The interactions of design, control and operability in reactive distillation systems

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Abstract

In this work the design and control of a reactive distillation column, described by a rigorous dynamic model, is tackled via two different optimization approaches. In the first, the steady-state process design and the control system are optimized sequentially. It is shown that operability is a strong function of the process design and potential operability bottlenecks are identified. In the second approach, the process design and the control system are optimized simultaneously leading to a more economically beneficial and better controlled system than that obtained using the sequential approach. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Reactive distillation systems involving reaction and separation in a single unit have the potential to reduce capital and operating costs, particularly when reversible reactions occur or when azeotropes exist making conventional separation difficult and expensive. However, reactive distillation is not extensively used in industry since it is perceived that its operation will always be more difficult and will pose higher requirements on the quality of the design and control system than conventional flowsheet in which a reactor is typically followed by a train of distillation columns. This behaviour can be mainly attributed to the complex interactions between the underlying physical phenomena taking place in reactive columns, having a significant influence on the robust operation under variations.

Initial research in reactive distillation focused mainly on the development of design procedures under steady-state conditions. A key contribution in this area is the work of Doherty and coworkers (Doherty & Buzad, 1992; Buzad & Doherty, 1995; Okansinski & Doherty, 1998). Ciric and Gu (1994) presented a mathematical programming model for synthesizing kinetically controlled (rate-based) reactive distillation processes. The dynamic modelling of reactive distillation has received considerable attention over the last 10 years with more emphasis on MTBE and ETBE productions. An excellent review in modelling reactive distillation has recently been presented by Taylor and Krishna (2000). To mention some of the advances, Abufares and Douglas (1995) developed a dynamic model for an MTBE process. Pilavachi, Schenk, Perez-Cisneros, and Gani (1997) discussed extensively a number of important aspects that effect the modelling and simulation of reactive distillation processes. Sneesby, Tade, Datta, and Smith (1997a) developed a model for the synthesis of ETBE and discussed several design and operating aspects. Gani, Jepsen, and Perez-Cisneros (1998) presented a generalized reactive separation model capable of considering multiple process unit configurations. Schenk, Gani, Bogle, and Pistikopoulos (1999) described in considerable details a hybrid modelling environment in which a reactive distillation process can be simulated using a combination of equilibrium and non-equilibrium models, both in steady-state and dynamic modes.

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Another area of research was focused on studying and identifying multiple steady-states (output multiplicity) in different reactive distillation systems (Guttinger & Morari, 1997; Gehrke & Marquardt, 1997; Mohl, Kienle, Gilles, Rapmund, Sundmacher, & Hoffmann, 1997; Hauan, Hertzberg, & Lien, 1997; Sneesby, Tade, & Smith, 1997).

The control of reactive distillation has received some attention only recently. Based on dynamic simulations, Sneesby, Tade, Datta, and Smith (1997b) presented general recommendations for the control of reactive ETBE columns, and the need of addressing control issues early in the design process was recognized. Bock, Wozny, & Gutsche (1997) proposed a control scheme for a reactive column with a recovery column. Sneesby, Tade, and Smith (1999) discussed the advantage of a combined composition and conversion control scheme for an ETBE column. Kumar and Daoutidis (1999) addressed the dynamic modelling, dynamics and non-linear control of an ethylene glycol reactive distillation column. A control system was designed that performs well with stability in the high purity region. Monroy-Loperena, Perez-Cisneros, and Alvarez-Ramirez (2000) studied the control problem of the same system and proposed a robust PI control configuration. Luyben (2000) presented a comparison of the dynamic behaviour and steady-state economics of two alternative reactive distillation systems. Al-Arfaj and Luyben (2000) systematically explored a variety of control structures for an ideal two-product reactive column. They identified the need to detect the inventory of one of the reactants in order a feedback trim can balance the reaction stoichiometry. Vora and Daoutidis (2001) studied the dynamics and control of an ethyl acetate reactive distillation system and proposed a different feed configuration for the two reactants that allows higher conversion and purity than the original configuration. More recently, Seferlis and Grieves (2001) presented a systematic approach for the optimal design of staged reactive distillation units using both rigorous optimization and sensitivity analysis.

Finally, the synthesis and design problem of reactive distillation systems has also received some attention. Kenig et al. (1999) described a software package for the synthesis and design of reactive distillation operations. Melles, Grieves, and Schrans (2000) discussed several aspects which facilitate the design and optimization procedure in a kinetically controlled distillation column. Giessler, Savilov, Pisarenko, Serafimov, Hasebe, and Hashimoto (2001) proposed a systematic method for generating different structural alternatives of reactive distillation processes.

In the open literature and to the best of our knowledge, only one work addresses (Heath, Kookos, & Perkins, 2000), the interactions of design and control for a reactive distillation column (ethylene glycol reactive column). However, no studies exists in the literature, in which in-depth comparisons are made between sequential and simultaneous approaches to design and control using advanced optimization techniques. The aim of this work is to address these issues. A rigorous and high fidelity (hybrid) dynamic model that has been validated against experimental data is first described and then used to study the interactions of design and control in a reactive column involving the production of ethyl acetate from the esterification of acetic acid with ethanol (Schenk et al., 1999). The problem is posed as a dynamic optimization problem and solved using control vector parameterization techniques. Two state-of-the-art optimization strategies are employed. In the first strategy, the design and control tasks are optimized sequentially while in the second, design and control are optimized simultaneously. The potential synergistic benefits of this simultaneous approach are investigated. In both cases, multi-loop proportional-integral (PI) controllers are used. Optimization results of the simultaneous approach indicate promising process designs and illustrate how careful design can result in significantly improved controllability without necessarily having to pay economic penalties.

2. Problem description

The production of ethyl acetate from the esterification of acetic acid with ethanol is considered in a reactive distillation column (see Fig. 1). As discussed by Bock, Jimoh, & Wozni (1997), Chang and Seader (1988) there is a number of problems in achieving high purity ethyl acetate. However, despite this disadvantage, there is one big advantage for this system: experimental data is openly available in the literature. This was our major consideration when selecting this reactive system in order to be able to validate our results and the application of novel techniques (experimental or plant data for many reactive systems is not readily available in the open literature).

In the reactive column, a saturated liquid mixture consisting of acetic acid, ethanol and water is fed to stage 6 at a rate of 4885 mol/h in order to produce a top product with at least 52% ethyl acetate composition (product specification). Reaction takes place in all 13 trays of the column, with sulfuric acid as catalyst. The rate of reaction used in this work is taken from Sujuki, Yagi, Komatsu, and Hirata (1971), where an Arrhenius-type expression accounts for the reversible reaction of acetic acid and ethanol to produce ethyl acetate and water. The maximum conversion is obviously limited by the reaction equilibrium conversion.

The mixture is highly non-ideal mainly due to the presence of alcohol, acid and water. Five normal-
Azeotropes exist in this mixture and then the separation of pure components is very difficult. Sujuki et al. (1971) also determined the phase equilibrium for the system taking the reaction into account (they fitted 16 coefficients in a Modified Margules equation, for calculating the VLE-model of this mixture), and this is the thermodynamic model employed in our studies.

2.1. Objectives of this work

The aim of this work is to design a reactive column together with the control scheme able to maintain feasible operation in the presence of given disturbances over a certain time horizon (24 h) subject to:

- A high-frequency sinusoidal disturbance in the acetic acid inlet composition (see Fig. 2);
- A ‘slow-moving’ disturbance in the cooling water inlet temperature representing diurnal, ambient variations (see Fig. 2);
- Product quality specifications;
- Minimum column diameter to avoid flooding;
- Fractional entrainment limits;
- Temperature driving forces in the reboiler and condenser drums;
- Limit on the heat flux in the reboiler;

- Limit on the cooling water outlet temperature;
- Above atmospheric pressure operation;
- Limits on the flowrates of steam and cooling water.

![Fig. 1. Reactive distillation column for the production of ethyl acetate.](image1)

![Fig. 2. Disturbances in acetic acid inlet composition and cooling water inlet temperature.](image2)
In general, the solution of this type of problem will require the determination of:

- the optimal process design, in terms of the number of trays and feed location (discrete decisions), and the column diameter, condenser and reboiler surface areas (continuous decisions); and
- the optimal control scheme design, in terms of the pairings of the manipulated and controlled variables (discrete decisions) and the tuning parameters for the given control structure (continuous decisions).

Thus, the problem can be mathematically represented as a large-scale, mixed-integer dynamic optimization (MIDO) problem. It is made more complex by the fact that there are a large number of structural alternatives, both from a process point of view (number of reactive trays and/or non-reactive trays, feed tray location), and from a control point of view (different pairings of controlled-manipulated variables), and that the optimal control scheme is likely to depend strongly on the process structure and design (and vice versa). Furthermore, due to the large-scale nature of the problem, the time horizon considered must be short enough to reduce the computational effort associated with the solution, yet long enough to capture the important dynamic features so that any conclusions do not change if longer time horizon is considered.

Given also the complexity of the interactions that exist between the physical phenomena (simultaneous reaction and separation) taking place in a reactive column, it is likely that simplified process models are inadequate for realistically portraying the operability characteristics over time, and hence for drawing proper conclusions about the interactions of process design and process control in reactive distillation systems.

In view of all these complexities, in this work a fixed column configuration is used (fixed feed tray location and number of reactive trays), as well as fixed control structure, using the efficient structure found by Schenk (1999) based on a detailed controllability analysis (with an additional pressure control loop). According to this, the process model is first linearized and the relation between process inputs–outputs is quantified. Then, a number of controllability indices are computed including: (i) right half plane zeroes and time delays; (ii) singular values decomposition; (iii) condition number; and (iv) relative gain array. Finally, an extensive analysis of the results obtained is performed. It should be noted that similar structure was also found to be efficient for the synthesis of ETBE (Sneesby, Tade, Datta & Smith, 1997b). So that, by fixing the discrete decisions, the problem can be solved as a dynamic optimization problem. Since the period of the ‘slow-moving’ disturbance in the cooling water temperature is 24 h, it is deemed that these 24 h is an adequate time horizon, whilst rendering the large-scale dynamic optimization problem tractable. It is also assumed that the operation of the process is periodic over 24 h.

In the following sections, first the dynamic model is described and then two state-of-the-art optimization techniques are presented to explore the interactions between design and control in a reactive distillation system.

3. Dynamic model

Due to the complexity and highly constrained nature of the problem described in the previous section, it is likely that a simplified dynamic model using ‘traditional’ assumptions (such as constant molar overflow, constant relative volatility, constant liquid and negligible vapour hold-ups) will be inadequate for capturing the dynamic characteristics of the reactive distillation system over time. We have thus chosen to use and extend a rigorous dynamic model that relaxes many of these assumptions. The basis of this model has been presented in our previous work (Schenk, Gani, Bogle & Pistikopoulos, 1999). It is important to emphasize that this model has been validated against experimental data and a satisfactory agreement was found with the work of Sujuki, Komatsu, and Hirata (1970); Sujuki, Yagi, Komatsu and Hirata (1971). In order to illustrate the detail and rigorous of this model Appendix A shows the equations for a single reactive sieve tray within the column. Models for other units such as heat exchangers are similar but with the addition of heat transfer equations and without the pressure drop equation, flooding and entrainment correlations. The dynamic equations of PI controllers have been properly incorporated into the model. Adequate capital cost equations (Douglas, 1988) (see Appendix B) have also been added to the model in order to calculate the total annualized cost of the column shell, trays, reboiler and condenser drums (assuming a 3 year pay-back period).

The key features, however, which set this model apart from previous works are summarized below:

- dynamic models for every reactive tray, reboiler and condenser (both mass and energy);
- consideration of both liquid and vapour, mass and energy hold-ups;
- accurate representation of the vapour–liquid equilibria using non-ideal physical properties models (in this case, the modified Margules equation for activity coefficients);
- consideration of non-phase equilibrium through use of Murphree tray efficiencies;
- consideration of liquid hydraulics and liquid level on each tray and in the auxiliary units by using modified Francis weir formulae;
- equations for the pressure drop from tray to tray by considering the pressure drop incurred by the vapour in flowing through the openings at the bottom of each tray and the hydrostatic pressure on each tray; and
detailed flooding and entrainment calculations for each tray and subsequent evaluation of ‘critical points’ in the column where constraint on the minimum allowable diameter are most likely to become limiting.

This dynamic model and its steady state analogue have been successfully implemented within gPROMS (Process Systems Enterprise, 2000a). The closed-loop simulation discussed in the following sections typically take about 1 min CPU time on a Dec Alpha 500/500 Server.

4. Sequential design and control

The steps of the sequential approach used for optimal design and control of the reactive distillation system are outlined schematically in Fig. 3.

4.1. Nominal steady-state optimal design

The gPROMS/gOPT (Process Systems Enterprise, 2000b) tools were used to solve the non-linear program (NLP) corresponding to steady-state optimization with the disturbances, cooling water inlet temperature and the feed compositions of ethanol and acetic acid, at their nominal values. Table 1 presents the annualized capital and operating costs along with the optimal values of the continuous design variables. The dominant operating cost is mainly due to the cost of steam.

4.2. Steady-state design under uncertainty

Since the nominal column design is not feasible for the whole range of the disturbance in the cooling water inlet temperatures, $T_{\text{w,in}}$, a multi-period opti-
mization approach was used to obtain an economically optimal and flexible design, as studied by Grossmann and Sargent (1978), Grossmann, Halemane, and Swaney (1983). At least, three degrees of freedom, reflux ratio, steam flowrate and cooling water flowrate (the same as in a normal distillation column) can in principle, be adjusted to offset the effects of the disturbances. The following two cases were considered:

**Case 1:** All three degrees of freedom are allowed to vary depending on the value of \( T_{w,in} \): ‘best-case’ flexible design.

**Case 2:** None of the degrees of freedom are allowed to vary as the value of \( T_{w,in} \) changes: ‘worst-case’ flexible design.

The different optimal designs and resulting annual costs for the two cases are shown in Table 1 where they are also compared with the nominal values. Note that \( D \) refers to the diameter of the column and \( S \) refers to the surface area of the heat exchange coil in the reboiler.

Table 1: Comparison of different economically optimal and flexible designs

<table>
<thead>
<tr>
<th>Design variable</th>
<th>Nominal</th>
<th>Case 1</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D ) (m)</td>
<td>6.09</td>
<td>6.09</td>
<td>6.12</td>
</tr>
<tr>
<td>( S_{\text{Reb}} ) (m²)</td>
<td>280</td>
<td>286</td>
<td>325</td>
</tr>
<tr>
<td>( S_{\text{Cond}} ) (m²)</td>
<td>417</td>
<td>458</td>
<td>498</td>
</tr>
<tr>
<td>Capital cost (million$)</td>
<td>0.45</td>
<td>0.46</td>
<td>0.47</td>
</tr>
<tr>
<td>Operating cost (million$)</td>
<td>3.95</td>
<td>3.99</td>
<td>4.35</td>
</tr>
<tr>
<td>Total cost (million$)</td>
<td>4.40</td>
<td>4.45</td>
<td>4.82</td>
</tr>
</tbody>
</table>

Both, the ‘best-case’ and the ‘worst-case’ flexible (steady-state) designs were dynamically tested in the presence of the sinusoidal feed composition disturbance and the ‘slow-moving’ profile for the cooling water inlet temperature which ranges between suitable lower and upper bounds (Fig. 2). As expected, there were a large number of constraints violations for both designs, and so they both require a control scheme in order for feasibility to be maintained. The pairings of the controlled-manipulated variables in the control structure considered are depicted in Fig. 4. The control loops are \( R−X_d \), \( (F_{\text{steam}}−X_b) \), \( (F_{\text{water}}−P_c) \) where \( R \) is the reflux ratio, \( F_{\text{steam}} \) is the steam flow rate, \( F_{\text{water}} \) is the cooling water flow rate. Finally, \( X_d \), \( X_b \) and \( P_c \) are the distillate and bottom product (ethyl acetate) compositions and pressure in the condenser, respectively.

No set of controller’s tuning parameters (gains, reset times and set-points) could be found for either design that would enable all the system feasibility constraints to be satisfied over the entire time horizon. This was confirmed by solving a dynamic optimization problem for each design where the controller’s tuning parameters were selected to minimize the sum of the constraint violations. For the ‘best-case’ design, the solution of this problem gave large violations in a number of constraints. Although, several attempts were made it was not possible to successfully modify the design and make it controllable. For the ‘worst-case’ design the solution of the dynamic optimization problem showed that the main operability bottleneck was due to violations in the minimum column diameter constraints (related to flooding). There was also one small violation in a thermodynamic feasibility constraint in the reboiler. In this case, the minimum column diameter was modified accordingly and a new steady-state flexible design was obtained (see Table 2). It is interesting to note that the modified design naturally has a larger column diameter while the heat exchanger areas are the same and the total costs of the two designs are very similar. This illustrates how controllability is a strong function of the process design and how careful design

![Control structure in the reactive distillation column.](image)
Table 2
Comparison of unmodified and modified ‘worst-case’ designs

<table>
<thead>
<tr>
<th>Design variable</th>
<th>Case 2</th>
<th>Modified Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D(m) )</td>
<td>6.12</td>
<td>6.3</td>
</tr>
<tr>
<td>( S_{\text{Rab}}(m^2) )</td>
<td>325</td>
<td>325</td>
</tr>
<tr>
<td>( S_{\text{Cond}}(m^2) )</td>
<td>498</td>
<td>498</td>
</tr>
<tr>
<td>Capital cost (million$)</td>
<td>0.47</td>
<td>0.48</td>
</tr>
<tr>
<td>Operating cost (million$)</td>
<td>4.35</td>
<td>4.35</td>
</tr>
<tr>
<td>Total cost (million$)</td>
<td>4.82</td>
<td>4.83</td>
</tr>
</tbody>
</table>

The sequential strategy outlined above illustrates that interactions do exist between process design and process control. However, a more systematic approach for exploiting these interactions is to include the process design variables as optimization variables whilst, at the same time, optimizing the controller tuning parameters. The potential economic benefits of such a simultaneous approach are therefore investigated.

Fig. 5 illustrates the steps of the general mathematical framework for simultaneous design and control as originally proposed by Mohideen, Perkins, and Pistikopoulos (1996). In their formulation, an iterative decomposition strategy alternates between a multi-period design sub-problem (which determines an optimal process design and control system able to tolerate a given set of critical uncertainty/disturbance scenarios) and a time-varying feasibility analysis step (which identifies a new set of critical scenarios for the fixed structure and design). Both sub-problems involve the solution of MIDO problems. In the multi-period sub-problem, integer variables correspond to discrete design decisions (such as the control structure), whereas in the feasibility analysis sub-problem integer variables arise from the active set strategy used to determine new critical scenarios.

As a first attempt in applying this novel technique to a reactive distillation system, and given the complexity and large-scale of the ethyl acetate production, it was decided to address a simplified version of the above problem. This simplification involves fixing the integer decisions pertaining to the existing process and control structure as well as assuming the disturbances take the forms shown in Fig. 2. The resulting problem may then be posed as a dynamic optimization over a fixed time horizon, \( t_f \), as follows:

5. Simultaneous design and control strategy

The sequential strategy outlined above illustrates that interactions do exist between process design and process control. However, a more systematic approach for exploiting these interactions is to include the process design variables as optimization variables whilst, at the same time, optimizing the controller tuning parameters. The potential economic benefits of such a simultaneous approach are therefore investigated.

4.4. Optimal controller tuning (Case 1 and modified Case 2)

Optimal tuning of the controller’s gains, reset times and set-points was carried out for two different cases. In the first case, the expected total annualized cost of the system over the whole time horizon was minimized. In the second case, a normalized integral square error (ISE) function was minimized in order to keep the controlled variables’ values as close to their set-points as possible. These problems correspond to large-scale dynamic optimization problems consisting of approximately 2000 variables (120 differentiable states). The system where the ISE is minimized leads to an ISE of 38 and a total cost of $4.99 million. On the other hand, the system where the total cost is minimized gives an ISE of 135 and a total cost of $4.85 million. This clearly demonstrates the potential trade-off between the quality of control and the economics of the process. A pareto curve of ISE vs. cost could be drawn up by solving the economic problem with an extra inequality constraint to bound the value of ISE. However, given the very high price one has to pay in order to minimize the ISE ($140,000 per year in utility cost), and that all the process feasibility constraints are enforced in both cases, it is logical to use the economically tuned control scheme. Furthermore, the difference in the two ISEs over 24 h operation is not significant and this does not translate to much noticeable tighter control. Thus, it is better to choose the controller’s tuning parameters based on the minimum cost results. Here, the total cost of the system, $4.85 million, is very close to the cost of the original steady-state flexible design, $4.83 million. By paying a slight economic penalty of $20,000 per year it is possible to obtain a fully operational design, over the entire time horizon considered.
\[
\min_{d_p, d_c, t_f} J(d_p, d_c, t_f)
\]
subject to:
\[
F(x_d(t), x_d(t), x_d(t), d_p, d_c) = 0 \quad \forall t \in [t_0, t_f]
\]
\[
q(x_d(t), x_d(t), x_d(t), d_p, d_c) \leq 0 \quad \forall t \in [t_0, t_f]
\]
\[
d_p \in D_p, \quad d_c \in D_c
\]
\[
x_d \in X_d \subseteq \mathbb{R}^{n_d}, \quad x_a \in X_a \subseteq \mathbb{R}^{n_a}.
\]

The large-scale system \( F \) comprises the process model, disturbance description and control scheme equations. \( x_d \) are the differential state variables, \( x_a \) are the algebraic state variables, \( q \) is the set of path inequality constraints, \( d_p \) are the variables being optimized including process decisions (column diameter and heat exchanger areas) and \( d_c \) are the PI controller design decisions (gain, reset time, set point or bias).

The optimal design, controller tuning parameters and associated costs for our reactive system are shown in Table 3 and are compared with the results obtained using the sequential strategy with economically tuned controllers. The simultaneous strategy has the same capital costs and lower operating costs leading to a 5% total annual cost savings ($220,000 per year). It should be emphasised here that an integrated sensitivity analysis would be useful to sustain the gains of the simultaneous approach. However, this is beyond the scope of the present work. It is interesting to note that the simultaneous approach is able to give a fully operational system with an annual cost in between the costs of the ‘best-case’ and ‘worst-case’ while the sequential approach gives a system which is more expensive than the ‘worst-case’ optimal flexible design.

It is also interesting to observe the different control settings adopted by the two approaches. As can be seen from Table 3 and the corresponding dynamic profiles (Figs. 6–8) the simultaneous approach gives tighter bottom product composition control; comparable top product composition and pressure control. Moreover, the ISE for the simultaneous approach is 10% less than of the sequentially obtained system. This clearly demonstrate how a simultaneous approach can exploit the interactions between design and control to give process designs which are less expensive and more satisfactorily controlled than those found by even state-of-the-art sequential approaches. The overall economic impact of this action is the reduction in the operating costs.
Appendix A. Dynamic model of a reactive sieve tray

In a typical distillation column the liquid flows over the tray’s weir down a narrow channel called downcomer and into the liquid held by the tray below. The liquid in the downcomer forms a seal that forces the vapour to flow through the openings in the main tray surface.

A.1. Modelling assumptions

- Perfect mixing of the liquid and vapour phases.
- Thermodynamic and mechanical equilibrium between both phases.
- Negligible ‘weeping’ of liquid through the openings on the tray surface.
- Negligible downcomer dynamics.

A.2. Equations

A.2.1. Component molar balance

\[
\frac{dM_i}{dt} = F_{in,liq} z_{i,in} + F_{in,vap} z_{j,vap} + F_{feed} z_{i,feed} - F_{out,liq} x_i - F_{out,vap} y_i + R_i \quad i = 1, \ldots, NC,
\]

where \( M_i \) is the total molar hold-up of component \( i \); \( F \) refers to the molar flowrate; \( z_i \) refers to the molar fraction of component \( i \) in an inlet stream; \( R_i \) is the rate of reaction for component \( i \) and \( x_i \) and \( y_i \) are the molar fractions of component \( i \) in the liquid and vapour phases, respectively, in an outlet stream. The overall rate of reaction used in the work is as follows (Schenk, 1999):

\[
R = k_1 \exp\left(-\frac{E}{RT}\right) C_{AA} C_{Et} - k_2 \exp\left(-\frac{E}{RT}\right) C_{W} C_{EtAc},
\]

where \( k_1 = 483.3, k_2 = 123, E = 54970.5 \) and \( C_{AA}, C_{Et}, C_{W}, C_{EtAc} \) represent the concentration of acetic acid, ethanol, water and ethyl acetate, respectively.

A.2.2. Energy balance

\[
\frac{dU}{dt} = F_{in,liq} h_{in} + F_{in,vap} h_{vap} + F_{feed} h_{feed} - F_{out,liq} h_{liq} - F_{out,vap} h_{vap},
\]

where \( U \) is the internal energy hold-up and \( h \) refers to molar enthalpies. The heat of the reaction is calculated implicitly and does not need to be separately specified.

A.2.2.1. Component molar hold-up.

\[
M_i = M_{liq} x_i + M_{vap} y_i \quad i = 1, \ldots, NC.
\]
A.2.2.2. Energy hold-up.
\[ U = M^{\text{liq}} \varphi_{\text{liq}} + M^{\text{vap}} \varphi_{\text{vap}} - P V_{\text{tray}}, \]
where \( P \) is the pressure and \( V_{\text{tray}} \) is the free volume between trays.

A.2.3. Volume constraint
\[ M^{\text{liq}} \varphi_{\text{liq}} + M^{\text{vap}} \varphi_{\text{vap}} = V_{\text{tray}}, \]
where \( \varphi \) refers to molar volume.

A.2.3.1. Definition of equilibrium vapour phase composition.
\[ \Phi_i^{\text{vap}} y^*_i = \Phi_i^{\text{liq}} x_i, \quad i = 1, \ldots, NC, \]
where \( \Phi_i \) refers to the fugacity coefficient of component \( i \). The fugacity coefficient for the vapour phase, \( \Phi_i^{\text{vap}} \), can be taken equal to one for the current study (ideal gas phase).

A.2.3.2. Definition of Murphree tray efficiency.
\[ E_{\text{mu},i} = \frac{y_i^* - z_i^{\text{vap}}}{y_i^* - z_i^{\text{vap}}} = \frac{y_i^* - z_i^{\text{vap}}}{y_i^* - z_i^{\text{vap}}}, \quad i = 1, \ldots, NC. \]

A.2.4. Mole fraction normalization
\[ \sum_{i=1}^{NC} x_i = \sum_{i=1}^{NC} y_i = 1. \]

A.2.5. Level of liquid on the tray
\[ L^{\text{liq}} = \frac{M^{\text{liq}} \varphi_{\text{liq}}}{A_{\text{tray}}}, \]
where \( A_{\text{tray}} \) is the active area of the tray.

A.2.5.1. Flow of liquid over the weir. If \( L^{\text{liq}} < h_{\text{weir}} \), then \( F_{\text{out}}^{\text{liq}} = 0 \).
ELSE (modified Francis weir formula for a rectangular notch weir, Coulson, 1990)
\[ F_{\text{out}}^{\text{liq}} = 1.84 \frac{L_{\text{weir}}}{\rho_{\text{liq}}} (L^{\text{liq}} - h_{\text{weir}})^{3/2}, \]
where \( L_{\text{weir}} \) and \( h_{\text{weir}} \) are the length and height of the weir, respectively.

A.2.5.2. Pressure driving force for vapour inlet (McCabe, Smith, & Harriott, 1993).
\[ P^{\text{vap}} - P = z \left( F_{\text{in}}^{\text{vap}} \rho_{\text{in}}^{\text{vap}} \right)^2 \rho_{\text{vap}} + \beta \rho_{\text{liq}} g L^{\text{liq}}, \]
where \( A_{\text{holes}} \) is the total area of all active holes; \( z \) and \( \beta \) are parameters; and \( \rho \) refers to molar density.

A.2.5.3. Tray geometry.
\[ A_{\text{col}} = \frac{\pi}{4} D_{\text{col}}^2, \]
\[ A_{\text{downcomer}} = 0.1 A_{\text{col}}, \]
\[ A_{\text{tray}} = A_{\text{col}} - 2 A_{\text{downcomer}}, \]
\[ A_{\text{net}} = A_{\text{col}} - A_{\text{downcomer}}, \]
\[ V_{\text{tray}} = t_{\text{ap}} A_{\text{tray}}, \]
\[ A_{\text{holes}} \approx 0.12 A_{\text{col}}, \]
\[ L_{\text{weir}} \approx 0.73 D_{\text{col}}, \]
where \( A_{\text{net}} \) is the net area available for the vapour–liquid disengagement; \( t_{\text{ap}} \) is the tray spacing; and \( L_{\text{weir}} \) is calculated using simple circular geometry.

A.2.5.4. Flooding and minimum column diameter calculations (Lygeros & Magoulas, 1986).
\[ u_1 = \left( \frac{u_{\text{liq}}}{20} \right)^{0.20} K_1 \left( \frac{\rho^{\text{vap}} - \rho^{\text{liq}}}{\rho^{\text{liq}}} \right)^{0.5}, \]
\[ F_{\text{in}}^{\text{liq}} = \frac{K_1}{F_{\text{in}}^{\text{vap}}} \left( \frac{\rho^{\text{vap}}}{\rho^{\text{liq}}} \right)^{0.5}, \]
\[ F_{\text{out}}^{\text{liq}} = F_{\text{in}}^{\text{liq}} \sum_{i=1}^{NC} x_i M W_i, \]
\[ F_{\text{vap}}^{\text{vap}} = F_{\text{in}}^{\text{vap}} \sum_{i=1}^{NC} z_i^{\text{vap}} M W_i, \]
\[ u = F_{\text{in}}^{\text{vap}} u_0, \]
\[ u = \frac{F_{\text{in}}^{\text{vap}} F_{\text{vap}}^{\text{vap}}}{A_{\text{net.min}}} \]
\[ A_{\text{col.min}} = \frac{A_{\text{net.min}}}{0.90}, \]
\[ D_{\text{col.min}} = \left( \frac{4 A_{\text{col.min}}}{\pi} \right)^{1/2}, \]
\[ \psi = 0.224 \times 10^{-2} + 2.377 \exp(-9.394 F_{\text{in}}^{\text{vap}}), \]
Here, \( u_t \) is the flooding velocity; \( \sigma_{\text{liq}} \) is the liquid surface tension; \( K_1 \) is an empirical coefficient; \( F_{\text{in}}^{\text{vap}} \) is the Sherwood flow parameter; \( F_{\text{in}}^{\text{liq}} \) refers to mass flowrates; \( u \) is the design velocity for the vapour; \( \psi \) is the fractional entrainment correlation for flooding factor, \( F_{\text{in}}^{\text{vap}} \); and the subscript \( \text{min} \) refers to the minimum allowable magnitude based on the flooding considerations.

A.2.6. Physical properties
\[ h_{\text{liq}} = h_{\text{liq}}(P, T, x), \]
\[ \tilde{h}_{\text{liq}} = \tilde{h}_{\text{liq}}(P, T, x), \]
\[ \Phi_i^{\text{liq}} = \Phi_i^{\text{liq}}(P, T, x), \quad i = 1, \ldots, NC, \]
Appendix B. Cost equations

The total annualized cost of the column is defined by:
\[
C_{\text{total}} = C_{\text{cap}} + C_{\text{op}}.
\]

The total annualized capital cost is calculated as:
\[
C_{\text{cap}} = C_{\text{shell}} + C_{\text{trays}} + C_{\text{reb}} + C_{\text{cond}},
\]

where the annualized installed cost of a column shell (with a 3 year payback), \(C_{\text{shell}}\) (Douglas, 1988) is given as follows:
\[
C_{\text{shell}} = \frac{1}{3} \left( \frac{M&S}{280} \right) 101.9 D_{\text{col}}^{1.066} H_{\text{col}}^{0.528} (2.18 + F_c) F_{\text{fac}},
\]

where \(M&S\) is the Marshall and Swift index taken equal to 1050; \(D_{\text{col}}\) is the column diameter (ft); \(H_{\text{col}}\) is the height of the column (ft) (determined by the tray spacing, number of trays and excess height at the top and bottom of the column). \(F_c\) is a material construction factor, taken with a value of 1; \(F_{\text{fac}}\) is a scale-up factor to account for the fact that Guthrie correlations underestimate real capital costs. A value of 2 was decided similar to the work of Bansal (2000).

The annualized installed cost of a column’s internal (with a 3 year payback), \(C_{\text{trays}}\) is given as follows (Douglas, 1988):
\[
C_{\text{trays}} = \frac{1}{3} \left( \frac{M&S}{280} \right) 4.7 D_{\text{col}}^{1.55} H_{\text{stack}} F_c F_{\text{fac}},
\]

where \(H_{\text{stack}}\) is the height of the tray stack (ft).

The annualized installed cost of a reboiler and condenser (with a 3 year payback), \(C_{\text{reb}}\) and \(C_{\text{cond}}\), respectively is defined as (Douglas, 1988):
\[
C_{\text{reb}} = \frac{1}{3} \left( \frac{M&S}{280} \right) 101.3 S_{\text{reb}}^{0.65} F_c F_{\text{fac}},
\]
\[
C_{\text{cond}} = \frac{1}{3} \left( \frac{M&S}{280} \right) 101.3 S_{\text{cond}}^{0.65} F_c F_{\text{fac}},
\]

where \(S_{\text{reb}}, S_{\text{cond}}\), are the areas of the reboiler and condenser, respectively, and \(F_{\text{fac}}\) is the scale-up factor. A value of 3 is taken for this factor in the reboiler and condenser equations.

The annualized operating cost, \(C_{\text{op}}\), is calculated as follows:
\[
C_{\text{op}} = C_{\text{steam}} + C_{\text{water}},
\]

where, the annualized average steam, \(C_{\text{steam}}\), and cooling water cost, \(C_{\text{water}}\) are calculated as:
\[
C_{\text{steam}} = F_{\text{steam}} \text{Cost}_{\text{steam}} 8150; \quad C_{\text{water}} = F_{\text{water}} \text{Cost}_{\text{water}} 8150.
\]

References


