Semicontinuous, Middle-Vessel Distillation of Ternary Mixtures

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The operation of a semicontinuous, middle-vessel column (SCMVC) that separates a nearly-ideal ternary mixture is analyzed. MVCs have a large vessel between the rectification and stripping sections. In traditional batch rectification or stripping, a still is charged and distillate or bottoms products are removed, leaving heavy or light concentrates in the still, respectively. In contrast, the middle vessel of an MVC is charged, and, similar to a continuous process, both distillate and bottoms products are withdrawn. The process separates nearly-ideal ternary mixtures into three nearly-pure species, with the intermediate-boiling species concentrating in the middle vessel, and the light and heavy species concentrating in the distillate and bottoms products, respectively. Shortcut methods are adapted to determine the minimum number of trays and minimum reflux ratio. Alternative control configurations are considered to achieve suitable performance throughout the campaign. Two DB configurations are shown to be suitable for this process, with the middle vessel decoupling the composition control loops and permitting dual-composition control with little interaction. Simulations confirm that difficulties encountered when using a DB configuration for the dual-composition control of a continuous column do not occur for a SCMVC.

Introduction

Traditionally, distillation processes have been designed to operate in a batch column, in which a still is charged and distilled, or to operate continuously, in which a stream is fed to a column and distillate and bottoms products are withdrawn continuously. Batch distillation is usually preferred for low throughputs, when fine or specialty chemicals are produced, or when there is intermittent or seasonal chemicals production. In contrast, continuous distillation is favored for larger-scale throughputs and continuous upstream feeds.

In this article, the design, control, and operation of a semicontinuous, middle-vessel column (SCMVC) to separate nearly-ideal ternary mixtures is investigated. The middle-vessel permits semicontinuous operation to be an attractive policy for the separation of multicomponent mixtures. The MVC is a distillation column with a large vessel between the rectifying and stripping sections. One MVC configuration is shown in Figure 1, in which the liquid stream from the rectifying section is sent to an external middle vessel. Variations to this configuration include the use of a partial-liquid sidedraw, a heat stream added to the middle vessel, and the transmission

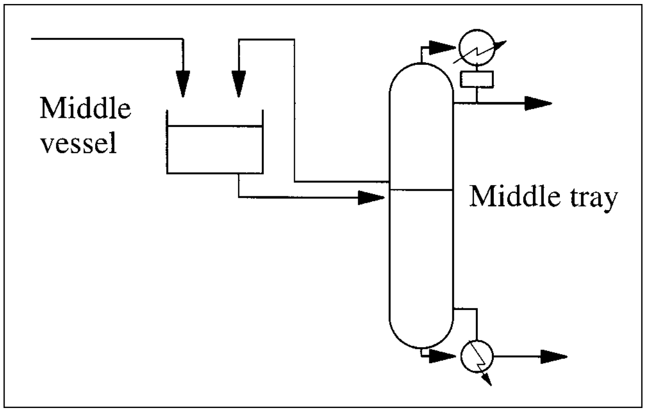

Figure 1. Middle-vessel column.

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of a vapor stream from the stripping section of the column to the middle vessel.

In a brief companion article (Phimister and Seider, 2000a), simulation studies of a SCMVC are presented for the separation of azeotropic mixtures in processes comparable to continuous extractive and azeotropic distillations. The MVC is shown to reduce capital investment, as compared with continuous processing. An MVC operated semicontinuously avoids column dumping and repeated startups, and allows for column automation, as compared with batch operation. In Table 1, several features of distillation processes are listed to compare a SCMVC with batch and continuous columns.

In this article, recent work on middle-vessel columns is reviewed. Then, the semicontinuous process is reviewed for the separation of three alkanes. Next, shortcut design procedures are adapted for semicontinuous columns. Several PI control configurations are examined, and for a *DB* configuration, the decoupling effect of the PI-composition controllers is shown. Finally, the three-alkane separation is considered in greater detail, with a column designed using the shortcut procedures and a *DB*-control configuration.

MV Distillation

Within the past decade, there has been much interest in the performance of alternative distillation configurations, including the MVC multivessel columns, series of heat-integrated, batch-distillation columns, and semicontinuous distillation configurations.

Although the MVC was initially suggested by Robinson and Gilliland (1950, p. 388), few papers appeared until the 1990s. One of the first articles, by Hasebe and coworkers (1992), reintroduced the MVC, presenting a campaign policy with simulation results. The simulations involve ideal mixtures, with the heavy and light impurities removed in the bottoms product and distillate, respectively, while the desired product concentrates in the middle vessel. In a subsequent article, Hasebe and coworkers (1996) conclude that a batch MVC consistently provides superior performance compared to batch rectification followed by batch stripping. Meski and Morari (1995) also conclude that MVC performance is superior to conventional batch distillation. When the middle vessel is charged with an ideal binary mixture, they conclude that the optimal operating strategy is to maintain constant distillate and bottoms flow rates, while holding the composition constant in the middle vessel. This strategy is shown consistently to outperform a conventional batch column.

Table 1. Comparison of Distillation Processes

	Batch	SCMVC	Continuous
Throughput	Low	Intermediate	High
Flexible *	Yes	Yes	No
Automatic control	Uncommon	Possible	Often
Investment	Lowest	Middle	Highest
Heat integration	No	No	Yes
Single column for ternary separation	Yes	Yes	No†
Slop-cut required for ideal ternary mixtures	Often	No	N/A

*The MVC can be designed to include the batch rectifier and batch stripper configurations as subunits within the MVC (Cheong and Barton, 1999a,b,c).

†However, a liquid side draw is possible over a narrow range of ternary compositions (Tedder and Rudd, 1978).

Davidyan et al. (1994) investigate the batch operation of the MVC for binary and ternary mixtures, and mixtures involving additional species. Two parameters related to the reflux and reboil ratios are introduced, and the regions of feasible product compositions are examined as these parameters are varied.

Lotter and Diwekar (1997) use shortcut methods and a simplified model to simulate the MVC. They show that the approximate model provides accurate and quick simulations for ideal systems.

Experimental results for a middle-vessel column are provided by Barolo et al. (1996). For a column with an external middle vessel, ethanol and water are separated, with the startup, control, and operation of the process discussed. The column is operated at total reflux until a steady state is achieved. Then, water is removed at a constant flow rate, until the bottoms product becomes off-specification.

Dual-composition control of an MVC is analyzed by Farschman and Diwekar (1998) who conclude that for the separation of binary pairs, provided sufficient holdup is maintained in the middle vessel, interaction between the two composition controllers is negligible. Their analysis is extended in this article for ternary mixtures.

Control of a multivessel column, a column with multiple intermediate vessels, is investigated by Skogestad et al. (1997). It is shown that the compositions in each vessel can be controlled by manipulating the reflux ratio (reflux flow rate/product flow rate) of each vessel to control the temperature on the tray below the returning reflux stream.

Safrit and Westerberg (1997) illustrate how acetone and methanol, a mixture exhibiting a low-boiling azeotrope, is separated in an MVC using water as an extractive agent. At the start of the campaign, water is fed to the top of the column, acetone is removed as the distillate, and the middle vessel, initially charged with acetone and methanol, increases in water concentration as acetone is removed. Subsequently, after the water feed is halted, streams concentrated in the acetone/methanol azeotrope and water are removed as the distillate and bottoms product, respectively, while the middle vessel becomes concentrated in methanol. Phimister and Seider (2000a) introduce the merits of a SCMVC for this separation. The latter uses a column with five interconnected hold vessels to separate three systems: an ideal ternary mixture, a low-boiling homogeneous azeotrope (acetone/methanol) using an extracting agent (water), and a low-boiling azeotrope with an intermediate entrainer. In a related article, Phimister and Seider (2000b) use a semicontinuous, pressure-swing distillation process to separate a pressure-sensitive binary azeotrope.

Finally, Cheong and Barton (1999a,b,c) analyze the performance of an MVC for separating azeotropic mixtures. First, a model is formulated for the MVC and potential operating lines are analyzed according to the ‘‘middle-vessel parameter,’’ the fraction of the product streams in the distillate (Cheong and Barton, 1999a). Next, the nonlinearities of separatrices are exploited to steer the middle vessel around previously perceived boundaries (Cheong and Barton, 1999b). Then, the conjectured policies, which are anticipated to provide complete separation of azeotropic mixtures in an MVC, are verified by simulation (Cheong and Barton, 1999c).

Semicontinuous Middle-Vessel Distillation of a Nearly-ideal Ternary Mixture

A semicontinuous MVC for the separation of a ternary mixture is shown in Figure 2. It is illustrated with a *DB*-control configuration, which will be discussed in the section on Decentralized Control. To introduce the SCMVC, consider the separation of 300 m^3 of an equimolar mixture of *n*-hexane, *n*-heptane, and *n*-octane using a 100 m^3 middle vessel. Two of the products, *n*-hexane and *n*-octane, are collected in tanks T2 and T4, respectively. After *n*-heptane builds to 98 mol % in the middle vessel, tank T1, this third product is dumped into product vessel T3, and, subsequently, tank T1 is recharged. This operating strategy is illustrated over the campaign by the trajectories of tank holdups and mol fractions, computed by integration of the MESH equations, shown in Figure 3. Tanks T2 and T4 fill nearly continuously, although slowly, as the intermediate mol fraction in the middle vessel approaches its set point. At 69, 133 and 197 h, the middle vessel is concentrated sufficiently in *n*-heptane to permit its contents to be dumped into tank T3, after which the vessel is recharged. The model assumes instantaneous discharges and recharges of the middle vessel. In practice, however, to facilitate rapid transfers, two middle vessels would be operated in parallel, with one feeding the column while the contents of the other are dumped and the vessel is recharged. Note that the initial cycle requires an additional five hours to achieve the concentration specification for the middle vessel because the column is loaded initially with the equimolar feed.

Unlike in batch processing, where manual control of the distillate and bottoms flow rates is often preferred, the product compositions, inferred from tray temperatures, are controlled by PI controllers. Level controllers maintain the liquid inventories in the sump and reflux drum. The pairings between the controlled and manipulated variables are discussed in the section on Decentralized Control.

Role of Semicontinuous Middle-Vessel Distillation

The decision to use a SCMVC is based primarily on the production rate. For the large production rates of commodity chemicals, a SCMVC compares unfavorably with continuous

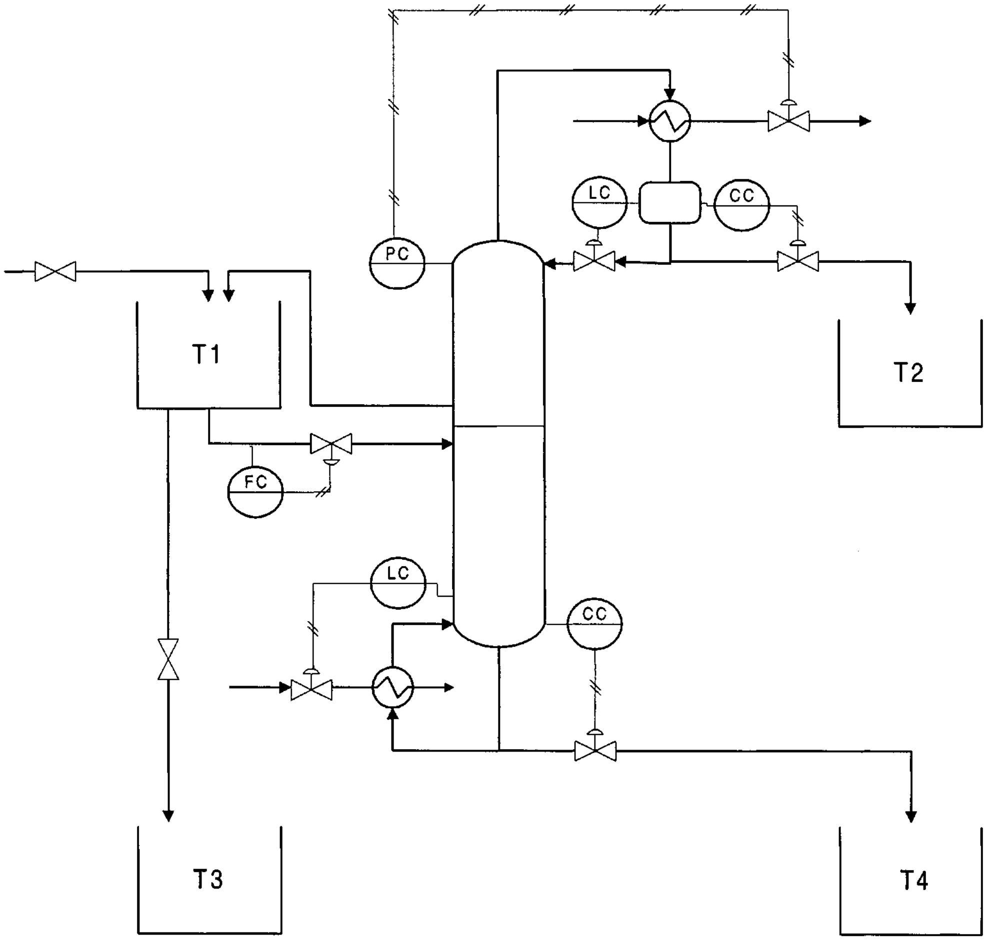

Figure 2. Semicontinuous middle-vessel column with *DB* configuration.

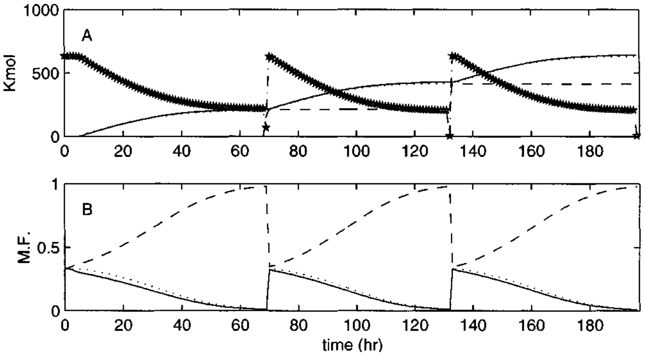

Figure 3. Trajectories of tank holdups and mol fractions in the middle vessel.

Holdups: *** T1, —— T2, – – – T3, · · · · T4. Mol fractions: —— *n*-hexane, – – – *n*-heptane, · · · · *n*-octane.

distillation. While a SCMVC for the separation of a ternary mixture is implemented with just one distillation column, compared with two normally required for continuous distillation, a key disadvantage is that heat integration cannot be implemented easily. For smaller production rates, such as 300 m^3 processed over 197 h, in the process considered herein, continuous distillation is impractical and the choice is between a SCMVC and batch processing. In this section, it is shown that, using nearly identical equipment to produce the same amount of product, the processing times associated with a SCMVC are smaller than for batch processing. This advantage translates to the greater availability of the equipment and greater profitability in the scheduling of batch and semicontinuous processes.

Given a small to moderate production rate, three considerations lead to a detailed comparison of a SCMVC:

(1) When the operating campaign can be implemented in periods of up to two months, with small- to moderately-sized equipment, a batch process is more economical than a continuous process. This heuristic is observed generally in industrial practice.

(2) The batch middle-vessel column provides superior performance compared to a batch column. And, hence, when a SCMVC is superior to batch middle-vessel distillation, it is superior to batch distillation. For discussions showing that batch MVCs outperform batch columns, see the articles by Hasebe and coworkers (1992), Davidyan and coworkers (1994), and Meski and Morari (1995).

(3) To compare a SCMVC with a batch MVC, it is helpful to consider two alternatives: (a) the feed is available entirely at the beginning of the process, or (b) the feed is available continuously during a portion of the process. The former typically originates from a process that produces sufficiently large batches. The latter originates from a process with a small continuous flow rate.

To illustrate these three considerations, return to the distillation of 300 m^3 of an equimolar mixture of *n*-hexane, *n*-heptane, and *n*-octane, a sufficiently small quantity to rule out continuous distillation. When the feed is provided in one charge, and the middle vessel is sufficiently large to hold the charge, the separation in a batch MVC is performed in 196 h. This is nearly identical to a SCMVC (with a 100 m^3 middle vessel), in which the separation is performed in 197 h. Note that both simulations were carried out using the same column. This result is expected because, with no constraints placed on the manipulated flow rates due to valve saturation, the processing times should be roughly proportional to the charge size. Consequently, three successive 100 m^3 charges and one 300 m^3 charge should be separated in the same time by a SCMVC or a batch MVC. With one large charge, it may be preferable to perform the separation in one batch, due to the economies of scale. The optimal batch size and processing schedule, however, also depends on available plant equipment.

For a small continuous feed, three operating policies are possible:

(1) Keep the distillation operation idle until the total charge is delivered to the middle vessel. Note that the middle vessel must be sufficiently large to accommodate the entire charge. Then, start the batch MVC.

(2) Use a "semibatch" operation. Place an initial charge in the middle vessel, start up the MVC, and operate the column continuously for the duration of the campaign. As upstream feed becomes available, it is added to the middle vessel. The middle vessel is discharged only when it has become suitably concentrated in the intermediate species.

(3) Use a SCMVC in which the middle vessel is filled, becomes concentrated in the intermediate species, and is discharged upon achieving its concentration specification. This cycle is repeated until the total charge is consumed. An additional vessel is required to hold the products from the upstream process during each cycle.

A batch MVC (1) is preferable to a SCMVC (3) only when

$$\tau_{tc} + \tau_{bd} \geq \tau_{ic} + \tau_{sd} \qquad (1)$$

where τ_{tc} is the time (s) for the middle vessel to receive the total charge, τ_{bd} is the time to distill the contents of the middle vessel in a batch MVC, τ_{ic} is the time for the middle vessel to receive an initial charge, and τ_{sd} is the time to distill the total charge semicontinuously in a SCMVC. Since $\tau_{bd} \approx \tau_{sd}$ and $\tau_{tc} \geq \tau_{ic}$, a SCMVC generally outperforms a batch MVC.

A SCMVC (3) can also prove superior to semi-batch operation (2). For an initial charge to the middle vessel at a composition along line X-X, x_M^i, in Figure 4A, Figure 4B shows the average sum of the distillate and bottoms flow rates starting from x_M^i. Note that the average sum of the distillate and bottoms flow rates decreases monotonically as $|x_{I,M}^{\text{spec}} - x_{I,M}^i|$ decreases. Let the middle vessel receive a 100 kmol charge with 68 mol % of the intermediate species. The charge decreases at an average rate of 1.8 kmol/h at point A ($x_{I,M}^{\text{spec}} - x_{I,M}^i = 0.98 - 0.68 = 0.3$). When 40 kmol of an equimolar feed is added, after the first charge is processed, it can be separated at an average rate of 7.1 kmol/h at point B. The overall average rate for both charges, using the lever rule, is 3.3 kmol/h, as shown at point D on line AB. Alternatively, let the second charge be added to the first charge before processing begins. The processing rate at point C is less than when the batches are processed separately. Consequently, the total charge is separated more rapidly by the SCMVC.

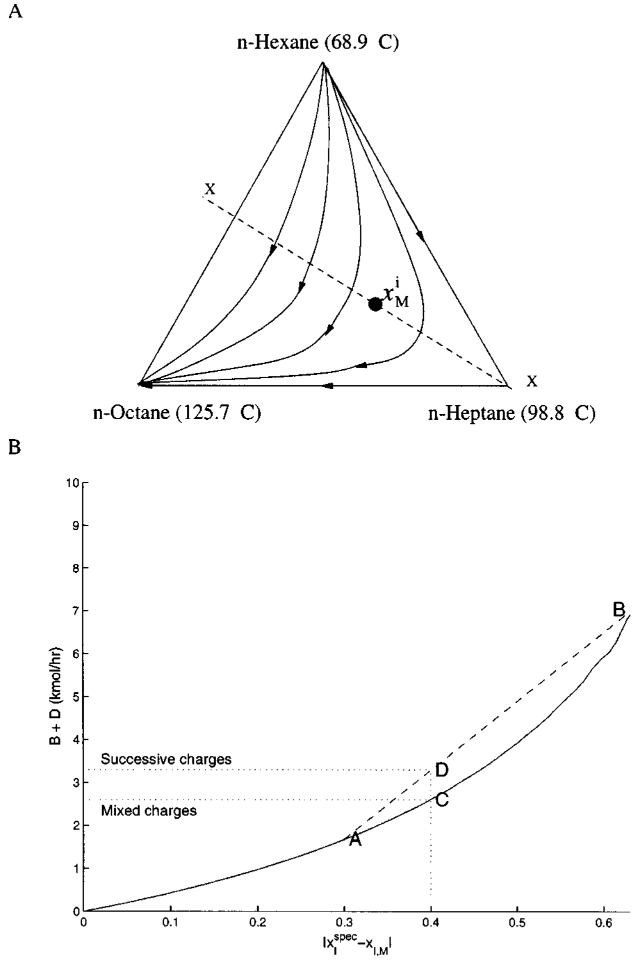

Figure 4. Comparison of a SCMVC with semi-batch operation.

(A) Residue curves at 1 atm with trajectories of mol fractions in the middle vessel on X-X; (B) average flow rate for the duration of the campaign with mol fractions in the middle-vessel initialized at x_M^i and $x_{I,M}^{\mathrm{Spec}} = 0.98$ along line X-X.

Due to the convexity of the curve in Figure 4B, assuming instantaneous transfers of the charges, it is always preferable to process the two charges separately regardless of the size of the charges. This is confirmed by simulation. With the same parameters as used to generate the trajectories of Figure 3, for an initial MVC charge of 100 m^3 and a column feed rate of 1.5 m^3/h, semi-batch operation requires 235 h to separate 300 m^3, compared to 197 h for a SCMVC. Hence, after the middle vessel is charged, it is optimal to complete the cycle without adding upstream feed.

Shortcut Design Procedures

Shortcut procedures provide initial estimates for the design parameters and help to assess the feasibility of a potential process. Herein, the Fenske and Underwood equations are adapted to determine the minimum number of stages and the minimum reflux ratio for a ternary system in a SCMVC. The minimum number of trays is estimated based upon operation near the end of each cycle, where the recirculation rate is highest, and the minimum reflux ratio is determined using the composition of the feed to the middle vessel. Then, using an estimate for the average reflux ratio, the Gilliland correlation provides an estimate of the number of trays required.

Minimum number of trays

Near the end of each cycle, between 60–69, 125–133 and 190–197 h in Figure 3, the rectifying section contains primarily the intermediate and light species, and the stripping section contains primarily the heavy and intermediate species. With most of the light and heavy species removed, the column operates at, or near, total reflux, and vapor-liquid equilibrium is assumed.

To estimate the minimum number of trays in the rectifying section, it is assumed that the heavy species does not appear in the rectifying section and the middle vessel. Then, the relative volatility of the light to intermediate species is defined as

$$\alpha_{LI} = \frac{y_L/x_L}{y_I/x_I} \tag{2}$$

where the L and I subscripts denote the light and intermediate species. The Fenske equation (Fenske, 1932) to estimate the minimum number of trays in the rectification section (including the middle vessel) takes the form:

$$N_{\min}^{\mathrm{rect}} = \frac{\log\left[\dfrac{x_{I,M}(1-x_{I,D})}{x_{I,D}(1-x_{I,M})}\right]}{\log \alpha_{LI}} \tag{3}$$

where $x_{I,M}$ and $x_{I,D}$ are the mol fractions of the intermediate species in the middle vessel, just prior to dumping, and the distillate, respectively.

To estimate the minimum number of trays in the stripping section, it is assumed that the light species is not present in the stripping section and the middle vessel. Then, the relative volatility of the intermediate to heavy species is defined as

$$\alpha_{IH} = \frac{y_I/x_I}{y_H/x_H} \tag{4}$$

where H is the subscript associated with the heavy species n-octane. The Fenske equation to estimate the minimum number of trays in the stripping section (excluding the reboiler) takes the form

$$N_{\min}^{\mathrm{strip}} = \frac{\log\left[\dfrac{x_{I,M}(1-x_{I,B})}{x_{I,B}(1-x_{I,M})}\right]}{\log \alpha_{IH}} \tag{5}$$

where $x_{I,B}$ and $x_{I,M}$ are the mol fractions of the intermediate species in the bottoms product and the middle vessel. Note that $1 - x_{I,M}$ is the mol fraction of the heavy species in the middle vessel, which is small just prior to dumping.

The minimum number of stages is rounded upwards for *each* section, and added to give the total minimum stages plus unity, since the middle vessel is counted twice. Hence, the estimate for the total minimum stages is

$$N_{\min}^{\mathrm{tot}} = RU\left(\frac{\log\left[\dfrac{x_{I,M}(1-x_{I,D})}{x_{I,D}(1-x_{I,M})}\right]}{\log \alpha_{LI}}\right) + RU\left(\frac{\log\left[\dfrac{x_{I,M}(1-x_{I,B})}{x_{I,B}(1-x_{I,M})}\right]}{\log \alpha_{IH}}\right) - 1 \quad (6)$$

Note that this estimate assumes different binary mixtures in the rectifying and stripping sections and constant relative volatility in each section of the tower.

Minimum reflux ratio

When designing an MVC, an estimate of the minimum reflux ratio provides a lower bound on the utility requirements, and, assuming steady-state operation, a lower bound on the internal flow rates and an upper bound on the product flow rates. These bounds enable the designer to assess whether the trays can weep, as well as to size the control valves.

Several methods for estimating the minimum reflux for multicomponent, nonideal systems have been reviewed by Koehler et al. (1995). In one approach, the reflux and reboil ratios are adjusted until the operating lines in the rectifying and stripping sections just touch (Levy et al., 1985; Julka and Doherty, 1990; Bausa et al., 1998). A less accurate method, which assumes constant relative volatilities, was developed by Underwood (1948). For nearly-ideal mixtures, such as examined herein, this method is easier to apply and provides a good estimate for the minimum reflux ratio.

In a SCMVC, the minimum reflux ratio is determined in accordance with the variation of the composition in the middle vessel. As an approximation, the minimum reflux ratio can be estimated using the Underwood equations developed for continuous distillation. Below, to minimize the reflux ratio, the feed composition is adjusted over the full range of middle-vessel compositions in a cycle.

To estimate the minimum reflux ratio, the Underwood equations are:

$$1 - q = \sum_{i=1}^{NC} \frac{\alpha_i x_{i,F}}{\alpha_i - \phi} \quad (7)$$

$$R_{\min} + 1 = \sum_{i=1}^{NC} \frac{\alpha_i x_{i,D}}{\alpha_i - \phi} \quad (8)$$

where x_F and q are the vector of feed mol fractions and the quality of the feed, respectively. The relative volatilities α_i, $i = 1, \ldots, NC$ are with reference to a base component. Furthermore, for the MVC, $\underline{x}_F = \underline{x}_M$.

The nonlinear program to find the smallest reflux ratio over all feasible mol fractions in the middle vessel is

$$\underset{\underline{x}_M}{Min}\, R_{\min}$$

$$\text{S.T.} \qquad \sum_{i=1}^{NC} \frac{\alpha_i x_{i,D}}{\alpha_i - \phi} - R_{\min} - 1 = 0 \quad (9)$$

$$\sum_{i=1}^{NC} \frac{\alpha_i x_{i,M}}{\alpha_i - \phi} - 1 + q = 0 \quad (10)$$

$$\sum_{i=1}^{NC} x_{i,M} - 1 = 0 \quad (11)$$

$$x_{L,M} \le x_{L,M}^{o} \quad (12)$$

$$x_{I,M} \ge x_{I,M}^{o} \quad (13)$$

$$x_{H,M} \le x_{H,M}^{o} \quad (14)$$

Equations 12–14 assume that the middle vessel concentrates in the intermediate species, with its mol fractions of the light and heavy species decreasing during each cycle.

The Lagrangian for this NLP is

$$L = \sum_{i=1}^{NC} \frac{\alpha_i x_{i,D}}{\alpha_i - \phi} - 1 + \lambda_1\left(\sum_{i=1}^{NC} \frac{\alpha_i x_{i,M}}{\alpha_i - \phi} - 1 + q\right) + \lambda_2(x_{L,M} + x_{I,M} + x_{H,M} - 1) + \lambda_3(x_{L,M} + a^2 - x_{L,M}^{o}) + \lambda_4(x_{I,M} - b^2 - x_{I,M}^{o}) + \lambda_5(x_{H,M} + c^2 - x_{H,M}^{o}) \quad (15)$$

where a, b, and c are introduced as slack variables. Consequently, the stationarity conditions are

$$\frac{dL}{d\phi} = -\sum_{i=1}^{NC} \frac{\alpha_i x_{i,D}}{(\alpha_i - \phi)^2} - \lambda_1\left(\sum_{i=1}^{NC} \frac{\alpha_i x_{i,F}}{(\alpha_i - \phi)^2}\right) = 0 \quad (16)$$

$$\frac{dL}{dx_{L,M}} = \frac{\lambda_1 \alpha_L}{\alpha_L - \phi} + \lambda_2 + \lambda_3 = 0 \quad (17)$$

$$\frac{dL}{dx_{I,M}} = \frac{\lambda_1 \alpha_I}{\alpha_I - \phi} + \lambda_2 + \lambda_4 = 0 \quad (18)$$

$$\frac{dL}{dx_{H,M}} = \frac{\lambda_1 \alpha_H}{\alpha_H - \phi} + \lambda_2 + \lambda_5 = 0 \quad (19)$$

$$\frac{dL}{d\lambda_3} = x_{L,M} + a^2 - x_{L,M}^{o} = 0 \quad (20)$$

$$\frac{dL}{d\lambda_4} = x_{I,M} - b^2 - x_{I,M}^{o} = 0 \quad (21)$$

$$\frac{dL}{d\lambda_5} = x_{H,M} + c^2 - x_{H,M}^{o} = 0 \quad (22)$$

$$\frac{dL}{da} = 2a\lambda_3 = 0 \quad (23)$$

$$\frac{dL}{db} = -2b\lambda_4 = 0 \quad (24)$$

$$\frac{dL}{dc} = 2c\lambda_5 = 0 \quad (25)$$

$$\sum_{i=1}^{NC} x_{i,M} - 1 = 0 \quad (11)$$

Since $\alpha_L \neq \alpha_I \neq \alpha_H$,

$$\frac{\lambda_1 \alpha_L}{\alpha_L - \phi} \neq \frac{\lambda_1 \alpha_I}{\alpha_I - \phi} \neq \frac{\lambda_1 \alpha_H}{\alpha_H - \phi} \tag{26}$$

it follows from Eqs. 17–19 that $\lambda_3 \neq \lambda_4 \neq \lambda_5$. Therefore, at least two of the multipliers λ_3, λ_4, and λ_5 must be non-zero, and, from the complementarity conditions (Eqs. 23–25), at least two of the slack variables a, b, and c must be zero. That is, at the stationary points, two of the species mol fractions must be at the mol fractions charged to the middle vessel. Consequently, from Eq. 11, the stationarity conditions are satisfied at the feed composition. As shown in Table 2, this stationary point is the minimum point in its vicinity.

Note that herein the reflux and reboil ratios are varied during each mode of the campaign, in the *DB*-control configuration, to be discussed below. To maintain concentration and level set points, the controllers keep the reflux ratio above $R_{\min}$ at all times. Consequently, the smallest $R_{\min}$ is computed to provide a design that maintains downcomer seals and avoids weeping at the smallest recirculation rates. If, instead, the reflux and reboil ratios are held constant, it is necessary to design the column to operate properly at the largest $R_{\min}$.

Equipment sizing

The trays are sized to provide sufficient residence time for the liquid while maintaining the vapor sufficiently below its flooding velocity at total reflux. The recirculation rate at total reflux and the heat duties for condensation and boiling are calculated, prior to design of the condenser, reflux accumulator, and reboiler. The MESH equations at steady state are solved to determine all of the internal flow rates. For the SCMVC to separate *n*-hexane, *n*-heptane, and *n*-octane, the total residence time in the liquid on a tray and in its downcomer is 8 s and the feed rate to the column at total reflux is 5 m^3/h. This gives a column diameter of 1 m. For sieve trays spaced 0.5 m apart, the flooding velocity varies from 1 m/s to 1.3 m/s. With an active area of 76% of the column cross-section and with the ratio of the area of the holes to the active area equal to 0.1, vapor velocities remain between 70–90% of the flooding velocity for the duration of the cycle.

Decentralized Control

In this article, focus is placed on the selection of a decentralized control configuration, rather than a multivariable predictive controller, primarily because of the middle vessel, which is shown to decouple simple PI-control loops. Controller pairings are selected and controllers are tuned to provide effective performance in response to disturbances and set point changes. Each PI controller adjusts its manipulated variable z by

$$z = z^* + K_c \left[e + \frac{1}{\tau_I} \int e \, dt \right] \tag{27}$$

where e is the error in the measured variable, z^* is the midpoint of the manipulated variable (or bias at $e = 0$), K_c is the controller gain, and τ_I is the integral time constant (s).

The selection of the manipulated and measured variables must utilize available degrees of freedom, aim to limit interactions between the controllers, and avoid operation near-limiting conditions (such as valve-saturation constraints). Since internal holdups in the sump and reflux drum, as well as the operating pressure must be maintained, desirable objectives, such as single- or dual-composition control, are applied with the remaining degrees of freedom. For continuous processes, a wealth of information is available to assist in selecting control loops (Shinskey, 1984; Skogestad and Morari, 1987; Skogestad et al., 1990; Skogestad, 1997).

To our knowledge, controller configurations for semicontinuous distillation have not been proposed in the literature. For this process, a steady state does not exist, and consequently, analysis techniques that assume steady-state operation must be applied more carefully. A drawback of semicontinuous distillation is that the column is not "self-regulating." In a continuous distillation column, when the concentration of the light species in the condenser is below specification, the distillate flow rate can be reduced, and reflux increased. As the light species is added continuously in the feed, the total holdup in the column of the light species increases, and the condenser concentration rises in turn; that is, its concentration in the distillate is self-regulated. This is not the case for a SCMVC, because, as distillate is withdrawn, the total holdup of the light species in the column and middle-vessel decreases. Hence, as the distillate (or bottoms product) is removed, set-point tracking of the product concentrations becomes increasingly difficult.

In spite of these limitations, PI controllers can be used effectively. Herein, three configurations commonly used for continuous, dual-composition control are considered. In the LV configuration, the reflux L_o (kmol/h) controls x_D, and the boilup rate V_b controls x_B. For the $(L/D)(V/B)$ configuration, the reflux and reboil ratios control x_D and x_B, respectively. Note that L/D can be manipulated using an internal controller, the set point of which can be adjusted by an external controller that measures x_D. The internal controller can measure D, which is manipulated by the level controller, and adjust the reflux flow rate L_o to achieve the desired R. A similar cascade loop can be implemented for the $V/B - x_B$ controller. Finally, in the DB configuration, the distillate and bottoms flow rates are manipulated to control x_D and x_B. To maintain the inventory in the sump and reflux drum, the manipulated variables for level control are selected next. In the LV- and $(L/D)(V/B)$ configurations, the distillate and bottoms flow rates maintain inventory control, while in the DB configuration, levels are controlled using L_o and V_b. A DB configuration that adjusts the feed flow rate to control the

Table 2. Minimum Reflux Ratios Near $\underline{x}^0 = [0.333\ \ 0.333\ \ 0.333]^T$ with $\alpha_L = 9$, $\alpha_I = 3$, and $\alpha_H = 1$

$X_{L,M}$	$X_{I,M}$	$X_{H,M}$	ϕ	$R_{\min}$
0.333	0.333	0.333	4.66	1.00
0.323	0.353	0.323	4.76	1.05
0.300	0.400	0.300	5.00	1.18
0.266	0.400	0.333	4.85	1.09
0.333	0.400	0.266	5.18	1.28

sump level is also considered. Uncommon configurations, in which the reflux or distillate flow rate is manipulated to control a bottoms mol fraction, or the boilup or bottoms flow rate is manipulated to control a distillate mol fraction, are not considered because the large holdup of the middle-vessel results in unacceptably slow responses.

For SCMVCs, in addition to interaction between the composition controllers, interactions between the composition and level controllers must be considered. Stated differently, for SCMVCs, it is not appropriate to assume perfect level control. Here, the control configuration must operate reliably throughout each cycle, especially in the rapid transients that occur after the middle-vessel is recharged. During this transitory period, the distillate and bottoms products are usually off-specification, and product is not taken until acceptable concentrations are recorded. Consequently, L_o and V_b (or F_c) *must* be used for level control, whether or not these variables are normally manipulated for composition control. Note that in a continuous column, when the distillate and bottoms products are off-specification and have small flow rates, flooding can result quickly, a situation that is avoided in MVCs with a full-liquid sidedraw.

This problem with off-specification distillate and bottoms products poses an important conflict between design and control. Clearly, composition control can be improved with an increased number of stages, also reducing the need to operate at large reflux ratios, but this is counter-balanced by increased capital costs.

(L/D)(V/B) configuration

Skogestad and Morari (1987) and Skogestad et al. (1990) generally find the $(L/D)(V/B)$ configuration (reflux-reboil ratio configuration) to be the most promising for binary dual-composition control in continuous columns. Typically, limited controller interaction is experienced, as one controller can be disconnected without sacrificing the performance of the other loop.

However, for semicontinuous middle-vessel distillation of ternary mixtures, two disadvantages are associated with the $(L/D)(V/B)$ configuration. First, the midpoint (or bias) of z^* is difficult to locate because, as the light and heavy species are removed, the reflux and reboil ratios can increase significantly. Furthermore, as the reflux and reboil ratios become large, L_o and V_b become sensitive to fluctuations in the distillate and the bottoms flow rates. This is exacerbated towards the end of each cycle, when the distillate and bottoms flow rates are small, such that changes in the distillate and bottoms flow rates cause large changes in the reflux and reboil ratios.

LV configuration

The LV configuration is popular for continuous towers in industry, and has some attractive features for the separation of ternary mixtures using a SCMVC, especially with regard to the ease of sizing the valves. Upper bounds for the flow rates are set slightly above L_o and V_b determined for the column at steady state and total reflux. For lower bounds, these flow rates are computed for a tower with the specified feed rate and composition, and the distillate on specification, at steady state and minimum reflux. The midpoints are the averages of the lower and upper bounds.

For a SCMVC, this control configuration has the disadvantage, discussed above, when the distillate and bottoms products are off specification shortly after the middle vessel is recharged. During the rapid transient, at total reflux, one (or both) of the reflux and boilup flow rates L_o and V_b must be used temporarily for level control, and, hence, is temporarily unavailable for composition control.

DB configuration

This control configuration intrinsically handles off-specification products. When the product concentrations are significantly below their specifications, operation moves toward total reflux with the liquid levels in the reflux drum and sump controlled using L_o and V_b. Its valves are straightforward to size, with the lower bounds on B and D at zero, and upper bounds at the feed flow rates of the species being removed.

For continuous distillation, the DB configuration can prove difficult for level control in the reflux drum due to a ‘‘pump-around’’ effect that occurs when the liquid entering the top tray is returned to the reflux drum through the vapor leaving the top tray. This is because, in continuous operation, the control system preserves the liquid inventory within the column. However, with an external middle vessel, the liquid overflows into the middle vessel and is removed from the column.

Yet, another disadvantage with the DB configuration for dual-composition control in a binary continuous column is that, due to the mass-balance constraints, composition control cannot be maintained when one of the control loops is set to manual with the distillate or bottoms flow rate fixed. For example, when the distillate flow rate is fixed, the composition of the bottoms product cannot be controlled due to the overall column mass balance

$$F_c = B + D \tag{28}$$

This does not occur for the separation of multicomponent mixtures using a SCMVC because this overall mass balance does not apply.

For the separation of ternary mixtures using a SCMVC (semicontinuous-middle vessel distillation), it is particularly important to reduce the interaction between the control loops because the composition of the stream from the middle vessel to the column changes throughout the cycle. One technique often used to assess the interaction between controllers is *relative gain analysis* (Bristol, 1966). As shown below, this analysis explains the desirable decoupling effect of the DB configuration.

The elements of the relative-gain array (RGA) for the two manipulated variables, D and B, and the two measured variables x_D and x_B are

$$\lambda_{i,j} = \frac{\text{Gain with all other loops open}}{\text{Gain with all other loops closed}} \tag{29}$$

where i and j are the manipulated and measured variable counters, respectively. For the DB configuration, assuming perfect level and pressure control, the relative gain for the

D-x_D pair is

$$\lambda_{x_D,D} = \frac{\left.\dfrac{dx_{I,D}}{dD}\right|_{B}}{\left.\dfrac{dx_{I,D}}{dD}\right|_{x_{I,B}}} = \frac{\left.\dfrac{dD}{dx_{I,D}}\right|_{x_{I,B}}}{\left.\dfrac{dD}{dx_{I,D}}\right|_{B}} \tag{30}$$

To evaluate this RGA element, assuming zero holdup on the trays (for calculation of relative gains only), the overall mass balance is

$$\frac{dH_M}{dt} = -(D+B) \tag{31}$$

and the balance for the intermediate species is

$$\frac{d(H_M x_{I,M})}{dt} = -(Dx_{I,D} + Bx_{I,B}) \tag{32}$$

where H_M is the molar holdup of the middle vessel. Differentiating by parts, discretizing, and rearranging

$$H_M\left(\frac{x_{I,M} - x^o_{I,M}}{\Delta t}\right) = B(x_{I,M} - x_{I,B}) + D(x_{I,M} - x_{I,D}) \tag{33}$$

where $x^o_{I,M}$ is the mol fraction of the intermediate species at the beginning of the time step Δt.

Taking the derivative of Eq. 33 with respect to $x_{I,D}$ and rearranging

$$(x_{I,M} - x_{I,D})\frac{dD}{dx_{I,D}} = \frac{H_M}{\Delta t}\frac{dx_{I,M}}{dx_{I,D}} - \frac{dB}{dx_{I,D}}(x_{I,M} - x_{I,B}) - B\left(\frac{dx_{I,M}}{dx_{I,D}} - \frac{dx_{I,B}}{dx_{I,D}}\right) - D\left(\frac{dx_{I,M}}{dx_{I,D}} - 1\right) \tag{34}$$

Substituting in the numerator (at fixed $x_{I,B}$) and in the denominator (at fixed B) of Eq. 30, an expression for the rela-

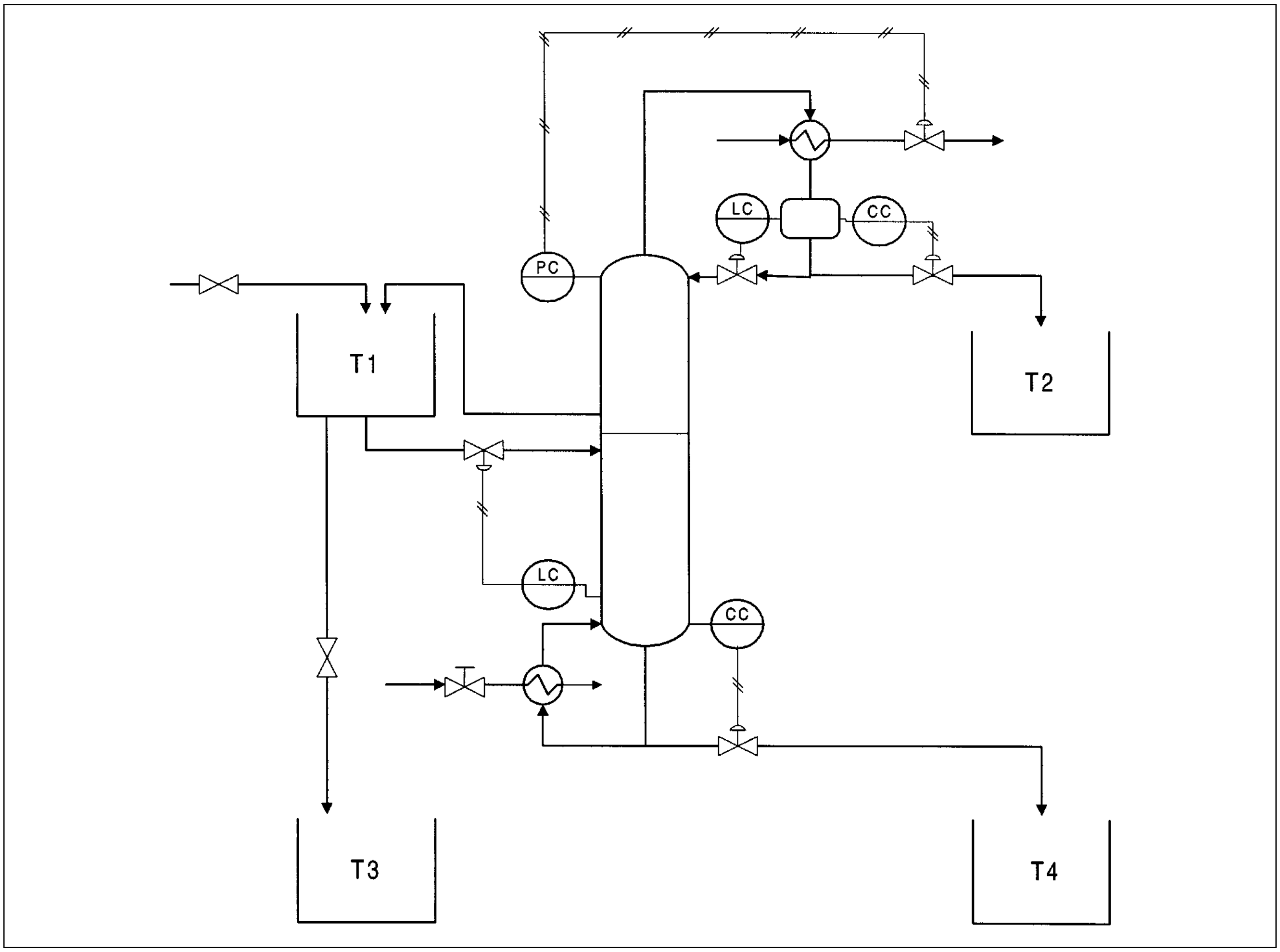

Figure 5. *DB* configuration with column feed control of the sump liquid level.

tive gain is obtained

$$\lambda_{x_D, D} = \frac{\dfrac{H_M}{\Delta t}\dfrac{dx_{I,M}}{dx_{I,D}} - \dfrac{dB}{dx_{I,D}}(x_{I,M} - x_{I,B}) - B\left(\dfrac{dx_{I,M}}{dx_{I,D}}\right) - D\left(\dfrac{dx_{I,M}}{dx_{I,D}} - 1\right)}{\dfrac{H_M}{\Delta t}\dfrac{dx_{I,M}}{dx_{I,D}} - B\left(\dfrac{dx_{I,M}}{dx_{I,D}} - \dfrac{dx_{I,B}}{dx_{I,D}}\right) - D\left(\dfrac{dx_{I,M}}{dx_{I,D}} - 1\right)} \tag{35}$$

The numerator and denominator differ by the term

$$\left(\frac{dB}{dx_{I,D}}\bigg|_{x_{I,B}}\right)(x_{I,M} - x_{I,B})$$

in the numerator, and the term

$$B\frac{dx_{i,B}}{dx_{I,D}}\bigg|_{B}$$

in the denominator. The derivative

$$\frac{dB}{dx_{I,D}}\bigg|_{x_{I,B}}$$

is approximately zero, since the bottoms flow rate does not change appreciably to maintain the set point mol fraction of the intermediate species, given a change in the distillate composition. Note that, in response to a step change in the distillate mol fraction, only the holdup in the middle vessel changes. Similarly, the derivative

$$\frac{dx_{I,B}}{dx_{I,D}}\bigg|_{B}$$

is approximately zero, since the intermediate mol fraction in the bottoms product can be maintained nearly constant at the same bottoms flow rate in response to a change in the distillate mol fraction. With these two derivatives nearly zero, the relative gain $\lambda_{x_D,D}$ is nearly unity. Consequently, this diagonal pairing in the RGA suggests very little interaction between the composition controllers.

DB configuration with feed manipulating sump level

In the typical *DB* configuration, a significant delay is experienced when manipulating the reboil rate to control the sump level. This configuration can be modified to overcome this delay, by manipulating the feed rate to the distillation column, as shown in Figure 5. While not appropriate for continuous distillation, where the feed rate cannot normally be adjusted for control purposes, it is quite promising for a SCMVC. Here, the inventory in the sump is maintained by adjusting the feed rate to the column, with the boilup rate constant, and the bottoms flow rate is adjusted to maintain the bottoms composition. Note that the distillate composition is controlled by adjusting *D*, or in alternate configurations L_o or R. Simulations show this configuration can be quite effective. One advantage is that the internal flow rates within the column are relatively constant throughout the cycle, as compared with alternate configurations. Hence, tray designs are simpler, with less uncertainty regarding performance. Note, however, that when the relative volatility of the intermediate/heavy species is close to unity, a large number of stages is required in the stripping section, which results in slow responses of the feed-flow/sump-level control loop.

Table 3. Physical Property Data

	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}
T_b (°C)	68.9	98.4	125.7
ΔH^v (kJ/kmol)*	28,931	31,956	34,876
ρ_L (kg/m^3)†	608	637	658

*Perry and Green (1984).

†Liquid densities (ASPEN PLUS, Version 10.1) reported at 75°C and at elevated pressures when 75°C exceeds the normal boiling point.

Simulation Results

Results are presented for the separation of 300 m^3 of an equimolar mixture of *n*-hexane, *n*-heptane, and *n*-octane using a SCMVC, with a 100 m^3 middle vessel and the flow rate of the feed to the column set at 5 m^3/h. Average relative volatilities are approximately $\alpha_{LI} = \alpha_{IH} = 3.0$, and, consequently, $\alpha_{LH} = 9.0$. Note that additional physical property data are shown in Table 3. To obtain 98 mol % pure products, using Eq. 6, the minimum number of stages is 15, with seven stages in the rectifying and stripping sections. Accounting for tray inefficiencies, a column consisting of ten stages in each section is specified. Using Eqs. 7 and 8, the minimum reflux ratio is estimated at 1.0. Upper bounds on the reflux and boilup flow rates, assuming total reflux, are $L_o = 29.0$ kmol/h (4.1 m^3/h) and $V_b = 35.0$ kmol/h (6.1 m^3/h). The initial feed flow rate is 31.7 kmol/h, with a maximum distillate rate of 10.6 kmol/h. For the *DB* configuration, where V_b varies slightly, or is held constant, since $R_{\min} = 1.0$ and the maximum distillate rate is 10.6 kmol/h, the lower bound on L_o is approximately 10.6 kmol/h. The rate of heat removal to condense 21.2 kmol/h (10.6 kmol/h × 2) of *n*-hexane in the distillate is equivalent to the rate of heat addition to vaporize 17.9 kmol/h of *n*-octane, providing a lower bound for the boilup rate.

The composition controllers have set points of 98 mol % *n*-hexane in the distillate, and 98 mol % *n*-octane in the bottoms product. Instantaneous measurements of the tray temperatures, and conversion to mol fractions, are assumed. Upper and lower bounds on the mol fractions are 0.995 and 0.96. Note, furthermore, that the product valves close when the mol fraction of the desired species is below 0.96, and are fully open when the mol fraction exceeds 0.995. The composition controller gains are set such that for a 1% change in the mol fraction over its permissible range (0.995 − 0.96), the corresponding manipulated variable changes by 1% over its permissible range. Note, also, that P control is used normally for the level and composition controllers, that is, τ_I is assigned a large value.

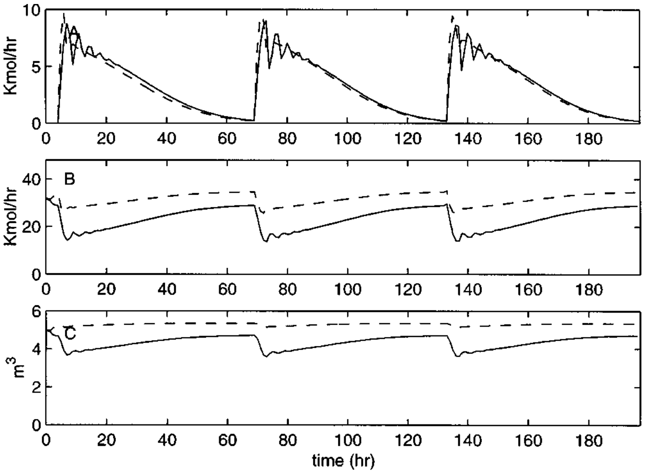

Figure 6. Trajectories of the manipulated variables for the *DB* configuration.

(A) Distillate (solid line) and bottoms (dotted line) flow rates; (B) L_o (solid line) and V_b (dotted line); (C) volumetric holdup in reflux drum (solid line) and sump (dotted line).

The column model is comprised of the MESH equations, assuming pseudo-steady-state heat balances [see, for example, the textbook by Seader and Henley (1998, p. 695)]. The MESH equations are integrated using an implicit integrator with step-size control, implemented in FORTRAN 90.

Figures 6 and 7 provide trajectories of the manipulated and controlled variables. As shown in Figure 6B, larger fluctuations occur at the top of the column, where the reflux rate has a maximum turndown of 43%. In comparison, at the bottom of the column, the boilup rate has a maximum turndown of 18%. Larger oscillations are observed in the distillate flow rate and the reflux drum holdup, than in the bottoms flow rate and sump holdup. Apparently, the process and its control configuration have directional interaction because the D-x_D controller and the level controller in the reflux drum are affected by fluctuations at the base of the column, whereas the controllers at the base of the column are not affected by fluctuations at the top of the column (due to the liquid sidedraw to the middle vessel.) As shown in Figure 6C, the level controller in the reflux drum performs satisfactorily, indicating that the "pump-around" effect is eliminated by the middle vessel. Thanks to the satisfactory performance of the level controllers, the sizes of the sump and reflux drums can be reduced.

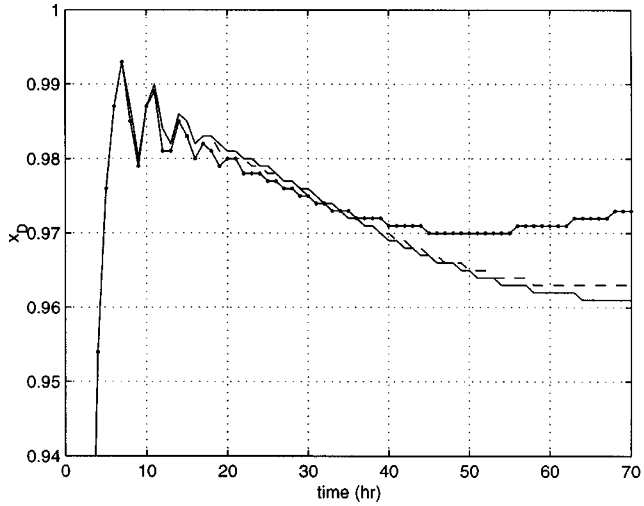

Figure 7. Trajectories of x_D for the initial cycle.

$\tau_i = 0.1$ h (dotted line), $\tau_i = 1$ h (dashed line), and without integral action (solid line). The integral term is initialized at $t = 5$ h.

The trajectories of $x_{I,D}$ in Figure 7 show the difficulty of maintaining the set point mol fractions over an entire cycle. Although integral action improves set point tracking, due to the diminishing holdups of the light and heavy species, it does not eliminate offset. Though, set point tracking proves difficult, the mol fraction in the distillate product tank settles at 0.980 and 0.981, without and with integral action, respectively. Although the mol fraction of n-hexane in the distillate is below its set point during much of the cycle, higher distillate flow rates occur while x_D exceeds its set point, and, hence, the mol fraction in the product tank settles near its set point.

Similar trajectories and results for $x_{H,B}$ are observed, and the mol fraction of n-octane in the bottoms product tank is 0.980 at the conclusion of the campaign, whether or not integral action is used.

While integral action does not improve control of the product tank composition, it can cause valve saturation, especially at low τ_I. The integral term must be reinitialized when this occurs. Consequently, it is recommended that proportional control be used.

Results are presented next for a *DB* configuration with the sump holdup maintained by adjusting the flow rate of the column feed. The boilup rate is fixed at 32 kmol/h (the average boilup rate for the previous configuration), and the midpoint of the feed flow rate is set at 5 m^3/h. The trajectories shown in Figure 9 are nearly identical to those presented in Figure 6. The mol fraction trajectories in Figure 8 are also similar, although mol fractions in the middle vessel are not displayed in Figures 6 and 7. The internal vapor flow rate

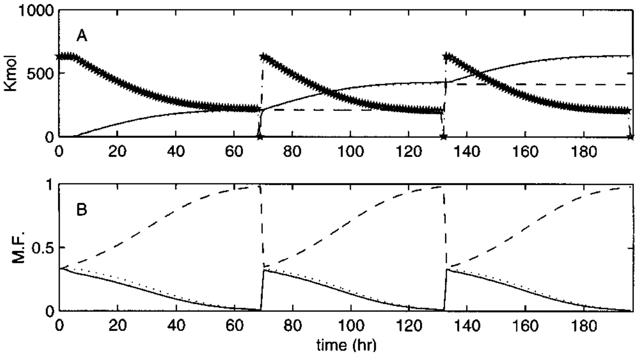

Figure 8. Trajectories of tank holdups and mol fractions in the middle vessel using the *DB* configuration with feed control of the sump level.

Holdups: *** T1, —— T2, – – – T3, · · · · T4. Mol fractions in the middle vessel: —— n-hexane, – – – n-heptane, · · · · n-octane.

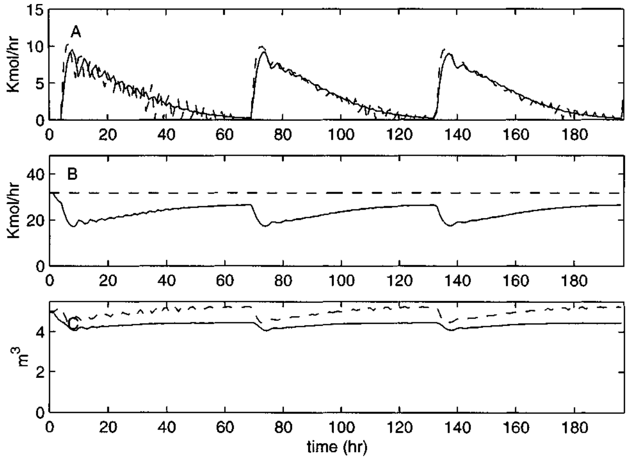

Figure 9. Trajectories of the manipulated variables for the *DB* configuration with feed control of the sump level.

(A) Distillate (solid line) and bottoms (dotted line) flow rates; (B) L_o (solid line) and V_b (dotted line); (C) volumetric holdup in reflux drum (solid line) and sump (dotted line).

shown in Figure 9B is fixed and the variation in the liquid flow rate is less than that shown in Figure 6B. Lowering the gain on the level controller for the sump reduces the deviation in the bottoms flow rate. As indicated in Figure 9C, this can be implemented without the sump over- or under-flowing, with the level maintained well within suitable operating bounds.

Conclusions

Effective use of a semicontinuous, middle-vessel column (SCMVC) is demonstrated for the separation of nearly-ideal ternary mixtures. Specifically, a design is presented to separate a mixture of *n*-hexane, *n*-heptane, and *n*-octane. The Fenske and Underwood shortcut methods are adapted to provide acceptable estimates of the minimum number of stages and the minimum reflux ratio to achieve a desired separation. Three control configurations are considered, and it is shown that, while less desirable for continuous separations, the *DB* configuration is more desirable for a SCMVC. For the example process, simulations show that this control configuration provides acceptable performance.

Acknowledgment

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Notation

a, b, c = slack variables

B = bottoms flow rate, kmol/h

D = distillate flow rate, kmol/h

e = error in measured variable

F_c = flow rate of feed to column, kmol/h

H_M = middle vessel holdup, kmol

K_c = controller gain

L = Lagrangian; Liquid flow rate, kmol/h

L_o = reflux flow rate (kmol/h)

$N_{\min}^{\text{rect}}$ = minimum number of trays in rectifying section

$N_{\min}^{\text{strip}}$ = minimum number of trays in stripping section

$N_{\min}^{\text{tot}}$ = minimum number of trays in column

q = quality of the feed

R = reflux ratio

R_B = reboil ratio

t = time, h

T_b = normal boiling-point temperature, °C

V = vapor flow rate, kmol/h

V_b = boilup rate, kmol/h

x = mol fraction (Subscripts: L, light species; I, intermediate species; H, heavy species; D, in distillate; B, in bottoms; F, in feed; M, in middle vessel. When species is not specified, it is the intermediate species. Superscripts: 0, at the start of a cycle; ave, average composition; spec, mol-fraction specification.)

y = vapor mol fraction

z = manipulated variable

α = relative volatility

ΔH^{v} = latent heat of vaporization, kJ/kmol

λ = Lagrange and Kuhn-Tucker multipliers

$\lambda_{I,j}$ = element of relative gain array for manipulated variable i and controlled variable j

Λ = relative gain array

τ = time, s

ρ_L = liquid density, kg/m^3

τ_I = integral time constant, s

ϕ = variable in Underwood Eqs. 7 and 8

Subscripts

bd = batch MVC distillation

ic = initial charge

sd = semicontinuous distillation

tc = total charge

Operations

RU = Round upward

Abbreviations

MESH = material balance, equilibrium, summation of mole fraction, and heat balance

MVC = middle-vessel column

PI = proportional-integral control

SCMVC = semicontinuous, middle-vessel column

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