# Optimal Operation of Extractive Distillation in Different Batch Configurations

**K. H. Low and E. Sørensen**
Dept. of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, U.K.

*Optimal operations of extractive distillation for regular and middle-vessel batch columns are presented based on a profit function. Detailed models are used for the rigorous dynamic optimization considering all operational decision variables, including reflux ratio, solvent feed rate, heat duties, and possible product withdrawals during the process. Optimal feed distribution and stream configuration at the middle section of the middle-vessel column are investigated. Separation of a minimum boiling azeotropic binary mixture (acetone and methanol using water as solvent) involving different separation duties and feed compositions is presented as a case study. The performance of the middle-vessel column is significantly influenced by the middle-section stream configuration, with the best profit when the stream configuration is allowed to vary during the operation. The optimal operating policy for the middle-vessel column involved the feed being charged mainly to the reboiler still with low holdup in the middle vessel during the operation.*

## Introduction

Azeotropic and low-relative volatility mixtures are commonly encountered in the fine-chemical and specialty industries, and many chemical processes depend on efficient and economical methods for their separation. These mixtures can be separated in a distillation column by altering the relative volatilities or shifting the azeotropic point to a more favorable position. Extractive distillation is defined as distillation in the presence of a miscible, high-boiling, relatively nonvolatile component—the solvent, which forms no azeotropes with other components in the mixture (Ruthven, 1997). The solvent breaks the azeotrope by altering the relative volatilities of the various components, which in the batch mode, permits the sequential withdrawal of different cuts, each one rich in one of the components of the feed from the reflux drum at the top. The solvent is retrieved in the bottom stream and can be reused.

Extractive distillation is widely used in the chemical industry and is commonly applied in a continuous multicolumn mode. In the current highly competitive environment of changing duty and demand, batch extractive distillation provides an attractive single-column alternative affording flexibility to tackle multiple feeds and product demand. However, no industrial attempt has been reported so far in the open literature to realize extractive distillation in a batch system. In this article, we attempt to study the operation of extractive distillation conducted in the batch mode using various column configurations.

Bernot et al. (1990) introduced a graphical technique that can be used to determine the sequence of distillate fractions in a batch distillation column from an initial composition. The method involved defining the different batch distillation regions on the state composition map in the limiting case of infinite number of stages and reflux or reboil ratio. Bernot et al. (1991) extended their method of sequence and feasibility prediction for inverted columns and quaternary mixtures.

Yatim et al. (1993) were the first to consider the application of batch extractive distillation via a pilot-plant column and a computer model for comparison. They proposed and simulated a four-step operating procedure for extractive batch distillation of binary minimum azeotrope mixtures. The model included dynamic material and energy balances, but constant liquid holdup and negligible vapor holdup was assumed. The group added some parametric studies in a later article (Lang et al., 1994). Using a similar model, the effects of various parameters like reflux ratio, solvent feed rate, solvent feed tray, reboiler heat duty, batch size, and feed composition were

Correspondence concerning this article should be addressed to E. Sørensen.

investigated using the method of varying one parameter individually while keeping the others constant. Although an optimal operation cannot be determined from these results as the parameters are interdependent; nonetheless, the parametric analysis demonstrated the significant effects of the operation parameters on the separation performance of the extractive batch distillation. Lang et al. (2000) investigated the performance of batch extractive distillation for the separation of maximum azeotropes. Again, the effects of various parameters were studied via simulation.

Safrit et al. (1995) is the first published work analyzing the potential of middle-vessel column for extractive distillation. In their article, the graphical analysis for continuous extractive columns by Wahnschafft and Westerberg (1993) was extended to batch distillation. Using the insight of the pinch-point curve technique, they were able to explain how the middle vessel can be steered toward the intermediate component to achieve high recovery in the distillate. They also noted that while the steering of the still path in the extractive middle-vessel column does determine the "optimal" solvent withdrawal-to-addition ratio, the flexibility of the middle-vessel column allows for many other column parameters to be optimized. For example, the results of their simulation show that although the recovery has been improved, large reflux and reboil ratios resulted in a long processing time. Safrit and Westerberg (1997) conducted simulation studies to find the sensitivity of the column parameters to a profit function, in particular, solvent flow rate and switching time between operational steps. Their work highlighted the need for a full optimal control study involving a wide range of degrees of freedom to find the best economic performance.

Lelkes et al. (1998a) extended the work of Lang et al. (1994) by considering other operating policies for the regular column. Instead of a constant reflux ratio during the last two steps of the operating procedure by Yatim et al. (1993), a constant distillate composition policy and a mixed policy of constant reflux ratio and constant distillate composition were considered and simulation results were compared to experimental results. Improvements in production rate, batch-processing time, energy, and solvent consumption were obtained in some cases. This again highlighted the need for rigorous optimization to explore the full potential of the batch extractive distillation.

Lelkes et al. (1998b) presented a method to assess the feasibility of batch extractive distillation for a ternary mixture using a graphical technique. When they compare the regular column to the middle-vessel column, they found, contrary to Safrit et al. (1995), that the middle-vessel column achieved smaller recovery under the same conditions. Warter and Stichlmair (1999) also compared the middle-vessel column with the regular column for batch extractive distillation. For the middle-vessel column, novel modifications of the stream configuration were proposed. The operation procedure is similar to Safrit et al. (1995) with constant solvent rate, fitted for every process, and constant product-composition withdrawal. The results showed that the temperature in the feed vessel, the solvent, and energy demand for the middle-vessel processes were significantly lower than those of the regular batch column. The comparisons were made via simulation without considering the full range of degrees of freedom available to each column configurations.

Milani (1999) conducted an experimental study on a batch distillation of acetone–methanol in a batch-feeding mode, whereby the solvent (that is, water) was charged together with the feed into the reboiler at the beginning of the operation. The purity and recovery of the acetone product were measured for various solvent-to-feed ratios. However, the operation of the column was not described, thus, the meaning of the results were vague. The results suggested no distinct trend between feed ratios and acetone purity, recovery, and productivity, but no explanation was given.

Studies so far have demonstrated the choice of various operating parameters has a significant effect on the performance of the batch operation (Yatim et al., 1993; Safrit et al., 1995; Safrit and Westerberg, 1997; Warter and Stichlmair, 1999; Milani, 1999). Despite this, to the best of our knowledge, no rigorous optimization studies have been reported in the literature. Recently, Mujtaba (1999) attempted dynamic optimization of batch extractive distillation for a regular column. However, he decomposed the overall optimization problem to separate independent single-period dynamic optimization problems. Reflux ratio and solvent feed rate were the resulting optimization variables after the decomposition. With this decomposition method, certain maximum time constraints were also needed to avoid exceeding the capacity of the reboiler.

The use of unconventional columns for batch extractive distillation has been proposed for a few years now, that is, the middle-vessel column by Safrit et al. (1995). The advantages of this complex column over the regular column, for example, with respect to product recovery, were claimed in the literature by Safrit et al. (1995) and Warter and Stichlmair (1999), but proved otherwise by Lelkes et al. (1998b). There are more decision variables available to this configuration, which increases the flexibility as well as the complexity of the column. Studies so far have mainly involved feasibility and column sequencing, as well as comparative studies via simulation.

Recently, Ruiz Ahon and de Medeiros (2001) presented an optimization study on extractive distillation of a near-azeotropic mixture with the solvent wholely charged together with the feed at the beginning of the operation. A simplified pseudostationary cascade model was used that assumed instantaneous dynamic response and McCabe–Thiele approximation. Due to this modeling simplication, the column initialized to a state of pure components at the top and bottom, causing immediate withdrawal. Thus, the full operating procedure, that is, similar to the steps described by Yatim et al. (1993) and others, was not investigated. Only one decision variable was considered, namely, the product fraction profile, while other degrees of freedom, like solvent rate and vapor boilup rate, were set as constant. Purity constraints were removed to ease optimization, and were replaced by a price function whereby every cut has a value corresponding to its purity. This is at odds with the fundamental purpose of industrial batch distillation, which is to obtain a predefined sufficient separation. Their work highlighted the difficulty in solving optimization problems associated with transient operation, nonideal systems, and complex configurations without discarding realistic models, degrees of freedom, and indeed, fundamental conditions like obtaining required product purities.

This work presents a first rigorous optimization case study of batch extractive distillation that explores the wide range of degrees of freedom available, including feed placement and stream configuration. Detailed models that take tray hydraulics, variable holdup, and operation practicalities into account are used. Optimal operations are obtained via a rigorous dynamic optimization technique based on a profit objective function. In the next section, we outline the different column configurations for batch extractive distillation and their degrees of freedom before introducing the optimization formulation and key features of our model. Next, the solution methodologies for the dynamic simulation and the optimization problem are presented. This is followed by a description of a case study involving the extractive separation of a binary minimum boiling mixture using both regular and middle-vessel columns. Finally, we compare the optimal operation of both columns.

## Column Configurations and Degrees of Freedom

The regular and middle-vessel column configurations for batch extractive distillation are shown in Figure 1. In the regular column, feed is charged into the reboiler. During operation, solvent may be added between the rectifying and extractive sections while product and offcuts are withdrawn from the top. The solvent is recovered in the reboiler at the end of the operation. The operating policy can be sufficiently described by the reboiler heat duty $Q_{\text{reb}}$, reflux ratio, $R(t)$, and solvent feed rate, $F_{\text{sol}}(t)$.

The middle-vessel column is split into three sections. Similar to the regular column, the rectifying section is above the point of solvent addition. Below the solvent feed point, the middle vessel is placed between the extractive and stripping sections. Due to the flexibility of this column, the feed can be charged either to the middle vessel or to the reboiler; hence, three different alternatives can be considered, namely, feed placed mainly in the middle vessel, feed placed mainly in the reboiler drum, and feed optimally distributed between these two. Previous studies on this column were always conducted with feed placed in the middle vessel. In this study, we relax this assumption and consider feed placement as a degree of freedom. We also allow material to be withdrawn into accumulators during the operation from both the reboiler, flow rate $F_{\text{reb}}(t)$, and the middle vessel, flow rate $F_{mv}(t)$.

Most studies on middle-vessel column involved only a fixed middle-section stream configuration. However, there are several combinations of vapor and liquid stream connections possible between the column and middle vessel, as shown in Figure 2. Studies on middle-vessel columns concentrated mostly on configuration A. The reason for this may be due to the practicality of this configuration where liquid stream, as a result of weir overflow of the bottom extractive tray, is diverted into a middle vessel. The liquid stream from the middle vessel is fed back into the column at the top stripping tray, and its feed rate, $L_{mv}(t)$, can be optimized. This configuration can operate without the addition of heat in the middle vessel, and can be easily modified from an existing regular column. In our study, the effect of the middle-section stream configuration on the column operation and performance is investigated.

Together with the initial feed distribution in the reboiler and middle vessel, $M_{\text{reb}}(0)$ and $M_{mv}(0)$, reboiler and middle-vessel heat duties, $Q_{\text{reb}}$ and $Q_{mv}(t)$, reflux ratio, $R(t)$, solvent feed rate, $F_{\text{sol}}(t)$, and both middle and bottom withdrawals, $F_{\text{reb}}(t)$ and $F_{mv}(t)$, the optimization determines all degrees of freedom available, and hence the best operating policy for the given feed composition and product requirement without any prior specification on feed placement or middle-section stream configuration. The degrees of freedom for both columns are summarized in Table 1.

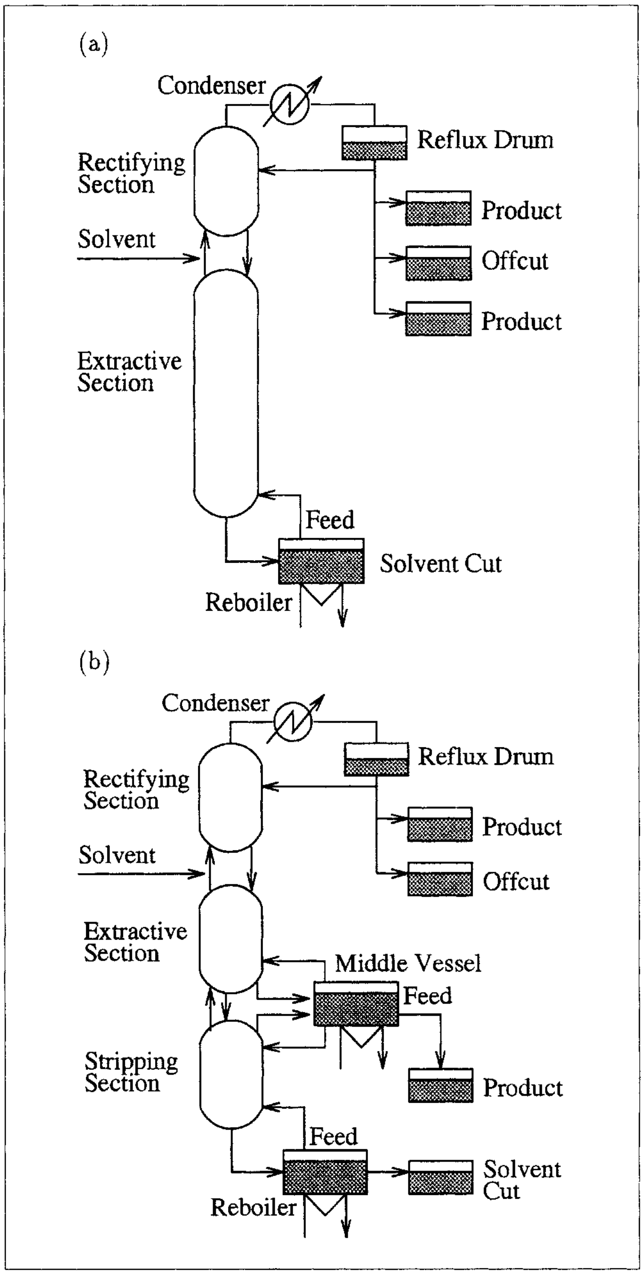



**Figure 1. Batch column configurations for extractive distillation.**

(a) regular column; (b) middle-vessel column.

## Optimization Formulation

The degree of purity of the main products is normally driven by customer demand, and distillation is undertaken to achieve these specifications. The optimal operation of batch

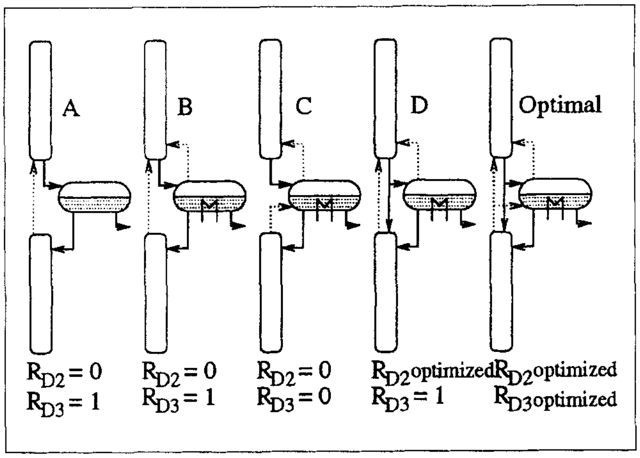



**Figure 2. Stream configurations at the middle section.**

distillation is dictated by the economics of the process, that is, to achieve the greatest profit at the shortest possible duration. The optimization problem considered here is therefore to find the operating variables (see Table 1) that maximize the operating profit per unit time. The profit can be calculated by taking into account sales revenue, inventory cost, utility cost, waste cost, and capital investment interest. If the *operation* of a column is to be considered, the capital investment costs associated with any existing column are fixed *a priori*, and thus would not be involved in any operating tradeoff (unlike optimal design studies, where this parameter must be included to account for the interaction between column sizing and the operation performance afforded by a particular column size). Provided the value of the desired products is greater than that of the cost associated with waste, the neglect of the waste cost parameter in the objective function would not affect the operation's optimal profile results. Since a significant fraction of the solvent used can be recovered at the end of the batch, only the makeup solvent is included in the objective function

$$\text{Profit} = \frac{\text{Sales revenue} - \text{feed cost} - \text{solvent cost} - \text{reboiler duty}}{\text{Batch processing time}} \tag{1}$$

Mathematically, the optimization problen can be written as

$$\max \frac{\sum_{i=1}^{N_C} C_i H_{A,i}(t_f) - C_{\text{feed}} H_{\text{feed}} - C_{\text{sol}} H_{\text{sol}}^{\text{makeup}} - C_Q \int_0^{t_f} Q_T(t)\,dt}{t_f} \tag{2}$$

subject to

- Model equations (equality constraints)
- Control variable bounds
- Product purities (inequality constraints)

$$x_{A,i}(t_f) \geq x_{A,i}^{\min} \qquad \forall i = 1, \ldots, N_C \tag{3}$$

- Recovered solvent purity (inequality constraints)

$$x_{A,\text{sol}}(t_f) \geq x_{\text{feed, sol}} \tag{4}$$

- Product and solvent recovery (inequality constraints)

$$\frac{H_{A,i}(t_f)}{H_{\text{feed},i}} \geq \Pi_i^{\min} \qquad \forall i = 1, \ldots, N_C \tag{5}$$

$$\frac{H_{A,\text{sol}}(t_f)}{\int_0^{t_f} F_{\text{sol}}(t)\,dt} \geq \Pi_{\text{sol}}^{\min} \tag{6}$$

If solvent feed rate is much higher than the distillate flow rate and withdrawals, the possibility exists that the reboiler drum may overflow, leading to operational problems. To prevent this situation from arising, a constraint is placed on the liquid level ($l_{\text{reb}}$) in the reboiler drum during the optimization:

$$l_{\text{reb}}(t) < \frac{v_{\text{reb}}}{A_{\text{reb}}} \qquad \forall t \in [0, t_f] \tag{7}$$

where $C_i$, $C_{\text{feed}}$, $C_{\text{sol}}$, and $C_Q$ represent the unit costs of product $i$, feed, solvent, and heating, respectively; $H_{A,i}$, $H_{\text{feed}}$, and $H_{\text{sol}}^{\text{makeup}}$ refer to the amounts of product $i$, feed, and makeup solvent, respectively; $Q_T(t)$ represents the total reboiler and middle-vessel heat duty; $t_f$ is the total batch processing time; $x_{A,i}$ and $x_{A,\text{sol}}$ refer to the recovered product and solvent purity respectively, and $x_{\text{feed,sol}}$ is the purity of

**Table 1. Decision Variables Considered**

| Column Configuration | Feed Location | Optimization Decision Variables |
|---|---|---|
| Regular | Reboiler drum | $Q_{\text{reb}}$, $R(t)$, $R_{\text{sol}}(t)$ |
| Middel vessel | Optimally distributed | $Q_{\text{reb}}$, $R(t)$, $F_{\text{sol}}(t)$, $L_{mv}(t)$, $F_{\text{reb}}(t)$, $M_{\text{reb}}(0)$, $M_{mv}(0)$, $R_{D2}$, $R_{D3}$, $Q_{mv}(t)$, $F_{mv}$(t) |

the solvent feed; and $\nu_{reb}$ and $A_{reb}$ are the reboiler volume and cross-sectional area, respectively. $H_{sol}^{makeup}$ is defined as

$$H_{sol}^{makeup} = \int_0^{t_f} F_{sol}(t)\, dt - H_{A,sol}(t_f) \qquad (8)$$

where $F_{sol}(t)$ is the solvent feedrate, and $H_{A,sol}(t_f)$ is the amount of solvent recovered at the end of the batch.

## Mathematical Model

In this study, a detailed model similar to that proposed by Furlonge et al. (1999) is used. The level of abstraction used disposes of the common modeling assumptions, such as negligible tray holdup and constant molal overflow, that may have a significant impact on the optimal solutions obtained, as demonstrated by Tomazi (1997) and Furlonge et al. (1999). The model includes the following main features:

- Dynamic energy balance instead of relying on the usual assumption of constant molal overflow.
- Takes account of both liquid and vapor tray holdups, their combined value being a function of the prevailing pressure and the intertray spacing.
- Tray hydraulics, the liquid flow rate from the tray being determined by a modified Francis weir formula.
- Pressure drop–vapor flow rate relationship that takes into account both dry and wet head losses on each tray.
- Rigorous thermodynamic model that replaces the usual constant relative volatility assumption through the use of liquid and vapor fugacities, which are a function of temperature, pressure, and composition.

Dynamic material and energy balances are used to model the accumulator, reflux drum, vessels, and reboiler. In each of these, both liquid and vapor holdups are taken into account. The condenser model assumes total condensation with no subcooling. The model assumptions retained include no entrainment effects, no downcomer dynamics, adiabatic operation with regards to the column's outer environment, phase equilibrium, and perfect mixing.

The model is constructed using the *gPROMS* modeling tool (Process Systems Enterprise Ltd., 2000). A schematic diagram of the column is shown in Figure 3 for the middle-vessel configuration. The rectifying, extractive, and stripping sections consist of a given number of trays. The stream configuration in the region between the extractive and stripping section is modeled using simple dividers (D2 and D3). Thus, the connections would encompass all the stream configurations possible in this region, and the split fractions, $R_{D2}$ and $R_{D3}$, can be treated as control variables to be determined by the optimization.

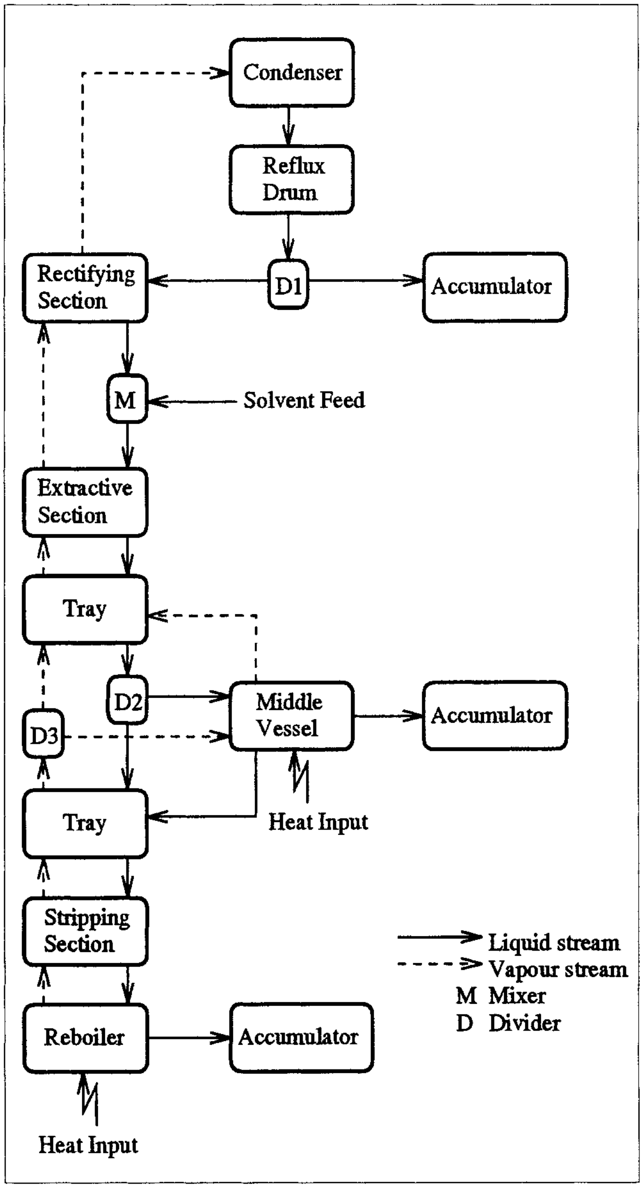



**Figure 3. Batch extractive distillation in a middle-vessel column.**

## Solution Methodology

### *Dynamic simulation*

The mathematical model describing the dynamic behavior of a batch distillation column consists of a set of differential and algebraic equations (DAE). Implicit numerical integration techniques were found to be better suited than explicit techniques, as they overcome the stiffness problem often exhibited by the batch distillation model. The *gPROMS* software (Process Systems Enterprise Ltd., 2000) used employs the backward differentiation formula approach, which is a class of implicit methods with varying time step and order of integration.

### *Dynamic optimization*

The optimization of batch distillation operations involves the solution of a dynamic optimization problem. A nonlinear programming technique is used in this article. The approach involves transforming the dynamic optimization problem, which is of infinite dimension, into a finite-dimensional nonlinear programming (NLP) problem. The control variable is restricted to a predefined form of temporal variation, that is, piecewise-constant, while the time horizon is discretized into a number of control intervals. The discretization technique used in this work is control vector parameterization (CVP) where the DAE system itself is not discretized, only the control variables, and integration is required in each iteration to evaluate the objective function and the constraints. The resulting finite-dimensional NLP problem is then solved using a sequential quadratic programming technique (Process Systems Enterprise Ltd., 2000).

In order to use the CVP technique, a feasible solution of the model equations must exist for every possible value that the optimization decision variables may take. In the middle-vessel column, for instance, the reflux flow rate ($L_{mv}$) from the middle vessel is allowed to vary within certain bounds in the optimization. Since the reflux flow rate may exceed the inlet flow rate ($L_{mv}^{in}$) to the middle vessel (which depends on the column equations), the liquid holdup ($M_{mv}$) in the middle vessel, determined by the equation

$$\frac{dM_{mv}}{dt} = L_{mv}^{in} - L_{mv} \tag{9}$$

may fall below zero. This situation is physically unrealistic and must be avoided. A technique (Furlonge et al., 1999) is employed whereby the mass balance just given is modified to

$$\frac{dM_{mv}}{dt} = L_{mv}^{in} - L'_{mv} \tag{10}$$

where $L'_{mv}$ is the *effective* reflux flow rate related to the control variable, $L_{mv}$, via

$$L'_{mv} = L_{mv}(1 - e^{-(M_{mv} - M^{\min})/M^*}) \tag{11}$$

where $M^*$ and $M^{\min}$ are constant holdup values. These are chosen such that, for $(M_{mv}(t) - M^{\min}) \gg M^*$, the preceding equation reduces to $L'_{mv} \approx L_{mv}$. On the other hand, as $M_{mv}(t) \to M^{\min}$, $L_{mv}$ tends to zero. Hence, assuming that the initial holdup value $M_{mv}(0) > M^{\min}$, $M_{mv}(t)$ can never become negative for any control profile of $L_{mv}(t)$.

Similarly, the effective liquid withdrawal rate, $F_{mv}(t)$, and effective middle-vessel heat duty, $Q_{mv}(t)$, are also used. The same technique is also employed to prevent the reboiler drum from going dry using an effective liquid flow rate leaving the reboiler drum, $F_{reb}(t)$, and an effective reboiler heat duty, $Q_{reb}$.

## Case Study: Separation of a Binary Azeotropic Mixture

Separation of an acetone–methanol mixture using water as solvent, a well-known industrial application, is considered. Many studies [Yatim et al. (1993) to Milani (1999)] have presented this mixture and solvent as their case study; therefore, the same are used here for easy comparison. The mixture forms a minimum boiling azeotrope at 55°C with about 0.8 mole fraction of acetone (Lang et al., 1994). The feed composition is 50 mol % each, and the batch size is taken to be 100 mol plus 5.7 mol initial total holdup on the trays.

The product specification for the acetone cut is 93 mol %, while the specification for water is 99 mol %, matching the initial purity of the solvent so the recovered solvent cut can be reused in successive batches. For the methanol-rich cut, it is either treated as an offcut or a product specification of 93 mol % is imposed on it. If it is treated as an offcut, it has negligible sale value. The cost parameters needed in the objective function are given in Table 2.

**Table 2. Cost Parameters for Case Study**

| | |
|---|---|
| Sale price of acetone, $C_1$ (\$/mol)* | 1.358 |
| Sale price of methanol, $C_2$ (\$/mol)* | 0.606 |
| Sale price of methanol, $C_2$ (\$/mol)** | 0.001 |
| Cost price of feed, $C_{feed}$ (\$/mol)* | 0.298 |
| Cost price of water, $C_{sol}$ (\$/mol)* | 0.0038 |
| Heating cost, $C_Q$ (\$/MJ)† | 0.019 |

*Taken from Mujtaba (1999).
**If treated as offcut.
†Taken from Sinnott (1993).

### Column configurations

The regular and middle-vessel tray column configurations are shown in Figure 1. Both columns have the same number of trays. The condenser pressure in both cases is atmospheric. Table 3 shows the column dimensions and other characteristics. The typical values of coefficients such as wall-correction factor, aeration coefficient, tray and condenser vapor flow coefficients were obtained from Perry and Green (1984).

The rectifying section of the regular column consists of six s. Below the point of solvent addition, the extractive section consists of 24 trays. Depending on the specifications, two or three overhead accumulators are used to collect the acetone product, methanol product, and offcut. The recovered solvent is taken to be the final content of the reboiler drum.

Similarly, the rectifying section of the middle-vesel column also consists of six trays. Both the extractive and stripping sections consist of 12 trays each, making the total number of trays equivalent to that of the regular column. An overhead accumulator is used for collecting the acetone product and another accumulator is made available for a possible offcut. The methanol-rich cut is produced in the middle vessel rather than being withdrawn overhead. The recovered solvent is taken to be the final content of the reboiler drum together with the liquid withdrawn to the bottom accumulator.

### Thermophysical model

Thermophysical properties, including density, enthalpy, and fugacity, are calculated using the *Multiflash* (Infochem Computer Services Ltd., 2000) physical-properties package inter-

**Table 3. Column Dimensions and Other Characteristics**

| | | |
|---|---|---|
| Accumulator | Volume | 0.0151 $m^3$ |
| Reflux drum | Volume | 0.000079 $m^3$ |
| Reboiler drum | Cross-sectional area | 0.03 $m^2$ |
| | Volume | 0.012 $m^3$ |
| Middle vessel | Volume | 0.012 $m^3$ |
| Trays | Number of trays | 30 |
| | Volume | 0.00012 $m^3$ |
| | Weir height | 0.006 m |
| | Weir length | 0.018 m |
| | Plate area | 0.00196 $m^2$ |
| | Total hole area | 0.0002244 $m^2$ |
| | Wall correction factor | 0.98 |
| | Aeration coefficient | 0.6 |
| | Tray vapor-flow coefficient | 0.003 |
| | Scale parameter | 1.0 |
| Condenser | Vapor-flow coefficient | 0.04 |

**Table 4. Wilson Binary Interaction Parameters**

| | $\lambda_{1,2}-\lambda_{1,1}$ | $\lambda_{2,1}-\lambda_{2,2}$ |
|---|---|---|
| Acetone (1) methanol (2) | −478.6693 | 2,281.5109 |
| Acetone (1) water (2) | 1,440.6960 | 6,201.5804 |
| Methanol (1) water (2) | 374.2201 | 2,178.3820 |

*Source:* Gmehling and Onken, 1977.

faced to *gPROMS*. The pressure range of the system is 1 bar with no liquid–liquid heterogeneity, hence, the Wilson model is chosen for the polar liquid phase while the Soave–Redlich–Kwong equation of state is used for the vapor phase.

The Wilson binary interaction parameters were obtained from Gmehling and Onken (1977), as shown in Table 4. The consistency of the parameters was checked by performing simple boiling-point flash calculations at atmospheric pressure, and the results obtained closely matched the values given by Safrit et al. (1995).

### *Initial conditions*

The startup period of operation, that is, starting from when the column is initially dry and cold feed is placed in the reboiler drum, is not simulated. Rather, it is assumed that the initial liquid composition throughout the column is that of the feed (50 mol %), and the liquid is at its boiling point (i.e., 330 K). This was shown by Sadotomo and Miyahara (1983) to be a reasonably accurate approximation for tray columns. The initial liquid holdup on the trays is 0.19 mol to allow liquid flow over the weir from the very beginning of the operation. The reflux drum and all accumulators are assumed to be empty at the start.

### *Bounds on decision variables*

For a fixed-column design, the operation is likely to be most profitable when operated at maximum available reboiler heat duty to provide maximal column loading and shorter process time. Thus, the optimal *time invariant* reboiler heat duty is determined. All other control variables are allowed to vary in a *piecewise-constant* manner. The bounds placed on the optimization decision variables are shown in Table 5.

### *Case I: single product*

The separation duty involving only one main product (acetone) and solvent recovery is considered (Table 6). The

**Table 5. Decision Variables Bounds**

| Decision Variables | Bounds |
|---|---|
| $Q_{reb}$ (kW) | [0.5, 20] |
| $Q_{mv}(t)$ (kW) | [0.5, 20] |
| $R(t)$ | [0.5, 1] |
| $R_{D2}(t)$ | [0, 1] |
| $R_{D3}(t)$ | [0, 1] |
| $F_{sol}(t)$ (mol/s) | [0, 0.1] |
| $L_{mv}(t)$ (mol/s) | [0.1, 1] |
| $F_{mv}(t)$ (mol/s) | [0, 0.5] |
| $F_{reb}(t)$ (mol/s) | [0, 0.5] |
| $M_{mv}(t)$ (mol) | [10, 90] |
| $M_{reb}(t)$ (mol) | [10, 90] |

**Table 6. Optimization Cases Considered**

| Case | Separation Duty (Purity) | Middle-Stream Configuration | Recovery Constraint |
|---|---|---|---|
| I | Acetone (93 mol %)<br>Solvent (99 mol %) | A | ≥ 20% |
| II | Acetone (93 mol %)<br>Methanol (93 mol %)<br>Solvent (99 mol %) | A, B, C, D, and optimal | ≥ 20% |

operating duration is divided into four time intervals (Yatim et al., 1993) for both regular and middle-vessel columns, the durations of which are allowed to vary in the optimization. In the case of the regular column, all of the feed is initially charged to the reboiler drum. The reflux ratio, $R(t)$, the reboiler heat duty, $Q_{reb}$, and the solvent feed rate, $F_{sol}(t)$, are optimized. The column is operated under total reflux (i.e., $R(t)=1$) in the first interval. All other decision variables in this interval, and all decision variables for the subsequent intervals, are free to be determined by the optimization. The acetone product cut is collected in the first overhead accumulator during the first three intervals. In the last interval, a methanol-rich offcut is withdrawn into the second accumulator while the solvent concentrates in the reboiler.

The simplest and most practical middle-vessel column configuration (configuration A) is considered with three different feed locations, namely, feed placed mainly in the middle vessel (90%), feed placed mainly in the reboiler drum (90%), and feed optimally distributed between these two. The reflux ratio, $R(t)$, the reboiler heat duty, $Q_{reb}$, the solvent feed rate, $F_{sol}(t)$, the reflux flow rate from the middle vessel, $L_{mv}(t)$, and the bottom product withdrawal flow rate, $F_{reb}(t)$, are optimized in all three situations. Similar to the regular column, except that the reflux ratio in the first interval is set to total reflux, the rest of the decision variables are optimized throughout the duration of the operation. The acetone product is collected in the first top accumulator, while high-purity solvent recovery is collected in the reboiler and bottom accumulator. A summary of the optimization results for case study I is given in Table 7.

*Optimal Operating Policy for Regular Column.* Although four control time intervals were allowed in the optimization, the optimal operating policy suggests only three steps are required to fulfil the separation duty. As can be seen from the

**Table 7. Optimal Results for Case Study I**

| Column | Regular | Middle Vessel | | |
|---|---|---|---|---|
| Feed location | Case $a^*$ | Case $a^*$ | Case $b^{**}$ | Case $c^\dagger$ |
| Reboiler/middle vessel (mol) | 100/– | 90/10 | 10/90 | 90/10 |
| Operating profit ($/h) | 149.8 | 122.5 | 111.8 | 122.5 |
| Batch-processing time (min) | 16.6 | 18.9 | 21.5 | 19.0 |
| Heat consumption (MJ) | 19.9 | 20.2 | 22.4 | 20.3 |
| Acetone recovery (%) | 93.0 | 89.3 | 91.3 | 89.7 |
| Methanol recovery (%) | — | — | — | — |
| Solvent recovery (%) | 69.9 | 52.0 | 52.7 | 52.2 |
| Amount solvent used (mol) | 78.2 | 94.8 | 96.4 | 95.4 |

*Reboiler Drum.
**Middle vessel.
†Optimized.

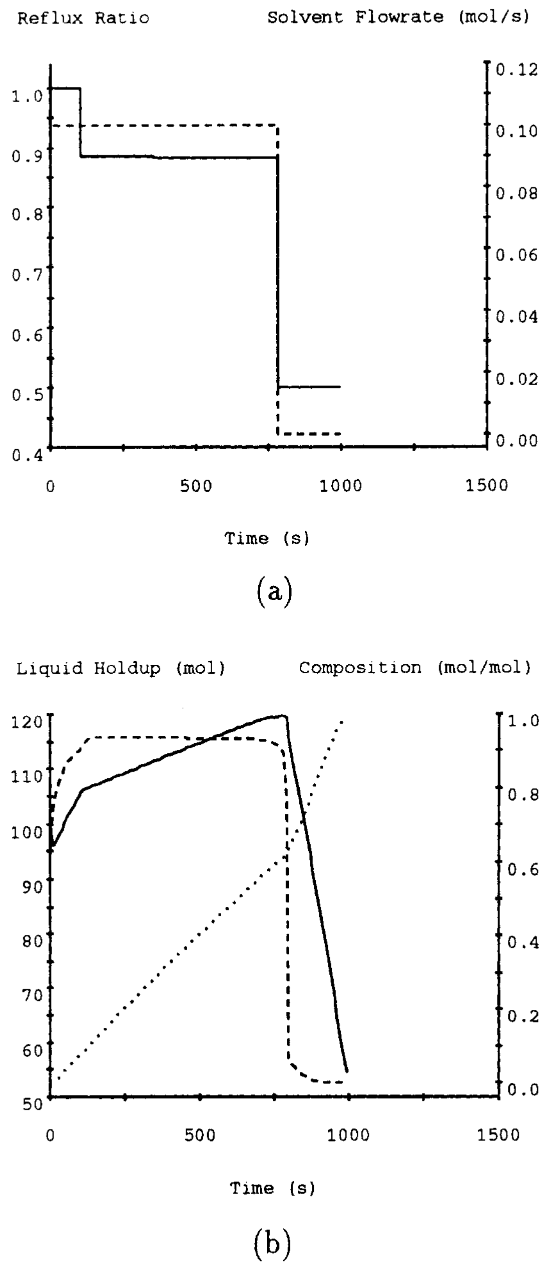



**Figure 4. Case I optimal results for regular column.**

(a)——Reflux ratio, - - - $F_{sol}$; (b)——reboiler holdup, - - - composition of acetone in distillate, ... composition of solvent in reboiler.

reflux ratio profile in Figure 4, the first step is a short period of total reflux operation (121 s duration), with solvent introduced right from the very beginning of the process. Thus, the first period of total reflux without solvent addition, as proposed by Yatim et al. (1993), is found here to be redundant for this case, reducing the minimum number of operation steps required to three. The acetone composition in the distillate rises steeply and above the azeotropic composition (80 mol %) during this period. The reboiler holdup slightly dips before rising due to the introduction of the solvent.

Withdrawal of the acetone product cut occurs in the second period of operation. The withdrawal period is relatively lengthy compared to the first period due to the high reflux ratio required to maintain a high distillate composition. This reflux ratio is maintained at the same value (0.884 and 0.883) in the two intervals (of 282 s and 520 s). Solvent feed rate and reboiler duty close to the maximum bounds are chosen. The reboiler liquid holdup gradually increases, as solvent addition exceeds the product removal rate.

In the final period of operation (217 s duration), solvent feeding terminates and solvent purification takes place. This involves the withdrawal of a methanol-rich cut overhead. Intuitively, a low reflux ratio is used in order to reduce the length of time taken, particularly since no specification is placed on the purity of the methanol-rich cut, as it is treated as a waste cut. The reboiler liquid holdup dips sharply as the offcut is withdrawn into the second accumulator at the top, until the purity specification on the solvent in the reboiler (99 mol %) is reached.

*Optimal Operating Policy for Middle-Vessel Column.* The optimal operation of the middle-vessel column with feed mostly charged to the reboiler drum (Table 7, case *a*) is found to be quite similar to the optimal operation of the conventional regular column. Again, only three operation steps are required (Figures 5 and 6).

The first total reflux period (277 s) is much longer than that of the regular column. Again, the maximum allowable solvent feed rate is introduced to the column from the very beginning. A high reflux flow rate from the middle vessel is selected that maintains a low liquid holdup in the middle vessel (Figure 6). Note that the effective reflux flow rate, $L'_{mv}$, is lower than its control value, $L_{mv}$, as a reaction to the low middle-vessel holdup. This is a result of the mathematical technique used to prevent the vessel from going dry (as described in the Solution Methodology section).

In the second period of operation (two intervals of 439 s and 232 s, respectively), the acetone cut is withdrawn at a reflux ratio of 0.881, followed by 0.855. The solvent feed rate is kept at the maximum allowable value during this period. The middle-vessel liquid holdup is kept fairly constant and at a low value. Low liquid holdup in the column section tends to promote higher distillate composition profiles (Tomazi, 1997), which is likely to account for the behavior. As shown in Figure 6, the methanol composition profile in the middle-vessel profile rises steeply toward the end of this period.

In the final period (183 s), purification of the solvent in the reboiler drum occurs. Again, the reflux ratio is lowered to accelerate the removal of the offcut. The reflux flow rate from the middle vessel, $L_{mv}$, is substantially decreased causing the liquid holdup in the middle vessel to rise and deteriorating the methanol purity in the vessel. This is because no specification is imposed on the cut, hence all the decision variables are selected to speed up the concentration of the solvent in the reboiler. Note that, although bottom product withdrawal is allowed throughout the duration of the process, no bottom cut was withdrawn and the solvent concentration in the reboiler only reaches its specification at the end of the process.

Next, consider the case where the feed is charged to the middle vessel (case *b*). The optimal operation policy involves an initial total reflux period without solvent feeding (Figures 7 and 8). During this period, a high reflux flow rate from the middle vessel is selected, which causes most of the liquid holdup in the middle vessel to be transferred to the reboiler (Figure 8). By the end of the first period, the distillate com-

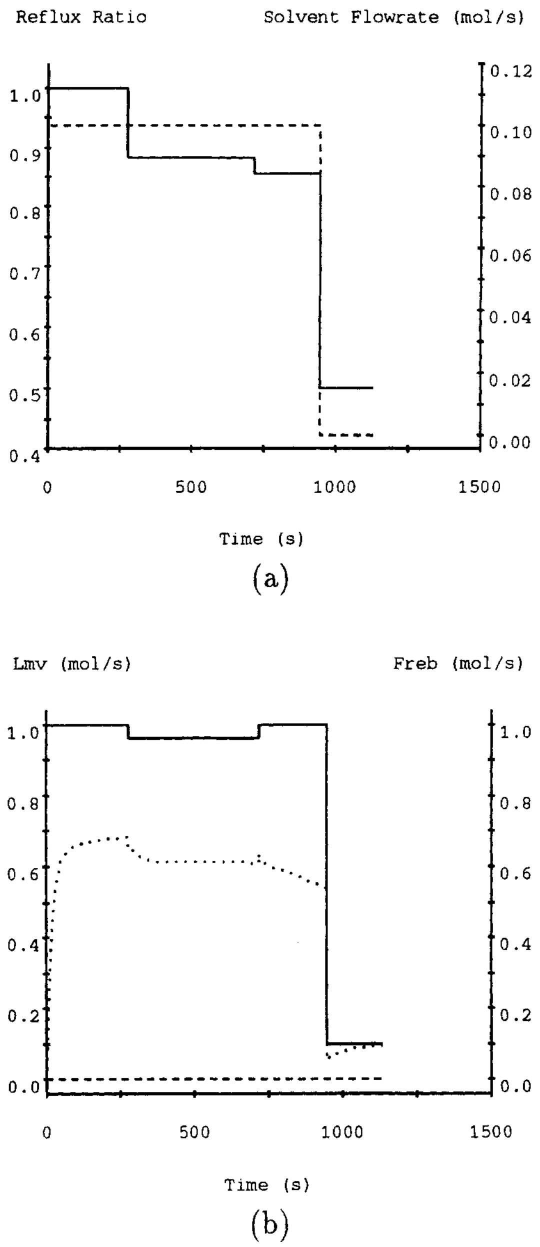



**Figure 5. Case I optimal control variables for middle-vessel column with reboiler charge.**

(a)——Reflux ratio, - - - $F_{sol}$; (b)——$L_{mv}$, ... effective $L_{mv}$, - - - $F_{reb}$.

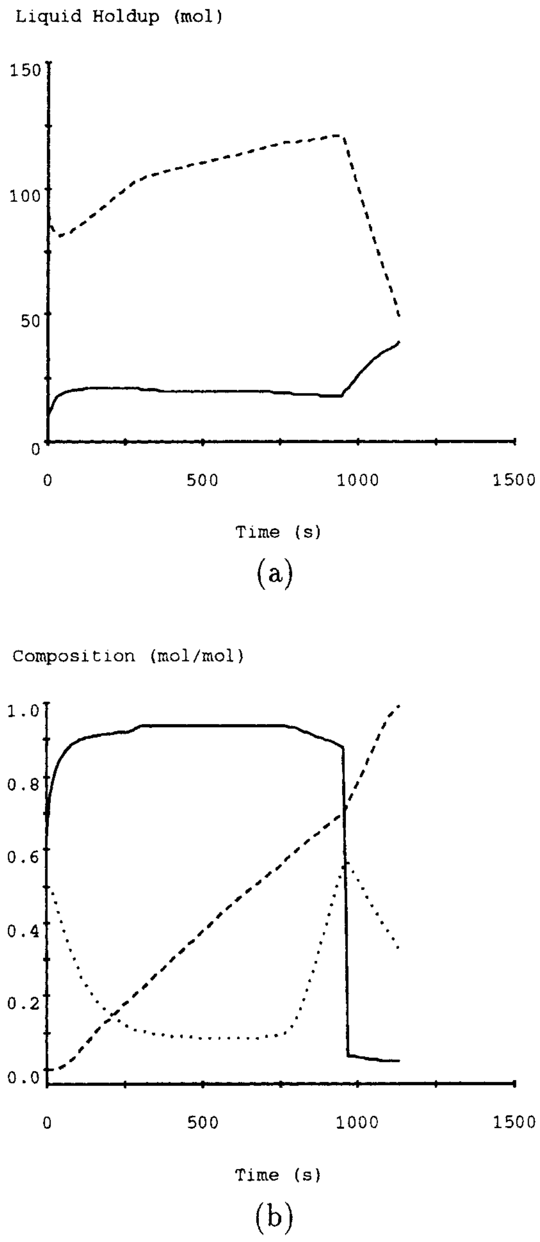



**Figure 6. Case I optimal holdup and composition for middle-vessel column with reboiler charge.**

(a)——middle vessel, - - - reboiler; (b)——acetone in distillate, - - - solvent in reboiler, ... methanol in middle vessel.

position reaches the azeotropic point. Then, maximum solvent feed rate is introduced into the column until the distillate composition approaches the purity specification. Hence, the combined total reflux period is longer (396 s) compared to the previous case (277 s), but the extra time is spent transferring material from the middle vessel to the reboiler.

Finally, the initial feed distribution was determined (case $c$). As expected, the optimal feed placement is in the reboiler (90 mol), and the control variables profiles are identical (bearing optimization accuracy) to those of case $a$.

*Comparison of Regular and Middle-Vessel Column.* For the middle-vessel column, the optimal operation for feed charged to the reboiler drum (case $a$) performed better than for feed charged to the middle vessel (case $b$). This was confirmed by the optimal feed location results (case $c$). The operating profit for case $b$ was about 9% lower than cases $a$ and $c$ due to the additional interval at the beginning of the operation to transfer the holdup from the middle vessel to the reboiler.

The optimal acetone and solvent recovery of the regular column were found to be higher than that of the middle-vessel column. Also, the operating profit of the regular column was 18% higher than the simple middle-vessel column configuration. This was in part due to the longer total reflux period in the middle-vessel column. In this specific case study, where

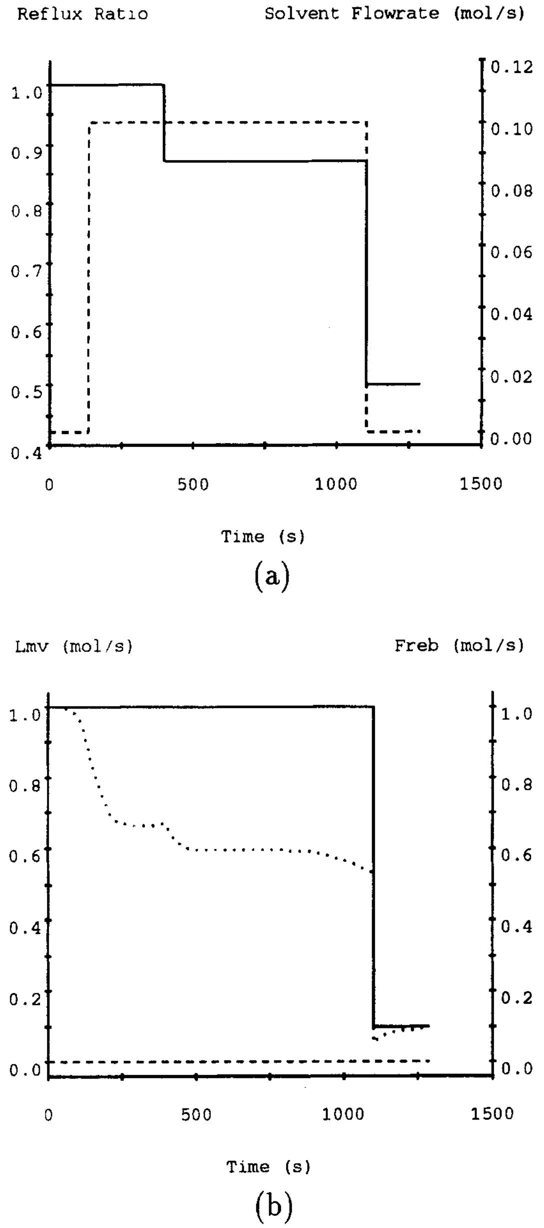



**Figure 7. Case I optimal control variables for middle-vessel column with middle charge.**

(a)——Reflux ratio, - - - $F_{sol}$; (b)——$L_{mv}$, ... effective $L_{mv}$, - - - $F_{reb}$.

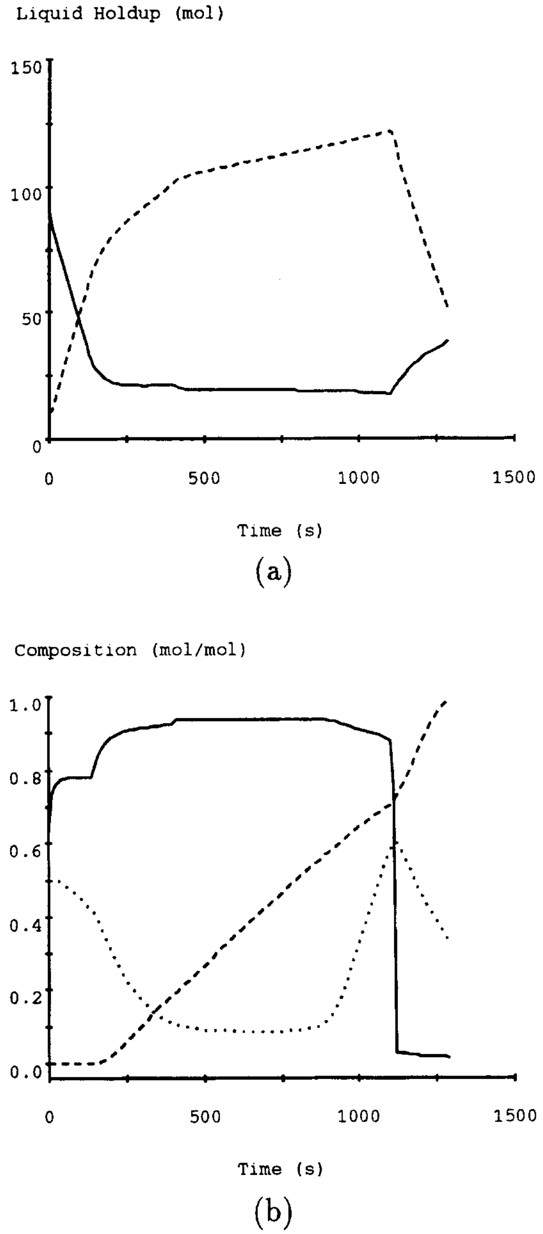



**Figure 8. Case I optimal holdup and composition for middle-vessel column with middle charge.**

(a)——middle vessel, - - - reboiler; (b)——acetone in distillate, - - - solvent in reboiler, ... methanol in middle vessel.

recovery of the intermediate component methanol was not considered, the middle vessel did not offer any functional advantage compared to the regular column other than acting as a low-level holdup through most of the operation duration.

### *Case II: multiple products*

In this example, the less volatile component, methanol, is also recovered at a purity specification of 93 mol % in addition to the specifications of acetone and solvent (Table 6). For the regular column, results from the first case study suggest that four control intervals are sufficient to fulfil the extra methanol specification. The methanol-rich cut is collected in the final accumulator, with an additional accumulator made available after the first acetone accumulator to collect a possible offcut. All the different stream configurations are now considered for the middle-vessel column. The methanol-rich cut is purified in the middle vessel and an additional accumulator is also made available for a possible offcut. The time interval is increased to five for all the middle-vessel configurations.

*Optimal Operating Policy for Regular Column.* The first period for the regular column is a short total reflux operation (99 s), with solvent feeding at the maximum rate (Figures 9

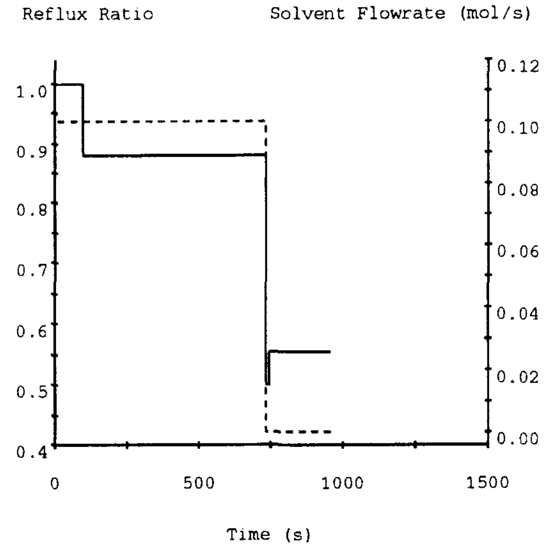



**Figure 9. Case II optimal control variables for regular column.**

———Reflux ratio, - - - $F_{sol}$.

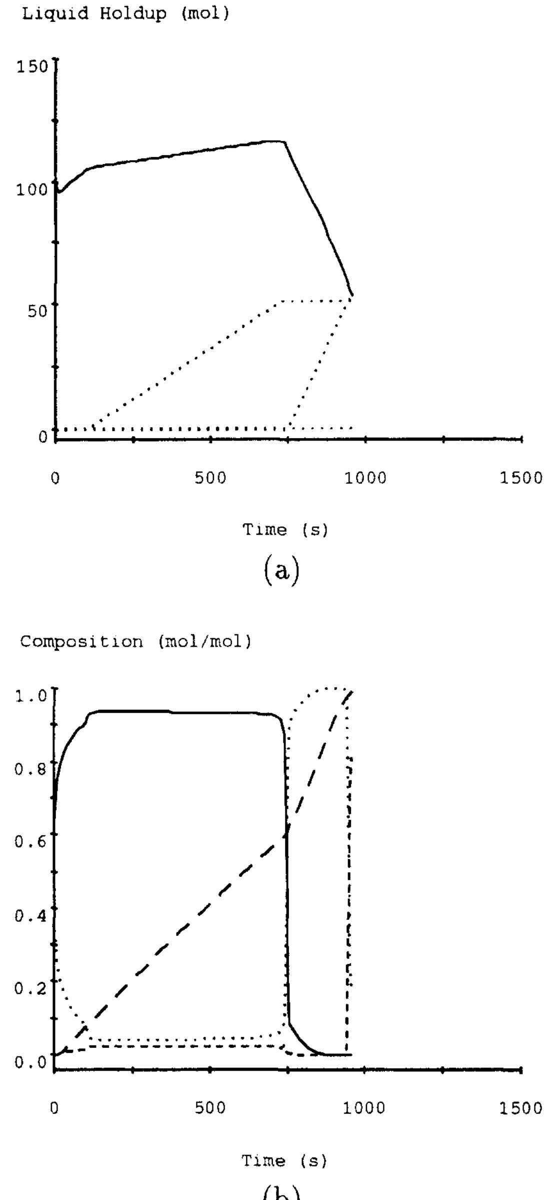



**Figure 10. Case II optimal holdup and composition for regular column.**

(a)———Reboiler, ... accumulators; (b)———acetone, ... methanol, - - - solvent in distillate; – – – solvent in reboiler.

and 10). The acetone composition at the top rises steeply from that of the feed to well above the azeotropic point (Figure 10). In the second period of operation (648 s), withdrawal of the first product cut of acetone occurs. This is done rather slowly with a high reflux ratio to maintain the distillate at a fairly constant level of just above the required 93 mol %. As shown in Figure 10, the liquid holdup of the first accumulator increases at a constant rate with a final acetone recovery of 90.4% with 93.0 mol % purity. At the end of the second period, the composition change in the distillate is very sharp, with the methanol profile shooting upwards almost instantaneously to well above the purity specification of 93 mol %. Hence, an offcut is not required in the optimal policy, as shown in Figure 9 where the offcut interval touches the minimum bound of 10 s. In the third period (211 s), solvent addition ceases and a lower reflux ratio is chosen to speed up the relatively easy separation of the remaining methanol from the solvent in the reboiler. As shown in Figure 10, the second accumulator fills up much faster than the first accumulator.

*Optimal Operating Policy for Middle-Vessel Columns.* Five different configurations of the middle-vessel column were investigated in this case study (Figure 2). For each configuration, the variables determined by the optimization include the reflux ratio, solvent flow rate, reflux from the middle vessel, reboiler and middle vessel heat duties, and withdrawals as well as the initial feed placement and duration of the process intervals. In addition, the split ratios of the liquid and vapor streams at the middle-vessel section were allowed to vary in the optimal case (refer to Table 1).

For the most practical configuration, configuration A (Figures 11 and 12), the optimal feed location is the reboiler drum. The total reflux period with solvent addition is followed by the acetone removal period at reflux ratios of 0.907 and 0.867. After a brief period of offcut, the solvent feed is stopped and another total reflux period resumes. Reflux flow rate from the middle vessel is reduced, allowing the methanol cut to accumulate and purify in the middle vessel. At the same time, the solvent is being purified in the reboiler drum. There was no withdrawal from the reboiler, nor from the middle vessel.

In configuration B, a heat input is introduced at the middle vessel and vapor is allowed to flow between the middle vessel and the bottom extractive tray. The optimal operating policy is similar to that of configuration A. The introduction of heating at the middle vessel improves the performance of the separation in terms of lower processing time and overall heat duty, as well as improvement in product recoveries. The objective function increased by 18% from 201.4 \$/h to 238.0 \$/h compared to configuration A (Table 8).

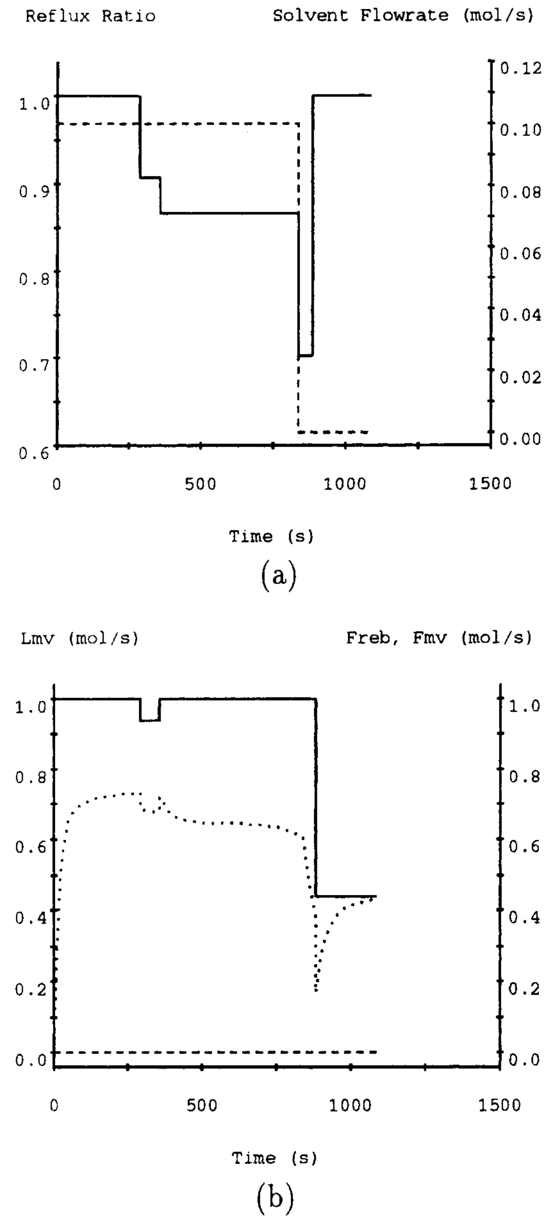



**Figure 11. Case II optimal control variables for middle-vessel column with configuration A.**

(a)——Reflux ratio, - - - $F_{sol}$; (b)——$L_{mv}$, ... effective $L_{mv}$, - - - $F_{reb}$, $F_{mv}$.

In configuration C, the vapor stream from the stripping section is fed to the middle vessel instead of to the extractive section. Of course, from a practical point of view, diversion of vapor between the trays into a heated middle vessel is difficult, unlike the liquid stream that may be easier to split via the downcomer. Nonetheless, in order to pursue a purely theoretical scenario, the model assumes the vapor stream to be driven by the usual intertray pressure difference. With this configuration, the column performance improved further with better processing time, overall heat duty, and product recoveries. The profit is 28% higher than that of configuration A.

A more practical approach to investigate a possible improvement to configuration B is to allow the direction of the liquid stream from the extractive section to be determined by the optimization, that is, configuration D. The downcomer flow could be split using a simple valve connection, with the ratio being the decision variable, $R_{D2}$. The optimal split ratio (0.8) is close to the upper bound during the initial total reflux and acetone withdrawal periods. In other words, the liquid stream is diverted to the stripping section, bypassing the middle vessel during the solvent-addition periods. This behavior can be explained by the fact that the solvent-rich stream would be directed toward the reboiler, where eventually it would be purified instead of forcing it through the middle vessel and possibly contaminating its content. During the final step, where methanol is purified in the middle vessel, the liquid stream switches its direction completely into the middle vessel. Configuration D has an operating profit 17% higher than that of configuration B and 28% higher than configuration A.

Lastly, for the optimal configuration case (Figures 13 and 14), all operational degrees of freedom available to this column were examined, including the optimal stream configurations between the middle vessel and the column, that is, both the vapor and liquid streams split ratios. The optimal feed placement is in the reboiler drum, as shown in Figure 14. The control variables profiles show that only three operating steps are required: a short period of total reflux with solvent feeding, a top withdrawal period with solvent feeding, and finally another total reflux period without solvent feeding. There is a very short offcut period (10 s, lower bound) before the final total reflux step.

Figure 15 illustrates the optimal operating steps of the middle-vessel column. In the first total reflux period, solvent is introduced at the maximum allowable flow rate. The heat duty in the middle vessel and reflux flow rate from the middle vessel are at their maximum bounds of 20 kW and 1.0 mol/s, respectively. This keeps the liquid holdup in the vessel low (Figure 14). The entire vapor stream from the stripping section is directed to the middle vessel instead of to the extractive section. Similar to previous observations, the liquid stream, which is rich in the added water solvent and ad-

**Table 8. Optimal Results for Case Study II**

| Column Configuration | Regular | Middle Vessel A | B | C | D | Optimal |
|---|---|---|---|---|---|---|
| Operating profit ($/h) | 270.8 | 201.4 | 238.0 | 257.9 | 278.7 | 291.1 |
| Batch-processing time (min) | 16.0 | 18.1 | 16.3 | 16.0 | 15.1 | 14.7 |
| Total heat consumption (MJ) | 19.1 | 21.0 | 20.0 | 19.6 | 18.5 | 18.0 |
| Acetone recovery (%) | 90.4 | 79.3 | 83.7 | 87.9 | 90.0 | 91.5 |
| Methanol recovery (%) | 94.6 | 86.7 | 88.4 | 90.0 | 89.9 | 90.4 |
| Solvent recovery (%) | 73.4 | 88.1 | 85.3 | 84.6 | 83.4 | 82.8 |
| Amount solvent used (mol) | 73.4 | 83.6 | 74.6 | 73.2 | 67.8 | 66.0 |
| Optimal feed location (mol) (reboiler/middle vessel) | — | 90/10 | 90/10 | 90/10 | 90/10 | 89/11 |

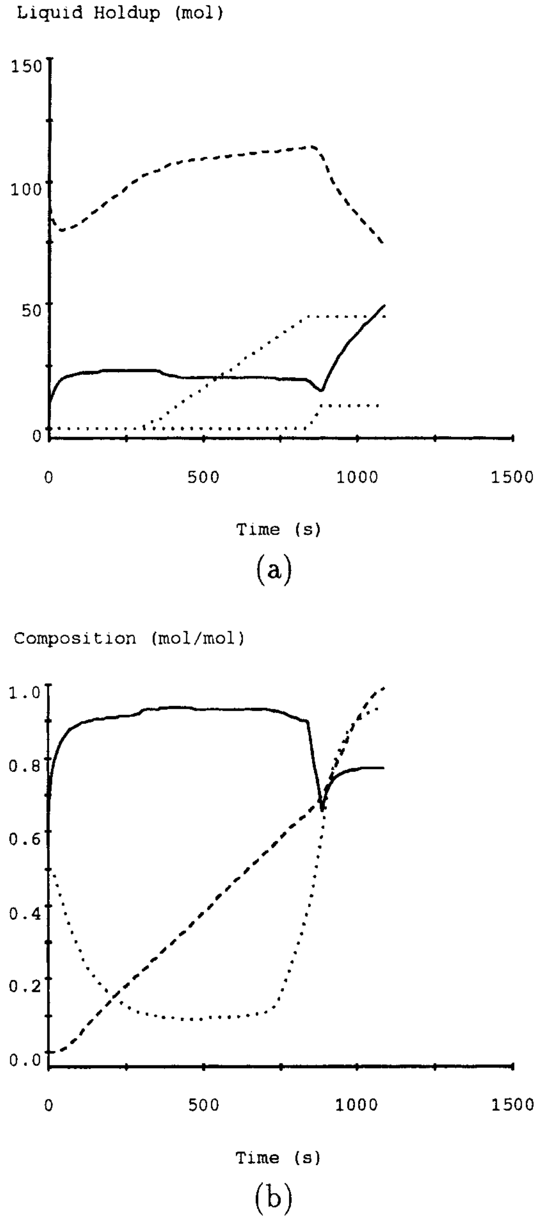



**Figure 12. Case II optimal holdup and composition for middle-vessel column with configuration A.**

(a)——Middle vessel, - - - reboiler, ... accumulators; (b)——acetone in distillate, - - - solvent in reboiler, ... methanol in middle vessel.

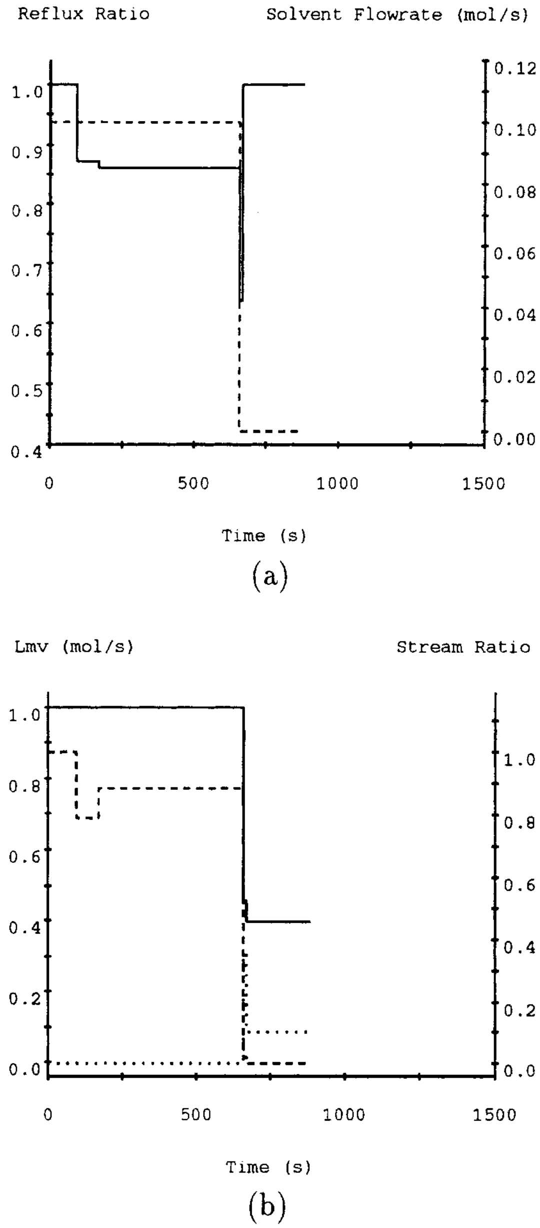


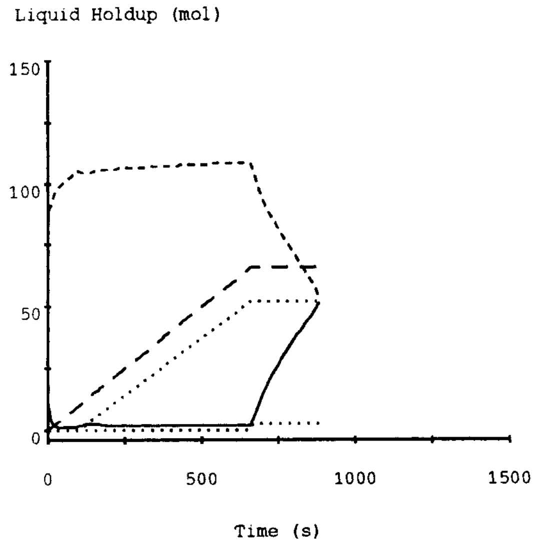

**Figure 13. Case II optimal control variables for middle-vessel column with optimal configuration.**

(a)——Reflux ratio, - - - $F_{sol}$; (b)——$L_{mv}$, - - - liquid-stream split ratio, ... vapor-stream split ratio.

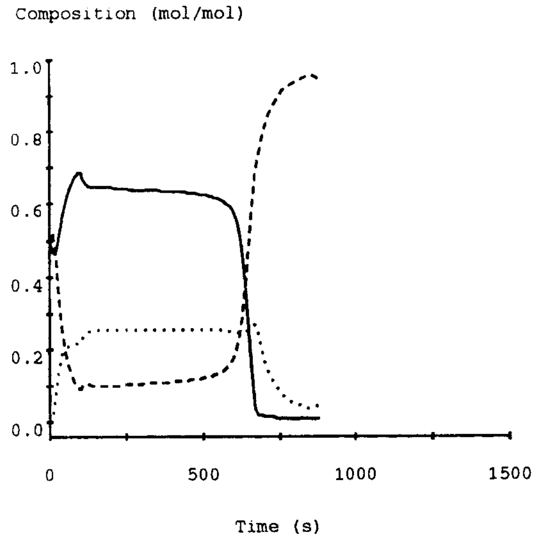
sorbed methanol, is directed straight down to the stripping section, bypassing the middle vessel. As shown in Figure 14, the acetone composition in the middle vessel improved and contamination by the solvent is kept low.

In the second period, solvent feeding is continued at a high flow rate, while the acetone product is being withdrawn at a fairly high reflux ratio. Only a minimal amount of heat duty is needed in the middle vessel (1.1 kW, then 0.5 kW, lower bound). During this period, the composition of the middle vessel is kept fairly constant, and so are the liquid holdups of the reboiler drum and middle vessel. This is because the rates of solvent addition and product removal are almost similar. Following a negligible offcut period (10 s, lower bound), the final period involves simultaneous purification of the methanol product and the solvent. Solvent feeding is terminated. No top offcut withdrawal is necessary as the column is switched back to total reflux mode. Purification is done by the middle-section stream configuration. All the liquid from the column, and most of the vapor stream, is diverted to the middle vessel where methanol is being accumulated. At the same time, the water solvent is being recovered in the reboiler drum at its original purity. No withdrawals were taken from either the middle vessel or the reboiler throughout the process operation.

By allowing both streams to vary in an optimal way, the operating profit increased by 45% from that of configuration




(a)




(b)

**Figure 14. Case II optimal liquid holdup and composition for middle-vessel column with optimal configuration.**

(a)——Middle vessel, - - - reboiler, ... accumulators, ——amount of solvent fed; (b)——acetone, - - - methanol, ... solvent in middle vessel.

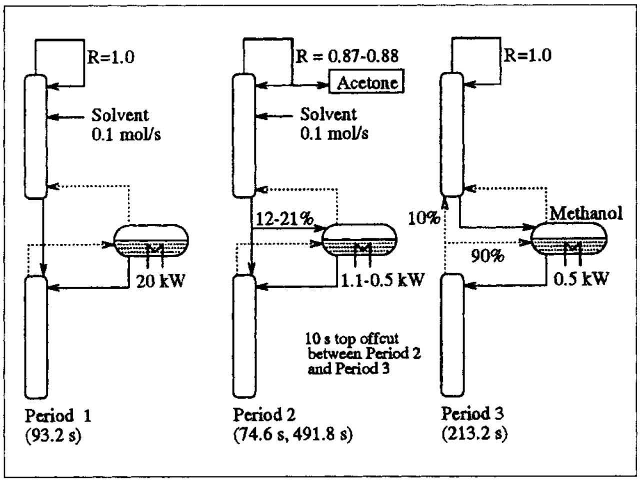



**Figure 15. Optimal operating policy of middle-vessel column.**

A in our case study. The batch-processing time and energy consumption decreased by 19% and 14%, respectively.

*Comparison of Regular and Middle-Vessel Columns.* For the middle-vessel column, Safrit et al. (1995) have proposed a middle-vessel steering operating policy that involved a period of solvent addition with no bottom removal but with distillate removal (acetone), followed by a period of normal distillate and bottom (water) removal. During the latter period, the reflux and reboil ratios were calculated in order to maintain the distillate and bottom purities while the middle vessel is being steered toward the required methanol composition. They claimed the advantage is high distillate recovery of up to 100% by overcoming the need for infinite reboiler size in the regular column. However, they observed high reflux ratio and reboil ratios toward the end of the operation. Thus, the proposed policy may not be attractive from an economic point of view due to requirements like high number of trays, high utility costs, and long processing times. They used a simple model assuming pseudo-steady-state on the trays and ignoring holdup effects, hence the operational feasibility is doubtful. Another study proposed by Lelkes et al. (1998b) has since refuted the study by Safrit et al., and even obtained an inverse result where the maximum recovery obtained using the batch rectifier was higher than the middle vessel.

From an industrial point of view, a comparison of operating procedures is best made via a detailed optimal control problem based on the economics of the process that takes into account all revenues and related costs. The optimal economic operation is seldom the maximum production operation, maximum revenue operation, or minimum processing time operation alone. The results of our study suggest that the middle vessel did not take up the functionality of being steered proposed by Safrit et al. (1995). In fact, the optimal feed location in this case study is the reboiler rather than the middle vessel. The optimal middle-section stream configuration in the first two steps (Figure 15) resulted in the holdup of the middle vessel remaining low, and thus did not exhibit any advantageous functionality over the regular column. Only in the final step did the middle vessel use this option to accumulate the methanol cut, and this is due to the product location being prespecified.

In this specific case study, it was found that the operating profit of the middle-vessel column can be improved by 45% from that of the simple configuration (configuration A) by allowing both liquid and vapor streams configuration to vary during the operation. The middle-vessel column with flexible middle-section stream configuration also performed 7.5% better than the conventional regular column in terms of operating profit. The middle vessel has a slightly shorter batch-processing time, lower heat duty, and higher acetone recovery, while the regular column achieved better methanol recovery. It should be noted that the profitability depends on the selling price of the products and other costs, and hence could alter significantly if these change.

### *Case III: various feed compositions*

In the previous case studies, equimolar mixture of the binary azeotropic feed was used. To the best of our knowledge, all studies of batch extractive distillation so far, including feasibility methods, simulation experiments, and optimization as reported in the literature review, involved only equimolar mixtures, and hence their conclusions are only valid for these mixtures. Here, the optimal operating profits and operations for both regular and middle-vessel columns using various feed compositions are presented. Both the simple configuration (configuration A) and optimal stream configuration of the middle vessel are used in our investigation. The production of both feed components and solvent recovery were taken into account, as in case study II. The results are displayed in Table 9 and the operating profits are as shown in Figure 16.

As can be seen from the results, when the molar ratio of a particular component is large in the feed mixture, the recovery of that component improves for both columns. The change in the amount of solvent used is small (18–47%) as compared to the change in feed composition (200%). In the case of the regular column, which has a fixed solvent feed rate capacity, this is because the extension of the total period of solvent feeding (total reflux and acetone withdrawal periods) was not significant, as a result of lower reflux ratios used for feed with more acetone.

Using the regular column to separate the various feed compositions, the optimal operating profiles are similar, each with negligible offcut. The main difference is the duration of the total reflux period. More time is needed to reach the purity specification for feed mixture with lower concentration of acetone (172, 99, and 61 s for feed compositions 25:75, 50:50, and 75:25, respectively). However, the total durations of the withdrawal steps of the operation are quite similar (865, 859, and 867 s, respectively), as the durations of the acetone withdrawal periods and the methanol withdrawal periods counterbalance each other for the various feed compositions. Thus, the optimal processing time of separating different feed compositions varies only insofar as the total reflux period at the beginning for a column with a maximum feed-rate capacity.

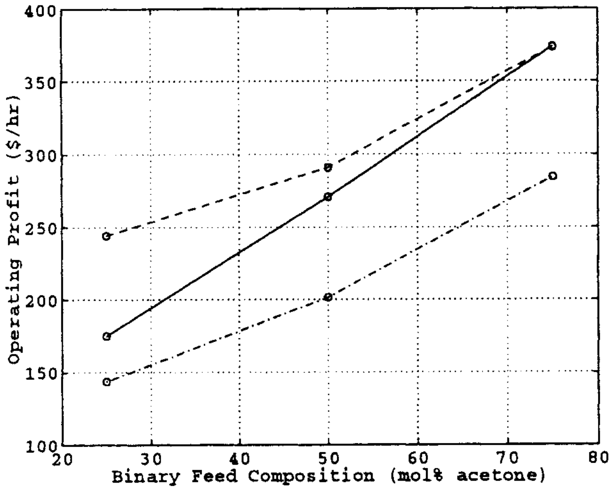



**Figure 16. Operating profits for various feed compositions.**

—·—·— simple configuration middle-vessel column, ——— regular column, - - - optimal configuration middle-vessel column.

For feed composition with a higher acetone fraction, the longer period of solvent addition results in a greater amount of solvent added, it would be intuitively assumed that the maximum reboiler still holdup would be greater. Contrary to that prediction, the maximum still holdup actually decreases, as shown in Figure 17. This is because as the acetone composition in the feed increases, the rate of acetone withdrawal is faster due to lower reflux ratio. For the case of feed composition 75:25, the withdrawal rate is actually greater than the rate of solvent addition. This causes the reboiler holdup to decrease rather than increase. Hence, for some separation duties, the capacity of the reboiler is not an operation limitation to batch extractive distillation, and in such cases, greater quantities of feed can be processed.

For the middle-vessel column, the optimal feed placement is in the reboiler for all feed compositions. The operating

**Table 9. Optimal Results for Regular and Middle-Vessel Columns Using Various Feed Compositions**

| Column | Regular | | | Middle Vessel Simple Configuration | | | Middle Vessel Optimal Configuration | | |
|---|---|---|---|---|---|---|---|---|---|
| Feed Composition* | 25:75 | 50:50 | 75:25 | 25:75 | 50:50 | 75:25 | 25:75 | 50:50 | 75:25 |
| Operating profit ($/h) | 175.0 | 270.8 | 373.7 | 143.7 | 201.4 | 284.4 | 244.2 | 291.1 | 373.3 |
| Batch-processing time (min) | 17.3 | 16.0 | 15.5 | 16.9 | 18.1 | 17.5 | 11.4 | 14.7 | 15.3 |
| Heat duty (MJ) | 18.3 | 19.1 | 18.6 | 17.2 | 21.0 | 21.1 | 13.0 | 18.0 | 18.8 |
| Acetone recovery (%) | 77.0 | 90.4 | 97.1 | 58.0 | 79.3 | 88.5 | 71.0 | 91.5 | 97.5 |
| Methanol recovery (%) | 98.7 | 94.6 | 83.8 | 93.3 | 86.7 | 64.2 | 94.8 | 90.4 | 74.4 |
| Solvent recovery (%) | 69.9 | 73.4 | 76.7 | 82.7 | 88.1 | 90.5 | 69.1 | 82.8 | 88.1 |
| Amount solvent used (mol) | 68.3 | 73.4 | 80.9 | 61.2 | 83.6 | 90.0 | 39.8 | 66.0 | 83.1 |
| Optimal feed location (mol) (reboiler/middle vessel) | — | — | — | 84/16 | 90/10 | 90/10 | 72/25 | 89/11 | 86/14 |
| Amount withdrawn from reboiler (mol) | — | — | — | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 |
| Amount withdrawn from middle vessel (mol) | — | — | — | 0.0 | 0.0 | 0.0 | 0.1 | 0.1 | 0.2 |

*Molar Ratio Acetone:Methanol.

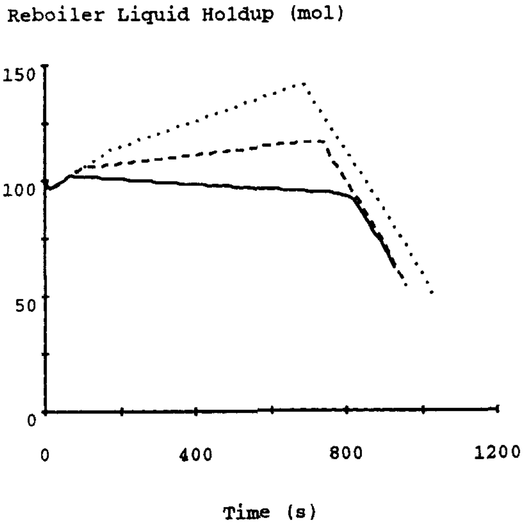



**Figure 17. Case III reboiler liquid holdup in the regular column for different feed compositions.**

... 25:75, - - - 50:50, ——— 75:25.

procedures are similar, beginning with a period of total reflux with solvent feeding followed by an acetone withdrawal period, offcut with solvent feeding stopped, and finally, a period of methanol concentration in the middle vessel. For feed mixtures richer in acetone, the initial total reflux period and the methanol concentration period gets shorter while the acetone withdrawal periods become longer.

Similar to the observation in the regular column, the maximum holdup in the reboiler is the lowest for the feed with 75 mol % acetone, although more solvent is used for separating a feed mixture rich in acetone. In fact, similar to the regular column, the holdup was below the initial charge throughout the operation. Unlike the previous two cases, accumulation of volume is not required in the middle vessel during the methanol concentration period with the middle-vessel reflux valve fully open ($L_{mv}$ maximum).

In comparison, the regular column performed better than the simple middle-vessel column for all three feed compositions investigated. Interestingly, a linear function can be seen, as shown in Figure 16, especially for the regular column. However, for feed with a low fraction of methanol, the advantage of the middle-vessel column with optimal stream configuration over the regular column is reduced, up to a point whereby the operating profit of the regular column began to overtake that of the middle-vessel column. This trend is in accordance with intuition, as when the feed to be processed approaches pure acetone, the functionality of the middle vessel, that is, to collect methanol, would diminish, and thus it would not be expected to perform better than a straightforward batch rectifier. Hence, it can be assumed that the performance of one column configuration over another is dependant on the composition of the feed mixture and that in certain cases, an advantage in performance may sometimes be reversed at some different feed composition, as found in our example. The same observation was also found by Sørensen and Skogestad (1996) when they compared the operation of the regular and inverted columns.

## Conclusion

In this article, we presented a study on optimal operation of batch extractive distillation operation involving a binary acetone–methanol azeotropic mixture, with water as solvent. Both conventional and complex columns with flexible stream configurations were considered and several comparative case studies presented. The dynamic model took into account variable liquid and vapor holdups, tray hydraulics, and rigorous mass and energy balances. A rigorous nonlinear programming technique was used for optimization and all the operational control variables available to both columns were taken into account, including reflux ratio, solvent feed rate, heating duties, stream ratios, and withdrawals. The effects of feed distribution and stream configuration were also investigated.

For the middle-vessel column, our results indicate that the operation is most economical when feed is fed to the reboiler; the holdup of the middle vessel was kept at a low level throughout the first two steps, and thus did not exhibit any functional advantages over the conventional regular column in the specific case studies. The batch rectifier performed better than the simple configuration middle-vessel column in terms of operating profit for various feed compositions. However, the performance of the middle-vessel column can be improved by optimizing the liquid and vapor stream configuration at the middle section.

Our example highlighted the need for thorough consideration when comparing the economical advantages of different column configurations and before making general conclusion, as the performance of a column may be influenced by various factors, such as feed composition.

The results obtained are specific to this case study in terms of mixture type, composition, feed amount, operation objective, pricing, column design as well as parameters specification, bounds, and constraints. Thus the guidelines drawn from this study are based on these conditions. This work shows that rigorous comparative optimization case studies are now possible with current numerical and computer technology and can be beneficial if applied during column and operational design for batch extractive distillation.

## Notation

$A_{reb}$ = cross-sectional area of reboiler drum, m$^2$
$C_{feed}$ = unit cost of feed, \$/mol
$C_i$ = selling price of product, $i$, \$/mol
$C_Q$ = unit cost of heating, \$/MJ
$C_{sol}$ = unit cost of solvent, \$/mol
$F_{mv}$ = liquid withdrawal flow rate from middle vessel, mol/s
$F_{reb}$ = liquid withdrawal flow rate from reboiler, mol/s
$F_{sol}$ = solvent feed flow rate, mol/s
$H_{A,i}$ = amount of accumulated product, $i$, mol
$H_{A,sol}$ = amount of recovered solvent, mol
$H_{feed}$ = amount of feed, mol
$H_{feed,i}$ = amount of component $i$ in feed, mol
$H_{sol}^{makeup}$ = amount of makeup solvent, mol
$l$ = liquid level, m
$L_{mv}$ = reflux flow rate from middle vessel, mol/s
$L'_{mv}$ = effective reflux flow rate from middle vessel, mol/s
$M$ = liquid holdup, mol
$N_C$ = number of components
$Q$ = rate of heat transfer, W
$R$ = internal reflux ratio
$R_{D2}$ = liquid-stream split ratio

$R_{D3}$ = vapor-stream split ratio
$t$ = time, s
$x_{A,i}$ = mole fraction of main component in product, $i$, mol/mol
$x_{A,\mathrm{sol}}$ = mole fraction of solvent in recovered solvent, mol/mol
$x_{\mathrm{feed,\,sol}}$ = mole fraction of solvent in solvent feed, mol/mol

### Greek letters

$\lambda$ = Wilson interaction parameter, J/mol
$v$ = volume, $m^3$
$\Pi$ = recovery, mol %

### Subscripts and superscripts

$A$ = accumulator
$C$ = total number of component
$D$ = divider
$f$ = final
feed = feed
$i$ = component
$mv$ = middle vessel
$Q$ = heating
reb = reboiler
sol = solvent
$T$ = total
in = inlet stream
min = specified lower bound
out = outlet stream

## Literature Cited


Bernot, C., M. F. Doherty, and M. F. Malone, "Patterns of Composition Change in Multicomponent Batch Distillation," *Chem. Eng. Sci.*, **45**, 1207 (1990).

Bernot, C., M. F. Doherty, and M. F. Malone, "Feasibility and Separation Sequencing in Multicomponent Batch Distillation," *Chem. Eng. Sci.*, **46**, 1311 (1991).

Furlonge, H. I., C. C. Pantelides, and E. Sørensen, "Optimal Operation of Multivessel Batch Distillation Columns," *AIChE J.*, **45**, 781 (1999).

Gmehling, J., and U. Onken, *Vapour-Liquid Equilibrium Data Collection*, Chemistry Data Series, DECHEMA, Frankfurt (1977).

Infochem Computer Services Ltd., *Multiflash Command Reference*, London (2000).

Lang, P., H. Yatim, P. Moszkowicz, and M. Otterbein, "Batch Extractive Distillation Under Constant Reflux Ratio," *Comput. Chem. Eng.*, **18**, 1057 (1994).

Lang, P., G. Modla, B. Kotai, Z. Lelkes, and P. Moszkowicz, "Homoazeotropic Distillation of Maximum Azeotropes in a Batch Rectifier with Continuous Entrainer Feeding II. Rigorous Simulation Results," *Comput. Chem. Eng.*, **24**, 1429 (2000).

Lelkes, Z., P. Lang, P. Moszkowicz, B. Benadda, and M. Otterbein, "Batch Extractive Distillation: The Process and the Operational Policies," *Chem. Eng. Sci.*, **53**, 1331 (1998a).

Lelkes, Z., P. Lang, P. Moszkowicz, and B. Benadda, "Feasibility of Extractive Distillation in a Batch Rectifier," *AIChE J.*, **44**, 810 (1998b).

Milani, S. M., "Optimization of Solvent Feed Rate for Maximum Recovery of High Purity Top Product in Batch Extractive Distillation," *Trans. Inst. Chem. Eng.*, **77**, 469 (1999).

Mujtaba, I. M., "Optimization of Batch Extractive Distillation Processes for Separating Close Boiling and Azeotropic Mixtures," *Trans. Inst. Chem. Eng.*, **77**, 588 (1999).

Perry, R. H., and D. Green, *Perry's Chemical Engineers' Handbook*, McGraw-Hill, New York (1984).

Process Systems Enterprise Ltd., *gPROMS Advanced User's Guide*, London (2000).

Ruiz Ahon, V., and J. L. de Medeiros, "Optimal Programming of Ideal and Extractive Batch Distillation: Single Vessel Operations," *Comput. Chem. Eng.*, **25**, 1115 (2001).

Ruthven, D. M., *Encyclopedia of Separation Technology*, Wiley, New York (1997).

Sadomoto, H., and K. Miyahara, "Calculation Procedure for Multicomponent Batch Distillation," *Int. Chem. Eng.*, **23**, 56 (1983).

Safrit, B. T., A. W. Westerberg, U. Diwekar, and O. M. Wahnschafft, "Extending Continuous Conventional and Extractive Distillation Feasibility Insights to Batch Distillation," *Ind. Eng. Chem. Res.*, **34**, 3257 (1995).

Safrit, B. T., and A. W. Westerberg, "Improved Operational Policies for Batch Extractive Distillation Columns," *Ind. Eng. Chem. Res.*, **36**, 436 (1997).

Sinnott, R. K., *Coulson and Richardson's Chemical Engineering*, Pergamon Press, Oxford (1993).

Sørensen, E., and S. Skogestad, "Comparison of Regular and Inverted Batch Distillation," *Chem. Eng. Sci.*, **51**, 4949 (1996).

Tomazi, K. G., "Limitations and Dynamics Imposed on Multicomponent Batch Distillation by Tray Hydraulics," *Ind. Eng. Chem. Res.*, **36**, 4273 (1997).

Wahnschaff, O. M., and A. W. Westerberg, "The Product Composition Regions of Azeotropic Distillation Columns. 2. Separability in Two-Feed Columns and Entrainer Selection," *Ind. Eng. Chem. Res.*, **32**, 1108 (1993).

Warter, M., and J. Stichlmair, "Batchwise Extractive Distillation in a Column with a Middle Vessel," *Comput. Chem. Eng. Suppl.*, **S23**, S915 (1999).

Yatim, H., P. Moszkowicz, O. A. Otterbein, and P. Lang, "Dynamic Simulation of a Batch Extractive Distillation Process," *Comput. Chem. Eng.*, **S17**, S57 (1993).


*Manuscript received Apr. 16, 2001, and revision received Nov. 27, 2001.*