading to waste salts generated in large amounts. Moreover, the unreacted AA remains in the HBA product, thus preventing its direct use as a raw material in some high-end applications.

The paper of [Yang et al. \(2008a\)](#) reports that the direct esterification reaction can be carried out using a solid catalyst, namely a strongly acidic ion-exchange resin such as Amberlyst 15. By using a heterogeneous catalyst, most of the problems related to using liquid catalysts can be avoided (including the recovery and re-use of the catalyst, difficult product recovery and purification, corrosion, and problems related to waste disposal). Nonetheless, the process remains challenging due to the side reaction that leads to the undesired BDA by-product.

The chemistry of the HBA synthesis is rather complex, as it involves several reactions leading to many unwanted by-products. Yet, it is well known that using inhibitors can reduce the formation of by-products. [Yang et al. \(2008a\)](#) reported the HBA synthesis using two

esterification reactions: the main reaction leading to the HBA product (equation (7.1)) and a side reaction forming the unwanted BDA by-product (equation (7.2)), along with water by-product that is formed in both esterification reactions which are equilibrium-limited. The kinetic model proposed in that research study is described by equations (7.3) – (7.8).



$$r_1 = k_1 \left(C_{AA}C_{BD} - (1/K_{eq,1})C_{HBA}C_{water} \right) \quad (7.3)$$

$$\ln(K_{eq,1}) = B_1 / T + A_1 \quad (7.4)$$

$$k_1 = k_{0,1} \exp(-E_{A,1}/RT) \quad (7.5)$$

$$r_2 = k_2 \left(C_{AA}C_{HBA} - (1/K_{eq,2})C_{BDA}C_{water} \right) \quad (7.6)$$

$$\ln(K_{eq,2}) = B_2 / T + A_2 \quad (7.7)$$

$$k_2 = k_{0,2} \exp(-E_{A,2}/RT) \quad (7.8)$$

In the equations (7.3) to (7.5) the variables subscript 1 refers to the 1st chemical reaction, while in the equations (7.6) to (7.8) the subscript 2 refers to the 2nd esterification reaction. Note that r [kmol/(kg_{cat}·s)] is the reaction rate, k [kmol/(kg_{cat}·s) / (kmol/m³)²] is the forward reaction rate constant, C_i are the liquid phase molar concentrations [kmol/m³] of component i (where $i = AA, BD, HBA, BDA, water$), K_{eq} [-] is the equilibrium constant based on molar concentration, A [-] and B [K] are constants in the equilibrium constant equations, k_0 [kmol/(kg_{cat}·s) / (kmol/m³)²] is the pre-exponential factor, E_A [kJ/kmol] is the activation energy, while R (=8.314 kJ/kmol/K) is the universal gas constant.

[Moraru et al. \(2022\)](#) used the experimental data reported in the paper of [Yang et al. \(2008a\)](#) to re-evaluate the values of all the kinetic parameters of this model. Table 7.1 gathers all these parameters, while Figure 7.2 provides a visual comparison between the reported experimental and the calculated molar fractions of the components. A good agreement between the experimental and calculated data is observed. During the first 200 min after the start, the experimental data compares well with the calculated data, but it begins to deviate towards the end, indicating that other side reactions may become more important at higher temperatures and longer residence times. It is worth noting that these calculations are made

for a temperature outside the range in which the pre-exponential factors were regressed. The *UNIQ-HOC* property model was used in Aspen Plus to calculate the properties required for rigorous process simulations. This particular method makes use of the UNIQUAC activity coefficient model to describe the liquid phase behavior, and the Hayden-O'Connell (HOC) equation of state to describe the vapor phase and account for the dimerization of carboxylic acids in vapor phase. Note that the VLE and LLE use the same sets of binary interaction parameters (BIPs) of the activity coefficient model.

Table 7.1 Parameters of the kinetic model based on the paper of [Yang et al. \(2008a\)](#)

Reaction	E_A [kJ/kmol]	A [-]	B [K]	k_0 [kmol/(kg _{cat} ·s) / (kmol/m ³) ²]
1	58300	-2.0212	1457.6	91.5
2	86700	-0.4614	810.36	181625

Notes: E_A – as reported by [Yang et al. \(2008a\)](#)

A and B – determined by regression using experimental data

k_0 – determined by regression using experimental data

The chemical system consists of five components: AA, BD, HBA, BDA, and water. However, the pure-component physical properties of only three of them (AA, BD, water) are present in the Aspen Plus database. The physical properties of the other two chemicals (HBA and BDA) were estimated based on their molecular structure, using the Property Constant Estimation System (PCES) available in Aspen Plus (with the exception of HBA vapor pressure). Notably, only 2 out of 10 BIP sets (water/AA and water/BD pairs) for the UNIQUAC activity coefficient model are available in the Aspen Plus database. Also, the association parameter for water/AA used in the EOS is available in the Aspen Plus databank. All the remaining (missing) BIPs were estimated using the UNIFAC group contribution method. The databanks from which the parameters are retrieved is indicated according to the naming in Aspen Plus (i.e. APV100 and NISTV100).

The vapor pressure of several components (AA, BD, water) is well described in the Aspen Plus database. For BDA there are no experimental data reported, thus its vapor pressure was estimated using methods based on the molecular structure. In case of HBA, the Antoine coefficients used in the vapor pressure equation were derived from data available in two brochures from BASF ([BASF, 2016a, 2016b](#)). More details on the physical properties are presented by [Moraru et al. \(2022b\)](#).

Figure 7.3 shows the vapor pressure curves for all the components involved in the system. Water and AA are the lightest components, and BDA is the heaviest component, thus an easy vapor-liquid-based separation should be possible. However, BD and HBA have very similar boiling points (suggesting a challenging fluid separation), and their vapor pressure curves cross each other meaning that BD is lighter at higher pressures and HBA is lighter at

lower pressures. In a process that employs a fixed bed reactor followed by a classic separation equipment (such as distillation), this behavior indicates a difficult separation between BD and HBA. This is crucial in the process, as BD is a reactant that needs to be recovered and recycled back to the reaction section, while HBA is the main product that needs to be separated and highly purified.

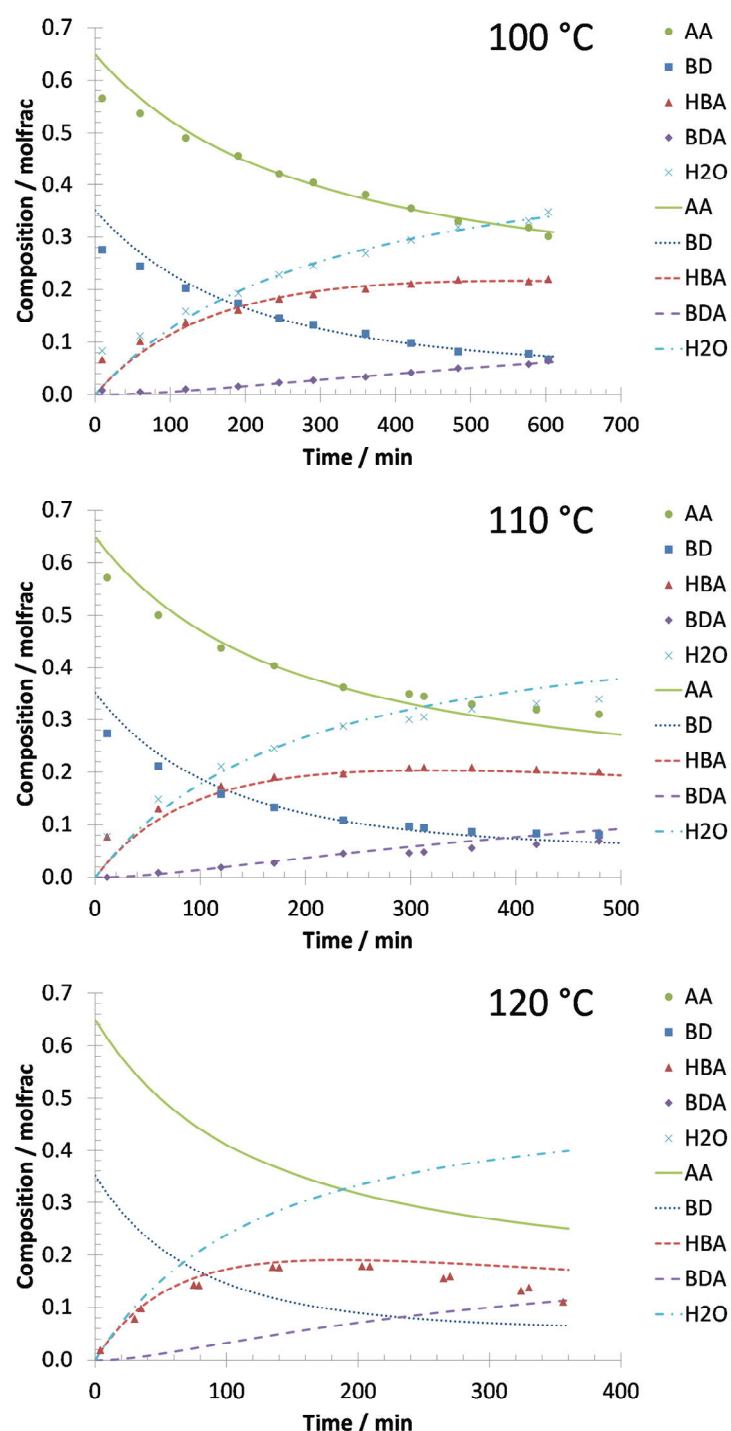


Figure 7.2 Comparison between experiments data (markers) from [Yang et al. \(2008a\)](#) and calculated (lines) mole fraction in time, at various temperatures; considering the same initial AA:BD mole ratio (1.85:1) and catalyst concentration (1.63 %mass) for all experiments.

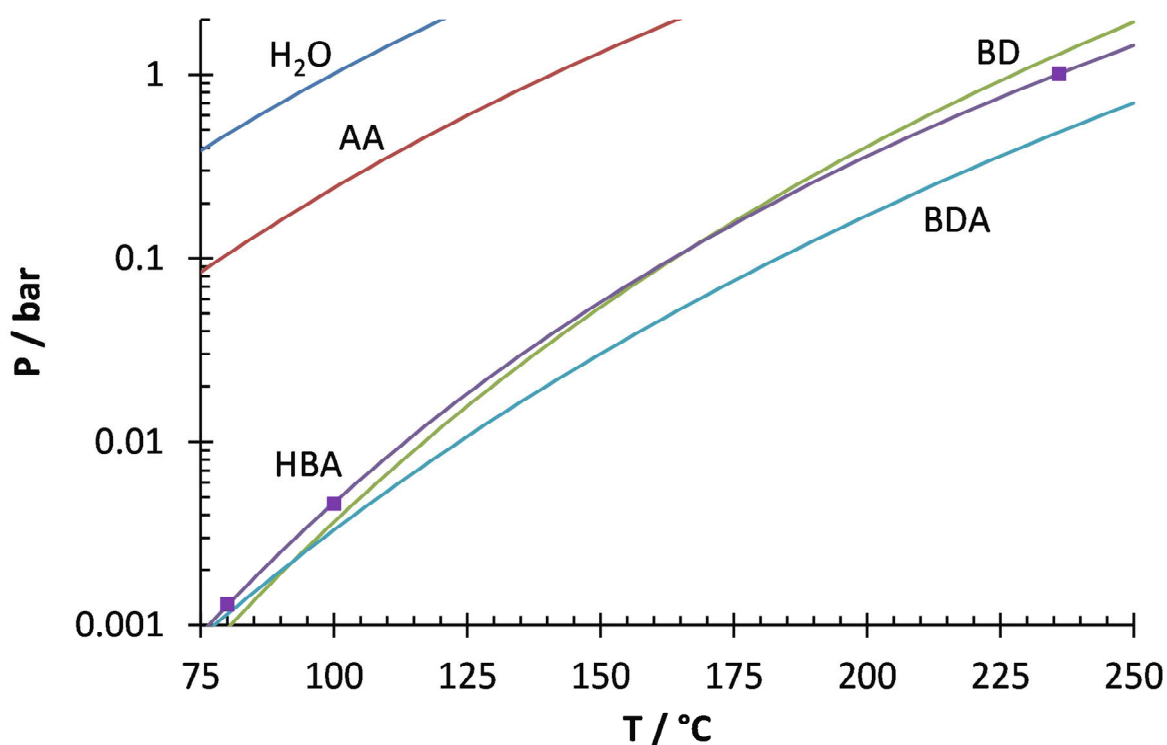


Figure 7.3 Vapor pressure of all components. Vapor pressure for HBA (squares) are taken from BASF brochures ([BASF, 2016a](#), [2016b](#))

The azeotrope searches, based on the *Distillation Synthesis* tool available in Aspen Plus, reveal that there are two azeotropes (at 0.1 bar) present in the system. Table 7.2 lists the boiling points of these azeotropes as well as of the pure components. The close-boiling components BD and HBA form a minimum-boiling homogeneous azeotrope (singular point SP #4), while BD and BDA form a heterogeneous azeotrope (singular point SP #3).

Table 7.2 Calculated singular points (SP) including pure components and binary azeotropes – composition (mass based) and boiling points at 0.1 bar

SP #	Type	Temp / [C]	H2O	AA	BD	HBA	BDA
0.1 bar							
1	hom	100.0	1				
2	hom	141.2		1			
3	het-az	158.1			0.707		0.293
4	hom-az	159.9			0.516	0.484	
5	hom	163.5				1	
6	hom	163.8			1		
7	hom	183.3					1

Figure 7.4 (constructed using the *Distillation Synthesis* tool in Aspen Plus) presents the ternary liquid-liquid diagram at 40 °C for the ternary mixture water-BD-BDA, which exhibits

two regions of liquid-liquid immiscibility gap. The other components (AA and HBA) do not present any immiscibility with the other components.

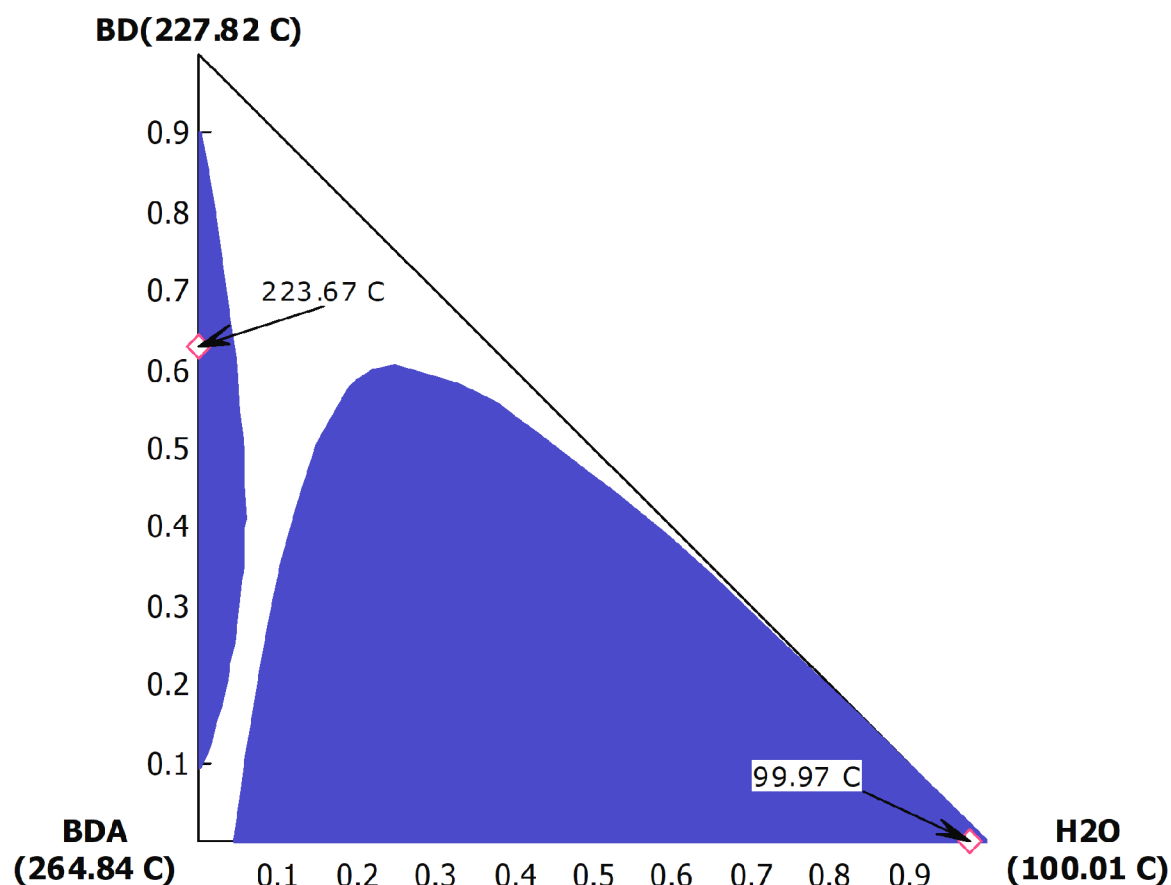


Figure 7.4 Liquid-liquid equilibrium diagram (mass based) for the ternary mixture water-BD-BDA at 40 °C and 1.013 bar (including the azeotropes of water-BDA and BD-BDA).

7.4.2 Process design

HBA could be conveniently manufactured in a process based on reactive distillation. The design of such a process considers a plant capacity of 22,900 t/a 4-HBA (at 99.4 %mass purity). One of our recent studies (Moraru et al., 2022) proved that a space-time-yield of $0.91 \text{ kg}_{\text{product}}/\text{kg}_{\text{cat}}/\text{h}$ in a catalytic fixed bed reactor placed in a classical reactor-separation-recycle (RSR) process is enough to accomplish a similar production capacity. This is equivalent to a catalyst amount of 2,500 kg, thus the results described hereafter are based on considering this amount of catalyst present in the reactive distillation column. The detailed process flow diagram is shown in Figure 7.5, while the mass balance is summarized in Table 7.3.

The RD column has a typical configuration, with the reactive zone (catalytic bed) placed in the middle of the column. The light reactant is added as vapor at the bottom of the reaction zone, while the heavy reactant is added as liquid at the top of the catalytic bed. As top distilled product of the RD column, high-purity water (>99.99 %mass) is obtained.

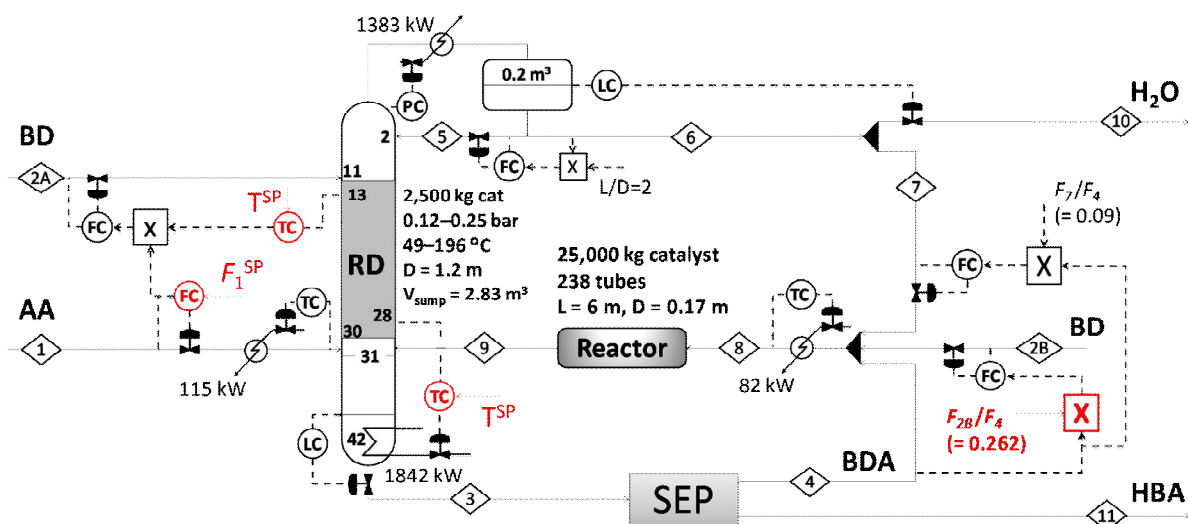


Figure 7.5 Process flow diagram of the RD process for HBA production

Table 7.3 Mass and energy balance of the RD process for HBA production

Stream	1	2A	2B	3	4	5	6	7	8	9	10	11
T / °C	35	35	35	195.6	190.6	49	49	49	87	106	49	168.1
P / bar	1.2	1.2	1.2	0.25	0.12	1.2	1.2	1.2	3	2.9	1.2	0.12
Flow / kg/h	1297	557	1081	6735	4125	1391	696	371	5577	5577	324	2611
Mass Fractions												
H2O						1	1	1	0.067	0.055	1	
AA	1					46 ppm	46 ppm	46 ppm	3 ppm	0.048	46 ppm	1 ppb
BD		1	1	0.002					0.194	0.134		0.006
HBA				0.385						0.288		0.994
BDA				0.612	1	3 ppm	3 ppm	3 ppm	0.740	0.476	3 ppm	

The heavier components (HBA and BDA) are removed as bottoms product, which is further split in the ideal separation block SEP (as the HBA/BDA split is very easy, a conventional distillation column can be used). In order to obtain on-spec HBA, it is imperative to avoid getting reactants in bottoms of the RD column; else these contaminating low-boiling components will end up in the lighter product (HBA) during the separation of HBA from BDA. The BDA stream is mixed with part of the H₂O stream (from the top of the RD column) and fresh BD reactant, and this mixed stream is fed to the reactor where BDA is hydrolyzed back to AA and HBA. The outlet stream from the reactor is fed to the RD column, below the reactive zone, providing the required separation of the heavier components (HBA and BDA) from the lighter reactants (AA and BD), and water by-product.

The equipment sizing is based on the rigorous process simulation results. The RD column

includes 2,500 kg of catalyst that ensures the same space-time-yield as the tubular reactor described in a previous research study (Moraru et al., 2022). The reactive distillation column has 9 rectifying stages (excluding the condenser), and 11 stripping stages (excluding the reboiler). These stages are enough to obtain high-purity water as distillate product, and a bottoms stream that contains only HBA and BDA (free of alcohol and acid). Structured packing MellapakPlus™ 252Y (with an *HETP* of 0.4 m) is used for the rectifying and stripping sections. Considering a structured catalytic packing, the maximum amount of solid catalyst ($m_{cat,max}$) that can be hosted per tray is estimated as follows:

$$m_{cat,max} = HETP \frac{\pi}{4} D_{packing}^2 \phi_{cat} \rho_{cat,bulk} \quad (7.9)$$

Dividing the total amount of catalyst to the number of 20 reactive trays, results in an actual amount of 125 kg catalyst per tray. Sulzer Katapak™-SP11 is employed for the reactive stages, having the solid catalyst immobilized in wire gauze layers which are combined with layers of MellapakPlus. The catalyst (with a bulk density of $\rho_{cat,bulk} = 740 \text{ kg/m}^3$) occupies $\phi_{cat} \approx 45\%$ of the volume of this packing (Gotze et al., 2001). The separation efficiency is about 2 *NTSM* (m^{-1}) which is equivalent to an *HETP* of 0.5 m (Gotze et al., 2001). Considering the density of the catalyst and a packing diameter ($D_{packing}$) equal to the column diameter (1.2 m) – which was determined using the pack sizing tool in Aspen Plus – this results in a maximum allowed amount of 188 kg catalyst per tray. Therefore, the condition of not exceeding the maximum amount of catalyst per tray is satisfied (i.e. 125 kg catalyst < max. 188 kg/tray). Note that the approach of simulating the heterogeneous catalyst in a reactive distillation column (using the RADFRAC block in Aspen Plus) is well described in the book of Luyben and Yu (2008).

The reactor is a fixed-bed tubular reactor operated adiabatically. The catalyst is inside the tubes. The amount of catalyst (25,000 kg) is determined for a BDA conversion of about 35 %. Note that the BDA hydrolysis back to HBA and AA is equilibrium limited, and only slightly exothermic. A brief sensitivity analysis shows that selecting a higher conversion does not justify the increase in the catalyst amount. Selecting a tube length of 6 m with a diameter of 0.17 m, the amount of catalyst required can be accommodated in a total of 238 tubes.

The sump of the RD column and the reflux accumulator are sized considering a residence time of 10 min. The heat exchangers (AA evaporator, column reboiler and condenser, and the reactor preheater) are designed using an overall heat transfer coefficient of 930 $\text{W}/(\text{m}^2 \cdot \text{K})$. An instantaneous model is used in the dynamic simulations, as the heat exchangers hold-up is neglected. The separation between BDA and HBA is not implemented in the design. Although a distillation column would add some material holdup, its impact on the overall dynamics are evaluated to be small. The focus here was kept on the dynamics of the RD capturing the influence of the recycle stream.

The SEP block used in this simulation can be seen as the equivalent of a conventional column. Rough calculations show that this binary mixture can be split using a column with 30 theoretical stages. The key figures of the overall process are presented in the process flow diagram (see Figure 7.5).

It is also worth mentioning some key information on how the final mass (and heat) balance was achieved. The most difficult task was to close the recycle, which was made in two iteration steps. In the first iteration, a preliminary mass balance was obtained in Aspen Plus, as mentioned, without being able to close the recycle. The preliminary sizing was also made, which meant finding the number of theoretical (catalytic, stripping and rectification) stages, as well as the column diameter, sump and main hydraulic parameters; the reflux vessel was also sized (note that when exporting the steady state simulation to dynamics, the holdup is necessary). Then, the simulation was exported to Aspen Dynamics. After implementing the main plantwide and some basic controls (please see the Process control section), the recycle was step-wise added as feed to the RD column, while the simulation was running. Once the simulation achieved steady state (i.e., the values of all variables remain do not change anymore), the steady state mass (and heat) balance was considered to be achieved. This ended the first iteration. In a second iteration, the preliminary mass (and heat) balance and the equipment sizing was updated in the Aspen Plus simulation. For some unknown reason, the recycle still did not close. Then, the simulation was exported in Aspen Dynamics and the same procedure was followed to close the recycle. The mass (and heat) balance presented in Table 7.3 is the result of the second iteration step.

7.4.3 Process control

The main objectives of any control structure are to achieve a desired production capacity, maintain the product purity at given set-points and keep the component inventory, all these despite any process perturbations. These are largely treated by well-known textbooks (e.g., Luyben et al., 1999; Skogestad and Postlethwaite, 2005; Dimian et al., 2014). Additional objectives can be defined like the economic plantwide control as largely described by Skogestad (2012). Here, we consider the first three objectives, namely the production capacity, product purity and component inventory. All the dynamic simulations have been carried out using Aspen Dynamics.

The control structure is presented in Figure 7.5, together with other process data. This control structure uses only PI controllers. At the plantwide level, the production capacity is set by the flow rate controller (marked in red) of the fresh acid. This is also known as the “throughput manipulator”. Note that there are also other options to set the production capacity. For example, one can chose the flow rate controller of the fresh alcohol that feeds the column.

The product purity is inferred by the temperature controller on stage 28 which manipulates the steam flow rate to the reboiler. By controlling the temperature on this stage at the required value, the bottom stream of the column is free of alcohol (the water and acid are lighter and are not expected to reach out in the bottoms). Thus, only the acrylate and the diacrylate are allowed to leave the column. This is important since the distillation column (modeled here as an ideal separation block) is left to perform the much simpler task of separating the acrylate as distillate at the required purity, and diacrylate as bottoms products. If the temperature controller on stage 28 fails, alcohol and even acid escape in the bottoms stream of the RD column. Since these components are lighter than the acrylate, they will find their way out from the process with the distillate of the distillation column contaminating in this way the acrylate product. Therefore, although the temperature control on the distillation column is important (for not allowing the diacrylate to escape in the distillate), the temperature control of the RD column is the key control element to achieve required product purity. Note that the main idea, independent of the implemented control, is to prevent the reactants escaping in the bottoms stream of the RD column.

In addition, a concentration controller in cascade with the temperature controller is also studied for two of the process changes. The results (i.e., with and without the concentration controller) are compared.

Achieving the component inventory is maybe the most difficult objective of the plantwide control structure. To a minimum, one needs to look at both the reactions stoichiometries, recycles, and at the inlet / outlet streams of the process when deciding on the control structure that might be capable of achieving the inventory. Regarding the process presented here, one key observation is that no reactants (i.e., acid and alcohol) leave the RD column. The other key observation is that only the acrylate and water leave the plant, while the diacrylate byproduct is recovered and converted to its reactants which are recycled back to the RD column. Roughly speaking, the question which is asked is how to feed the alcohol reactant (remember that the acid reactant is fixed, setting the plant throughput) such that no accumulation or depletion of reactants will occur. The strategy proposed here is to infer the necessity of alcohol, or lack of it, by temperature measurement in the column, and adjusting the flow rate of fresh alcohol to the column accordingly. Note that the recycle stream contains all components, including alcohol; however, since the temperature measurement is a good indication of the alcohol inventory in the column from which neither alcohol nor acid escape, the control strategy should be able to properly adjust the fresh alcohol, or the ratio between the two fresh feeds as shown in Figure 7.5, to balance the stoichiometries. The simulation results (not presented here) show that setting the two fresh feeds in ratio responds faster at throughput changes, giving lower settling times. Using the temperature profile in the column, the slope criteria (i.e., $\Delta T = T_{n+1} - T_n$, where T is the temperature and n

is the stage number) indicates that the temperature measurement and control should be made on stage 13. This is inside the top part of the reactive-distillation section, two stages below the stage where the fresh alcohol is fed to the column. The same procedure is applied to find a suitable stage for temperature control for the product purity.

Another important element of the proposed strategy for balancing the stoichiometry is in relation to the second feed of fresh alcohol which is added to the hydrolysis reactor. Overall, it seems that the presence of alcohol increases the conversion of the diacrylate back to its reactants (i.e., acid and acrylate), which is a desired outcome. This is because the alcohol reacts with the resulted acid, forming even more acrylate. Thus, this second feed of fresh alcohol is added in ratio with the flow rate of the diacrylate resulted from the RD column. Another reason for feeding alcohol to the reactor is to have a homogeneous liquid phase, since water and the diacrylate present a large heterogeneous area (see Figure 7.4). The water stream to the hydrolysis reactor is also set in ratio with the diacrylate flow rate.

For the rest of the variables, standard control is implemented. In the column, the top pressure is controlled by manipulating the cooling water flow rate. The level in the reflux vessel is controlled by manipulating the water flow removed from the process. The column is set to work at a fixed reflux ratio. The evaporation rate in the acid evaporator is controlled by manipulating the steam flow rate. The temperature at the reactor inlet is kept constant by manipulating the cooling water flow rate in the cooler. The reactor operation is adiabatic.

The PI-controllers are tuned by choosing reasonable ranges for the process variable (PV) and the controller output (OP) and then setting the controller gain to $1 \text{ } [\%OP \text{ range}] / [\%PV \text{ range}]$. The integral time is set equal to an estimated time constant of the process. The column temperature controllers are tuned by assuming 1 min measurement delay, and using the ATV (Auto-Tune Variation) method to find the ultimate gain and the period of oscillations at stability limit and using the Tyreus–Luyben rules. The parameters of the concentration controller are determined using the open loop method and using the IMC (Internal Model Control) tuning rules. 30 min sampling interval and 30 min dead time are assumed when tuning this controller.

The dynamic behavior of the plant is studied for two types of changes: (i) increase and decrease of the production capacity by approximately 10 %; and (ii) contamination with 3 %mass water of both fresh reactants. The changes are implemented one at a time, following the same procedure: After one hour of steady state, the new value of the manipulated variable is ramped during a two-hour interval, and the simulation continues until it reaches twenty process hours. The change of throughput is made by increasing / decreasing the fresh flow rate of the acid by 10 % from its nominal value. The contamination of the fresh feeds is made by (simultaneously) increasing the water concentration from 0 to 3 %mass

and decreasing the acid / alcohol concentration from 100 to 97 %mass. In the case of fresh alcohol, both fresh feeds are contaminated.

All results are presented in Figure 7.6, each graph showing the acrylate and water molar flow rates on the Y1-axis, and their mass purity on the Y2-axis. The graphs on the top show the results for 10% increase (top left) and 10% decrease (top right) in the fresh acid flowrate. As expected, both the acrylate and the water flow rates increase / decrease accordingly by 10%. In both cases, the water purity remains constant while the acrylate purity modifies slightly. If necessary, the off-set of the acrylate purity can be eliminated by using a concentration controller, as shown by the results (interrupted line) in the case of increasing throughput. The bottom left graph shows the results for fresh acid contamination with 3 %mass water. Since the fresh acid is the throughput manipulator and is set to a fixed mass flow rate, the acrylate flow rate decreases. The water flow rate increases since more water is fed to the process. The water purity remains unchanged, while the acrylate purity shows an offset. The bottom right graph shows the results for fresh alcohol contamination with 3 %mass water. As expected, the acrylate flow rate remains constant since the fresh acid is the throughput manipulator. The water purity remains unchanged, while the acrylate purity shows an offset which can be easily eliminated by using a concentration controller (results indicated by the interrupted line).

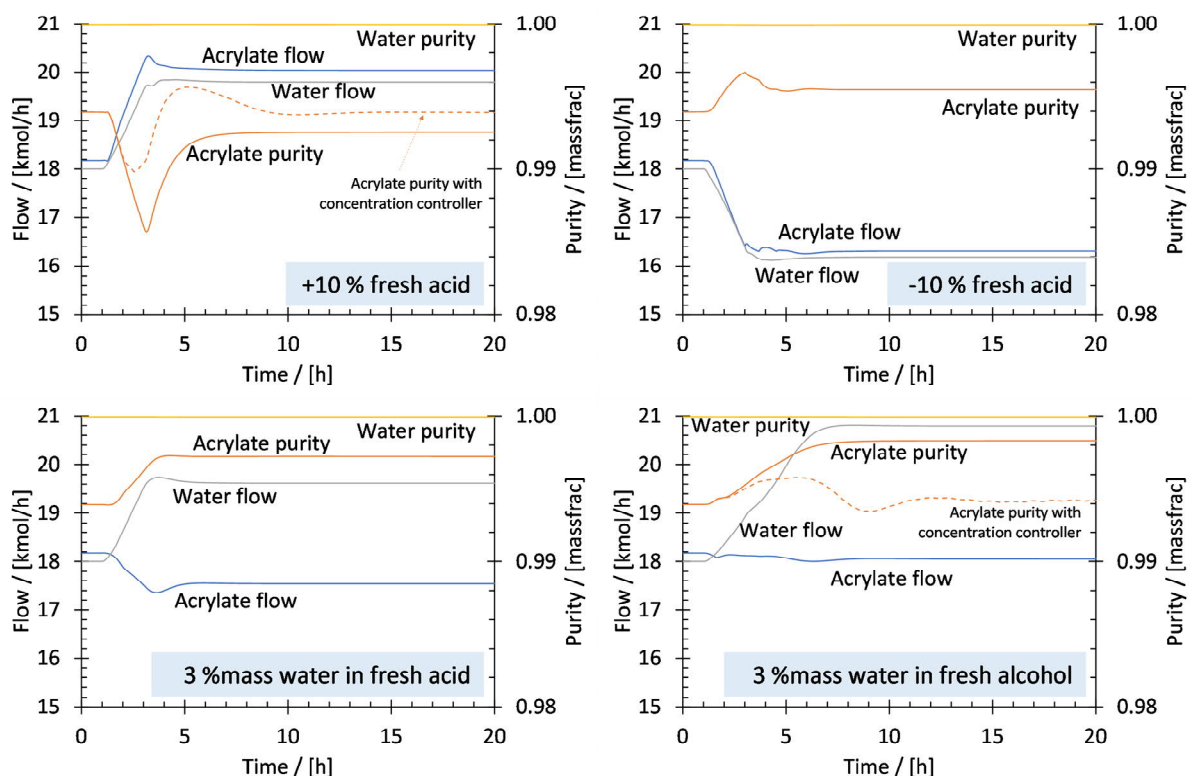


Figure 7.6 Dynamic simulation results: Acrylate and water flow rates and their purities for increase (top left) and decrease (top right) in capacity by approximately 10 %, and the contamination of fresh acid (bottom left) and fresh alcohol (bottom right) with 5 %mass water

7.4.4 Discussion

The manufacturing of 4-hydroxybutyl acrylate at industrial scale using catalytic distillation technology is promising and feasible. An annual production capacity of 22,900 t HBA can be achieved in a RD column using 10 m of Katapak™-SP11 packing hosting in total 2,500 kg of solid catalyst. The additional rectification section (3.6 m) and a stripping section (4.4 m) – both of them using MellapakPlus structured packing - are sufficient to obtain high-purity water as top stream, and a bottom stream (BDA and HBA) that is free of acid and alcohol. The BDA formed in the RD column is conveniently converted back to AA and HBA in a fixed bed catalytic reactor with a total of 25,000 kg catalyst Amberlyst 15. The process based on reactive distillation overcomes the difficult separation BD/HBA/BDA, by completely reacting BD in the RD column, and thus achieving the necessary HBA specification in a subsequent distillation column required for the HBA/BDA split. The complete conversion of BD reactant in the RD column and the hydrolysis of BDA in the additional fixed-bed reactor are the key elements in characterizing the technical feasibility of this novel process.

The proposed control structure is able to achieve the most important objectives (namely the production capacity, product purity and component inventory) when an increase / decrease in process throughput is required (for production changes), or when the fresh reactants are contaminated with significant amounts of water.

Due to material recycle, obtaining the mass and heat balance for this process is challenging. Both the Aspen Plus and Aspen Dynamics simulators were used to achieve the steady state mass and heat balance. In addition, a couple of iterations were necessary since the equipment design (mainly the column diameter and hydraulic parameters) had to be updated so that the system dynamics is properly captured in face of disturbances. Further iterations may refine the design, including the addition of a distillation column for HBA/BDA separation.

7.5 Conclusions

The design and control of reactive distillation columns in systems with recycles is more complex but closer to the industrial reality. The design is focused on developing the topology of the entire process that includes RD columns, and solving the mass and energy balance based on which key process performance indicators (e.g., reactants utilization, energy efficiency, material and energy intensity, carbon dioxide emissions) can be analyzed. Using process simulators is unavoidable during process flowsheet development due to complexities that both the process and equipment design pose, and their integrated and iterative nature. Closing material recycles for large processes is particularly challenging to obtain the steady state mass (and energy) balances. The process control is focused on developing a plantwide strategy to achieve the material inventory (balancing the

stoichiometry), alongside with achieving the desired production rate and product purities. Again, process simulators are key in testing and analyzing the feasibility of the proposed control structures.

In the case of RD coupled with a distillation-reactor system and recycle (HBA process), the process design of the RD column as integral part of a larger process is particularly challenging. This is because the material recycle is not easy to close, making difficult to achieve the material balance of the final process topology. The hydrolysis reactor for BDA conversion back to AA and HBA is another key element of the process design in achieving a highly selective process. This is because the BDA formation in the column is significant, and therefore BDA must be converted to its reactants before recycling them to the RD column. The reactor is also an integral element in achieving the reaction stoichiometry, hence contributing to maintaining the component inventory. An undersized reactor would lead to insufficient hydrolysis of BDA, hence leading to its accumulation in the process. The rigorous dynamic simulations show that the proposed control structure achieves the main task of maintaining the component inventory, as well as setting the desired production rate and keeping the products purity at the required values.

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