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SEPARATIONS

Optimization of Multicomponent Batch Distillation Columns

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The shortcut method described in earlier literature facilitates the optimal design of batch distillation columns using a relatively less amount of computer time and memory. The method can be extended to the more complex problem of optimal design of batch distillation columns in which multiple fractions are produced. In the present paper, optimization approaches using the shortcut method for the optimal design of single- and multiple-fraction batch columns operating under constant reflux and variable reflux conditions are presented.

1. Introduction

The shortcut method has been shown (Diwekar, 1988; Diwekar et al., 1987) to be extremely effective for performing a rapid design of batch distillation columns, without requiring extensive memory and computational time. Such a method thus is ideally suited for tackling problems in the optimal column design, which would call for extensive computational effort, if rigorous models are used for design.

The optimal design and operation of batch plants including distillation has been reviewed by Rippin (1983). The literature published on the optimization of a batch distillation column is mostly concentrated on the optimal control policies. Most of the published papers use Pontryagin's continuous maximum principle to solve the problem of optimal control. There is very little literature on the optimal design of batch distillation for performing a specified separation using a predefined policy of either constant reflux or variable reflux (Houtman and Hussain, 1956; Robinson and Goldman, 1969).

In this paper, the optimization problem is formulated with profit as an objective function. Since the shortcut method approximates the column operation with a set of nonlinear, noninteger equations, the optimization problems can be treated as a nonlinear constrained optimization problem. Formulation of the optimization problem is presented for the single-fraction and multifraction batch distillation columns operating under variable and constant reflux conditions.

2. Formulation of the Optimization Problem

2.1. Objective Function. The objective function considered here is annual profit P:

$$P = \text{annual sales value of distillate} - \text{annual cost of distillation} \quad (1)$$

The annual cost of distillation is based on the cost function of the continuous distillation column given by Happel

(1958). The cost function involves the following:

(a)

$$\text{amortized cost of the distillation equipment per year} = C1VN/Ga \quad (2)$$

where C1 is the amortized incremental investment cost, $/m^2/plate/year; V is the vapor boil-up rate, kg/h; N is the number of plates; and Ga is the allowable vapor velocity, kg/h/m^2.

(b)

$$\text{amortized cost of the reboiler and condenser per year} = C2V/Gb \quad (3)$$

where C2 is the amortized incremental investment cost in the tubular equipment, $/m^2/year; and Gb is the vapor handling capacity of the tubular equipment, kg/h/m^2.

(c)

$$\text{annual cost of the steam and coolant} = C3VtNB \quad (4)$$

where C3 is the cost of the steam and coolant to vaporize and condense, respectively, per kg of distillate; t is the time required per batch, h; and NB is the number of batches per year, $= 24(365/(t + ts))$, ts being the time required for startup and shutdown, h.

With the inclusion of cost terms in eq 1, the objective function becomes

$$P = \sum_{i=1}^{\text{nfr}} C(i)D(i)\text{NB} - C1VN/Ga - C2V/Gb - C3VtNB \quad (5)$$

where $C(i)$ is the cost of the product for the ith fraction, per kg; and $D(i)$ is the distillate in fraction i, per batch, kg/batch.

The degrees of freedom analysis (discussed in the next section) shows that, for the single-fraction case and for both the variable and constant reflux conditions, there are 3 degrees of freedom. For the constant reflux condition, if the reflux ratio is maintained constant throughout the operation (for all the fractions), the analysis of the mul-

tifraction case results in the same number of degrees of freedom, the same solution strategy, and the same number of constraints. However, for variable reflux conditions, the reflux pattern changes for each fraction, leading to more degrees of freedom, and introduces more constraints to the problem.

2.2. Constraints, Design Variables, and Solution.
2.2.1. Variable Reflux Condition. (a) Single Fraction.
The shortcut method described by Diwekar (1988) leads to the following constraint equations (for ready reference, the shortcut method model equations are given in the Appendix section):

The differential material balance has been approximated as

$$x_B^{(i)} = x_D^{(i)} - \frac{(x_D^{(i)} - x_B^{(i)})_{old}}{(x_D^{(1)} - x_B^{(1)})_{old}}(x_D^{(1)} - x_B^{(1)}) \quad i = 2, 3, ..., n \tag{6}$$

The equation for time t is

$$t = \frac{F(x_D^{(1)} - x_F^{(1)})}{V} \sum_{x_{B_\infty}^{(1)}}^{x_F^{(1)}} \frac{\Delta x_B^{(1)}(R + 1)}{(x_D^{(1)} - x_B^{(1)})^2} \tag{7}$$

In addition to the above two explicit equality constraints (eq 6 and 7), the problem has an implicit equality constraint, which, following the shortcut method, can be expressed as

$$N = f(r, x_D^{(1)}, x_F^{(i)}) \tag{8}$$

where

$$r = (R/Rmin)_{initial}$$

The general optimization problem has $n + 2$ degrees of freedom. For the condition where the product composition $x_D^{(i)}, i = 1, 2, ..., n$, approximately remains constant, $x_D^{(i)}$s can be specified or can be calculated by using additional $n - 1$ equations in the form of Hengestebeck–Geddes' equation given by

$$x_D^{(i)} = \left(\frac{\alpha_i}{\alpha_1}\right)^{C_1} \frac{x_D^{(1)}}{x_B^{(1)}} x_B^{(i)} \quad i = 2, 3, ..., n \tag{9}$$

So the degrees of freedom reduce to 3. The decision variables can be chosen as N or r, $x_{B_\infty}^{(1)}$ (termination criterion), and V.

Fixed Terminal Condition. For a problem with a fixed terminal condition, $x_{B_\infty}^{(1)}$ is fixed. If V is also fixed, then the column design becomes a single-variable optimization problem with r (or N) as the decision variable. In order to maintain the feasibility of the design, it is necessary to place appropriate limits on the value of r. The lower limit on r is governed by the value of Rmin and the upper limit by Nmin (Nmin is a measure of the total reflux condition). Since Nmin is expected to increase with the decrease in $x_B^{(1)}$, the initial choice of r should be such that the resulting N is greater than the maximum value of Nmin. To obtain the upper limit of r, Nmin is calculated at the terminal value of $x_B^{(1)}$, and this is taken as the limiting value of N. The value of r corresponding to this N is calculated at the initial condition of $x_B^{(1)}$ ($x_B^{(1)} = x_F^{(1)}$). This is taken as the limiting value rmax of r (Figure 1). The optimization problem is then solved with the inequality constraint

$$1 < r < rmax \tag{10}$$

Free Terminal Condition. When $x_{B_\infty}^{(1)}$ and V are not fixed, the problem becomes a multivariable optimization problem. In addition to the constraint on r discussed
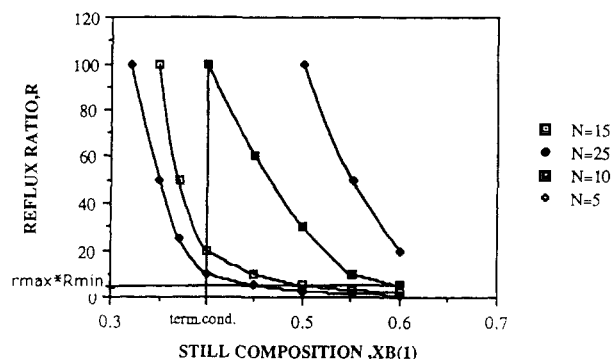

Figure 1. Concept of rmax.

the previous section, there is a constraint on $x_{B_\infty}^{(1)}$ given by

$$0 < x_{B_\infty}^{(1)} < x_F^{(1)} \tag{11}$$

and a constraint on V given by

$$0 < V \tag{12}$$

The optimization problem can be solved as a sequence of optimization problems (as indicated below):

$$\max P(r, x_{B_\infty}^{(1)}, V) = \max [f(x_{B_\infty}^{(1)}, r) = \max \{F(r)\}] \tag{13}$$

Since each inner optimization problem is of single variable by nature, the Fibonacci search technique can be used.

An alternate approach is to solve the problem as a NLP problem by using the sequential quadratic programming approach.

Formulation of NLP. The problem can be formulated as a nonlinear programming problem with the transformed decision variables $X(i)$, $i = 1, ..., 3$, as follows:

$$\min -P(X) \tag{14}$$

subject to $X(i) > 0$ for $i = 1, ..., 3$ where

$$X(1) = \frac{rmax - 1}{r - 1} - 1 \tag{15}$$

$$X(2) = \frac{x_F^{(1)}}{x_{B_\infty}^{(1)}} - 1 \tag{16}$$

$$X(3) = V \tag{17}$$

For the solution of this NLP, sequential quadratic programming is used. The first derivatives needed for the method can be evaluated analytically for the case where $x_D^{(i)}$, $i = 1, 2, ..., n$, approximately remains constant.

(b) Multifraction. The problem formulation is similar to that of the single fraction except for a few differences. The multifractions are treated as a number of single fractions in series. The termination conditions for the previous fraction are the starting conditions for the present fraction. So the implicit constraint (eq 8) in the single-fraction case can be modified for the multifractions case as follows:

$$N = f(r, x_{Df}^{(i,j)}, x_{Bf}^{(i,j)}) \quad i = 1, 2, ..., n;$$
$$j = 1, 2, ..., nfr \tag{18}$$

where $x_{Df}^{(i,j)}$ is the starting value of $x_D^{(i)}$ for fraction j, $x_{Bf}^{(i,j)}$ is the starting value of $x_B^{(i)}$ for fraction j, and nfr is the number of fractions.

So the degrees of freedom increase to $2 + nfr$, instead of 3. The decision variable can be chosen as N or r, $x_{Bf}^{(rk,j)}$, $j = 1, 2, ..., nfr$, and V.

Fixed Terminal Condition. Similar to the single-fraction condition, if the terminal conditions and V are fixed, then the column has the single decision variable r or N. The constraint on r is the same, except here rmax will take the value corresponding to the value of Nmin, which is the largest of all the fractions calculated at the terminal condition. The solution strategy is similar to that of the single-fraction condition.

Free Terminal Condition. The problem for multifraction optimization becomes comparatively more difficult because, along with the number of decision variables, the number of constraints also increases with the increase in the number of fractions. The constraints are

$$x_{Bf}^{(rk,2)} < x_{Bf}^{(rk,1)} < x_F^{(1)} \tag{19}$$

$$x_{Bf}^{(rk,j+1)} < x_{Bf}^{(rk,j)} < x_{Bf}^{(rk,j-1)} \qquad j = 2, 3, ..., \text{nfr} \tag{20}$$

and

$$0 < x_{Bf}^{(rk,nfr)} \tag{21}$$

The problem cannot be solved with single-variable techniques like the single-fraction condition. So the following strategy can be used:

$$\max P(r, x_{Bf}^{(rk,j)}, V) = \max [f(x_{Bf}^{(rk,j)}, r) = \max \{F(r)\}] \tag{22}$$

As stated earlier, the innermost problem can be solved by the Fibonacci search technique and the outer loop by the Golden complex method.

Formulation of NLP. Formulation of NLP is similar to that of the single-fraction case, where the constraints on $x_{Bf}^{(i,j)}$ are taken care of by formulating them as follows:

$$x_{Bf}^{(rk,1)} = \frac{x_F^{(1)}}{1 + xn(rk)} \qquad x_{Bf}^{(rk,j+1)} = \frac{x_{Bf}^{(rk,j)}}{1 + xn(j+1)} \tag{23}$$

where $xn(j)$ are transformed decision variables and

$$xn(j) > 0 \qquad j = 1, 2, ..., \text{nfr} - 1$$

2.2.2. Constant Reflux Condition. Similar to the variable reflux condition, the shortcut method results in the following equality constraints:

The differential material balance equation is given by

$$x_B^{(i)}{}_{new} =$$

$$x_B^{(i)}{}_{old} \exp\left[\frac{\Delta x_B^{(1)}}{x_D^{(1)} - x_B^{(1)}}\right]\left[\left(\frac{\alpha_i}{\alpha_1}\right)^{C_1}\frac{x_D^{(1)}}{x_B^{(1)}} - 1\right] \qquad i = 2, 3, ..., n \tag{24}$$

The equation for time t is

$$t = \frac{F(R+1)}{V}\left[1 - \exp\left(\sum_{x_{B\infty}^{(1)}}^{x_F^{(1)}}\frac{\Delta x_B^{(1)}}{x_D^{(1)} - x_B^{(1)}}\right)\right] \tag{25}$$

The Hengestebeck–Geddes' equation is

$$x_D^{(i)} = \left(\frac{\alpha_i}{\alpha_1}\right)^{C_1}\frac{x_D^{(1)}}{x_B^{(1)}}x_B^{(i)} \qquad i = 2, 3, ..., n \tag{26}$$

and the implicit equality constraint is

$$x_D^{(1)} = f(r, \text{Nm}, x_F^{(i)}) \tag{27}$$

where $r = R/\text{RMIN}$, RMIN being the minimum value of R required to obtain the initial distillate composition of the key component equal to the specified average composition, for the specific value of N (Figure 2); and Nm $= N/\text{Nmin}$, Nmin being the Fenske's value of the minimum number of plates (equivalent to C_1 of the Hengestebeck–Geddes equation) for the same value of distillate composition.
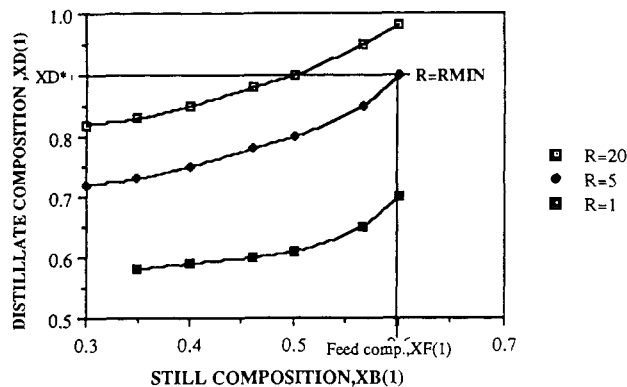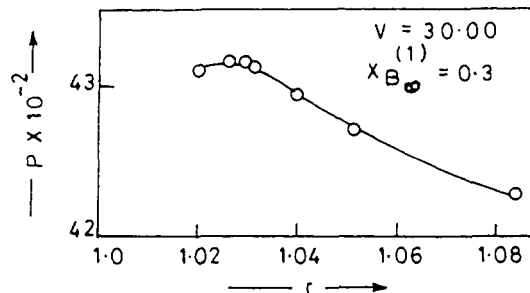

Figure 2. Concept of Rmin.

Figure 3. Single-fraction optimization, variable reflux condition (case 1, Table I).

Again the problem has 3 degrees of freedom for single-fraction as well as multifraction cases, so the decision variable can be chosen as Nm or initial $x_D^{(1)}$, r, or V.

Similar to the variable reflux condition, the decision variables are restricted by the following inequality constraints

$$1 < r \tag{28}$$

$$1 < \text{Nm} \tag{29}$$

and the nonnegativity of V

$$0 < V \tag{30}$$

Since, the variables are not bounded by limits, the bounded search techniques used for the variable reflux condition cannot be used here. The problem can be solved by using nonlinear programming techniques. The problem formulation is given below:

$$\min -P(X) \tag{31}$$

subject to

$$-X(1) > 1 \tag{32}$$

$$-X(2) > 1 \tag{33}$$

$$-X(3) > 0 \tag{34}$$

Since the constraints are linear, the VE01A subroutine of the Harwell library can be used. VE01A is based on the generalization of Davidon's method, enabling linear equality constraints to be dealt with by the projection technique.

3. Results and Discussion

3.1. Variable Reflux Condition. The results of the single-variable as well as multivariable optimization, for the single-fraction case, are shown in Figures 3–5 (ternary system, case 1 of Table I).

Figure 3 shows the objective function versus r curve for the specified $x_{B\infty}^{(1)}$ and V leading to optimum r.
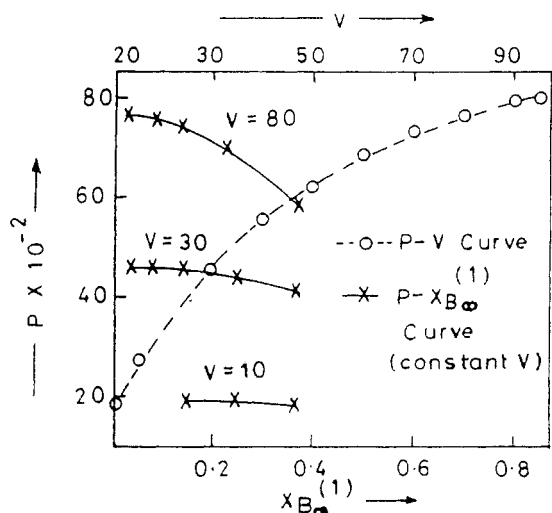
Figure 4. Single-fraction optimization, variable reflux condition (case 1, Table I).
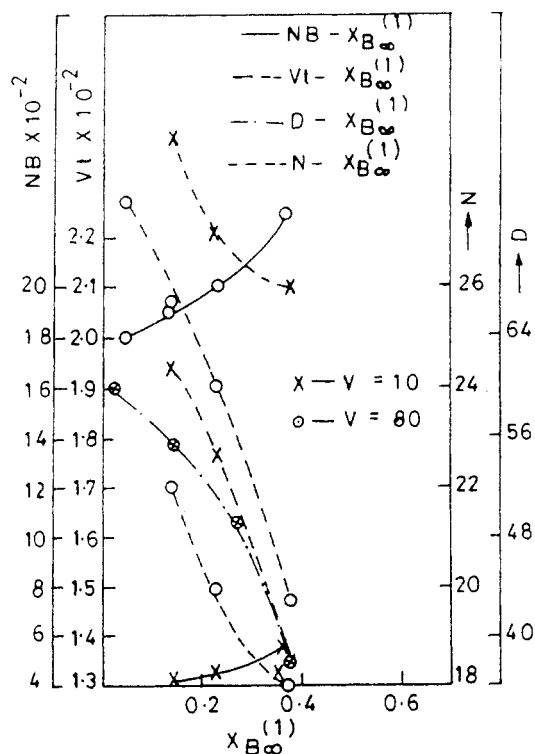

Figure 5. Single-fraction optimization, variable reflux condition (case 1, Table I).

Table I. Input Conditions[a]

case	rel volatility	feed composition	C(1)	C(2)
1	1.7	0.60	0.2	0.15
	1.16	0.04		
	1.0	0.36		
2	2.0	0.25	0.2	
	1.5	0.25		
	1.0	0.25		
	0.5	0.25		

[a] C1 = 27.5, C2 = 1.65, C3 = 0.00935, Ga = 15.0, Gb = 0.1028.

Figures 4 and 5 show the results of the multivariable optimization for the cases where V is fixed. It is seen that the optimum $x_{B_\infty}^{(1)}$ is very low, indicating that the separation problem selected is an easy separation problem. However, the effect of $x_B^{(1)}$ on the objective function is seen
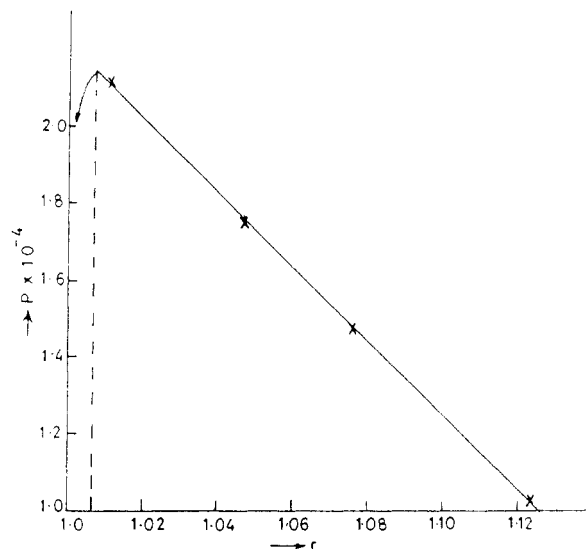

Figure 6. Multifraction optimization, fixed terminal condition (case 1, Table I).
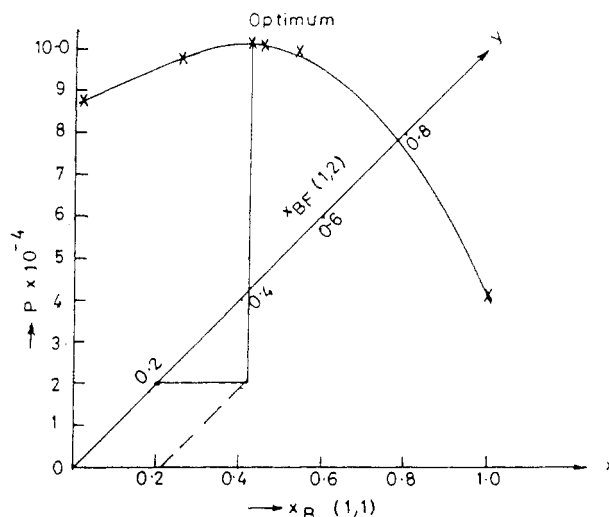

Figure 7. Multifraction optimization, free terminal condition (case 1, Table I).

to be decreasing as we go for lower V and is almost negligible for small V. This situation can be explained by considering the derivative of P, with respect to $x_{B_\infty}^{(1)}$ at constant V:

$$\left.\frac{\partial P}{\partial x_{B_\infty}^{(1)}}\right|_V =$$

$$C(1)D(1)\left.\frac{\partial NB}{\partial x_{B_\infty}^{(1)}}\right|_V + C(1)NB\frac{\partial D(1)}{\partial x_{B_\infty}^{(1)}}\frac{C1V}{Ga}\left.\frac{\partial N}{\partial x_{B_\infty}^{(1)}}\right|_V -$$

$$C3Vt\left.\frac{\partial NB}{\partial x_{B_\infty}^{(1)}}\right|_V - C3NB\left.\frac{\partial(Vt)}{\partial x_{B_\infty}^{(1)}}\right|_V \quad (35)$$

Figure 5 shows NB, D, Vt, and N versus $x_B^{(1)}$ for two values of V. The slopes of the curves for two different V's are almost the same. But Vt, NB, and V are very much larger in the case of large V, resulting in

$$\left.\frac{\partial P}{\partial x_{B_\infty}^{(1)}}\right|_{\text{large } V} \gg \left.\frac{\partial P}{\partial x_{B_\infty}^{(1)}}\right|_{\text{small } V} \quad (36)$$

Thus, at low values of V, the resultants of P for changes in $x_{B_\infty}^{(1)}$ are seen to be small (generally the effect of V is to magnify the profit and this is shown in section 3.2).
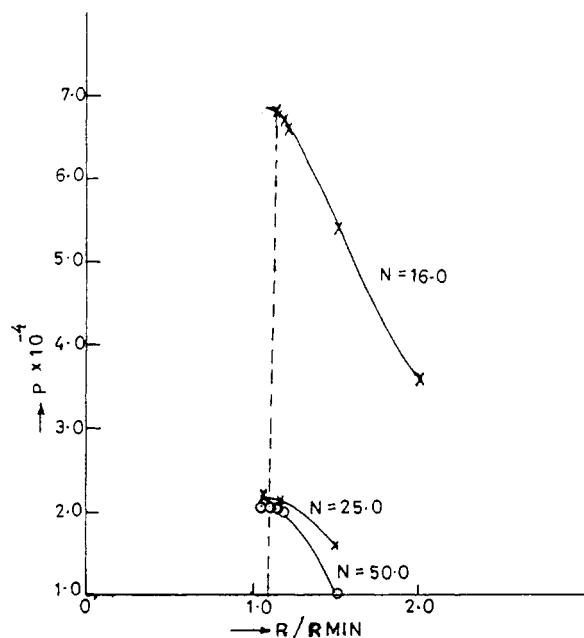
Figure 8. Single-variable optimization, constant reflux condition (case 2, Table I).

Similarly, in Figure 4, the effect of V is shown, leading to the optimum V.

Figures 6 and 7 show the results of two-fraction optimization for fixed terminal and free terminal conditions, respectively. The fixed terminal problem is similar to the single-fraction condition. The free terminal condition results in economic distribution of the fraction. It shows that the amount of the second fraction is very less compared to the first fraction because of its lower price.

Comparison of the Optimization Methods. The results obtained by breaking up the problem in stages and solving it by search techniques are similar to those obtained by NLP methods for the problem considered in this paper. However, the latter is recommended because of the computational efficiency.

3.2. Constant Reflux Condition. The results for a quaternary system (case 2, Table I) for the constant reflux condition are shown in Figures 8–10.

Figure 8 shows the results of the single-variable optimization for different values of N (or Nm). It can be seen that the curves for the different values of N show the same trend.

Similarly the curves for different V's (Figure 9) show the same trend, and it can be seen that the optimum value of Nm and r is unaffected by changes in V. This can be explained as follows:

In the expression of the objective function P, only NB and t are dependent on V, and it can be seen that

$$t \propto 1/V \qquad (37)$$

and

$$NB \propto V \qquad (38)$$

So, from eq 5,

$$P = V(V\text{-independent terms}) \qquad \text{when } t \gg ts \qquad (39)$$

So, when $t \gg ts$ (which is valid when V is small), the effect of V is to magnify P. This is also observed in Figure 10, where P versus V is plotted (the trend is similar as observed in the variable reflux condition, Figure 4).

4. Conclusions

In the present paper, we have presented the optimization problem for a single-fraction as well as multifraction batch
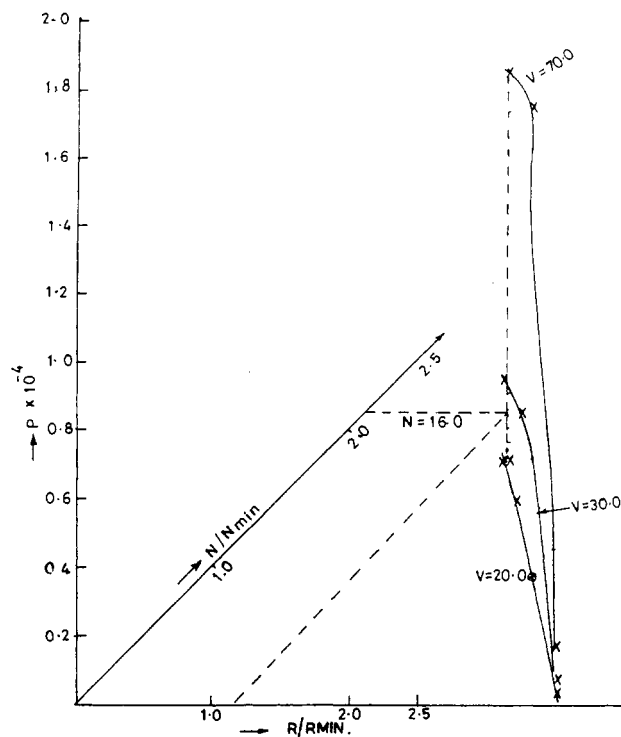

Figure 9. Multivariable optimization, constant reflux condition (case 2, Table I).
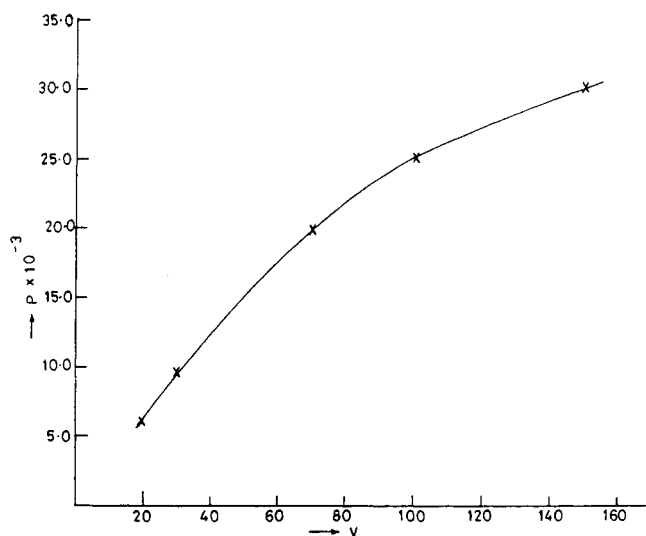

Figure 10. Multivariable optimization, constant reflux condition (case 2, Table I).

distillation column using the shortcut method.

It can be seen that the shortcut method, because of its noninteger algebraic equation oriented form (the number of equations is independent of the number of plates), is very useful in analyzing the optimization problem.

Nomenclature

B = amount of material remaining in the still, kg
C_1 = constant in the Hengestebeck–Geddes equation (equivalent to Nmin)
C1 = amortized incremental unit investment cost, \$/m²/plate/year
C2 = amortized incremental unit investment cost in tubular equipment, \$/m²/year
C3 = cost of steam and coolant to vaporize and condense respectively 1 kg of distillate, \$/kg
$C(i)$ = cost of product for the ith fraction per kg, \$/kg
$D(i)$ = distillate collected in fraction i per batch, kg/batch

F = amount of feed

Ga = allowable vapor velocity, $kg/h/m^2$

Gb = vapor-handling capacity in tubular equipment, $kg/h/m^2$

n = number of components

NB = number of batches per year

nfr = number of fractions

Nmin = minimum number of plates

P = objective function of profit, $/year

R = reflux ratio

Rmin = minimum reflux ratio

RMIN = minimum reflux ratio R, required to obtain initial distillate composition equal to the specified average distillate composition for given N

rk = reference key component

t = time per batch, h

ts = time required for startup and shutdown, h

V = vapor boil-up rate

$x_B^{(i)}$ = still composition of component i

$x_{B_\bullet}^{(i)}$ = final still composition of component i

$x_D^{(i)}$ = distillate composition of component i

x_D^* = average specified distillate composition

$x_F^{(i)}$ = feed composition of component i

Greek Symbol

α_i = relative volatility of component i

Appendix

Shortcut Method. Simplifying Assumptions:

1. Constant molal overflow.
2. Zero holdup.
3. Constant relative volatility throughout the column, which can be updated at each time step.

Model Equations. Differential material balance equation:

$$d \ln \left(\frac{B}{F} \right) = \frac{dx_B^{(i)}}{x_D^{(i)} - x_B^{(i)}} \qquad (A\text{-}1)$$

Hengestebeck–Geddes' equation:

$$x_D^{(i)} = \left(\frac{\alpha_i}{\alpha_1} \right)^{C_1} \frac{x_D^{(1)}}{x_B^{(1)}} x_B^{(i)} \qquad i = 2, 3, ..., n \quad (A\text{-}2)$$

Fenske's equation:

$$Nmin = \frac{\ln \left[\dfrac{x_D^{(lk)}}{x_B^{(lk)}} \dfrac{x_B^{(hk)}}{x_D^{(hk)}} \right]}{\ln \alpha_{lk}} \qquad (A\text{-}3)$$

Underwood's equations:

$$\sum_{i=1}^{n} \frac{\alpha_i x_B^{(i)}}{\alpha_i - \phi} = 0 \qquad Rmin + 1 = \sum_{i=1}^{n} \frac{\alpha_i x_D^{(i)}}{\alpha_i - \phi} \quad (A\text{-}4)$$

Gilliland's correlation:

$$y = 1 - \exp \left[\frac{(1 + 54.4X)(X - 1)}{(11 + 117.2X)X^{1/2}} \right] \qquad (A\text{-}5)$$

where

$$X = \frac{R - Rmin}{R + 1} \qquad y = \frac{N - Nmin}{N + 1}$$

Derivation of Equation 6. For the variable reflux condition, the change in the product composition $x_D^{(i)}$, $i = 1, 2, ..., n$, is negligible compared to the change in the still composition $x_B^{(i)}$s. Integrating eq A-1 from the old state to new state (for a small change in x_B) results in

$$\ln \left[\frac{(x_D^{(1)} - x_B^{(1)})_{new}}{(x_D^{(1)} - x_B^{(1)})_{old}} \right] = \ln \left[\frac{(x_D^{(i)} - x_B^{(i)})_{new}}{(x_D^{(i)} - x_B^{(i)})_{old}} \right] \qquad (A\text{-}6)$$

Rearranging gives

$$x_B^{(i)} = x_D^{(i)} - \frac{(x_D^{(i)} - x_B^{(i)})_{old}}{(x_D^{(1)} - x_B^{(1)})_{old}} (x_D^{(1)} - x_B^{(1)}) \qquad (6)$$

Derivation of Equation 7. The material balance for component 1 can be written as

$$Fx_F^{(1)} = Bx_B^{(1)} + Dx_D^{(1)} \qquad (A\text{-}7)$$

So

$$D = F \frac{x_F^{(i)} - x_B^{(i)}}{x_D^{(i)} - x_B^{(i)}} \qquad (A\text{-}8)$$

Differentiating eq A-8 with respect to t gives

$$\frac{dD}{dt} = F \frac{x_D^{(1)} - x_F^{(1)}}{(x_D^{(1)} - x_B^{(1)})^2} \frac{dx_B^{(1)}}{dt} \qquad (A\text{-}9)$$

Substituting

$$\frac{dD}{dt} = \frac{V}{R + 1}$$

gives

$$t = \frac{F(x_D^{(1)} - x_F^{(1)})}{V} \sum_{x_{B_\bullet}^{(i)}}^{x_F^{(1)}} \frac{\Delta x_B^{(1)}(R + 1)}{(x_D^{(1)} - x_B^{(1)})^2} \qquad (7)$$

Derivation of Equation 24. Substituting values of $x_D^{(i)}$ from eq A-2 in eq A-6 results in

$$d \ln x_B^{(i)} = \frac{dx_B^{(1)}}{x_D^{(1)} - x_B^{(1)}} \left[\left(\frac{\alpha_i}{\alpha_1} \right)^{C_1} \frac{x_D^{(1)}}{x_B^{(1)}} - 1 \right] \qquad (A\text{-}10)$$

For a small change, one can write

$$\ln \frac{x_B^{(i)}{}_{new}}{x_B^{(i)}{}_{old}} = \frac{\Delta x_B^{(1)}}{x_D^{(1)} - x_B^{(1)}} \left[\left(\frac{\alpha_i}{\alpha_1} \right)^{C_1} \frac{x_D^{(1)}}{x_B^{(1)}} - 1 \right] \qquad (A\text{-}11)$$

So

$$x_B^{(i)}{}_{new} =$$

$$x_B^{(i)}{}_{old} \exp \left[\frac{\Delta x_B^{(1)}}{x_D^{(1)} - x_B^{(1)}} \right] \left[\left(\frac{\alpha_i}{\alpha_1} \right)^{C_1} \frac{x_D^{(1)}}{x_B^{(1)}} - 1 \right]$$

$$i = 2, 3, ..., n \quad (24)$$

Derivation of Equation 25. Integration of eq A-1 results in

$$\frac{B}{F} = \exp \left(\frac{\Delta x_B^{(1)}}{x_D^{(1)} - x_B^{(1)}} \right) \qquad (A\text{-}12)$$

So, the total amount of distillate collected (D) is given by

$$D = F \left(1 - \exp \left(\frac{\Delta x_B^{(1)}}{x_D^{(1)} - x_B^{(1)}} \right) \right) \qquad (A\text{-}13)$$

Since

$$\frac{dD}{dt} = \frac{V}{R + 1} = \text{constant} \quad \text{(for constant reflux)}$$

then

$$t = \int \frac{dD}{V/(R + 1)} = \frac{D(R + 1)}{V} \qquad (A\text{-}14)$$

So

$$t = \frac{F(R+1)}{V}\left[1 - \exp\left(\sum_{x_{B_\infty}^{(1)}}^{x_F^{(1)}} \frac{\Delta x_B^{(1)}}{x_D^{(1)} - x_B^{(1)}}\right)\right] \quad (25)$$

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Supercritical Fluid Isolation of Monocrotaline from *Crotalaria spectabilis* Using Ion-Exchange Resins

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In our previous studies, we have successfully extracted monocrotaline, a hepatotoxic pyrrolizidine alkaloid of chemotherapeutic interest, from the seeds of *Crotalaria spectabilis* using supercritical carbon dioxide–ethanol mixtures. However, the presence of highly soluble lipid material in the seeds resulted in rather low monocrotaline purity in the extracts—24% by mass or less. The purity could be improved to values as high as 49% monocrotaline by mass by using a two-stage process in the temperature–solubility crossover region. However, pressure changes were still required to obtain the product. In this work, we show that monocrotaline purities greater than 95% by mass can be obtained by the combination of cation-exchange resins with supercritical fluid extraction without any pressure changes. This represents a new application of supercritical extraction which is particularly attractive for the isolation of alkaloids, drugs, and other biological materials.

I. Introduction

Supercritical fluid extraction has found increasing acceptance as a separation process in the biochemical and pharmaceutical industries principally due to the temperature sensitivity of the compounds of interest and the need for physiologically inert solvents. Its application, however, has been somewhat limited by the inherent nonselectivity of the preferred solvent—carbon dioxide—to the compounds of interest. Moreover, biomolecules often have low solubilities in supercritical fluids, and they occur only in trace amounts in mixtures containing highly soluble lipid materials, making isolation quite difficult. Judicious selection of a cosolvent by matching acid–base sites or polarity (Dobbs et al., 1987) can improve the extraction selectivity. However, further separations are still required to complete the isolation.

In a previous study (Schaeffer et al., 1988a), we showed that supercritical carbon dioxide–ethanol mixtures can be used to extract the pyrrolizidine alkaloid, monocrotaline, from the seeds of *Crotalaria spectabilis*. Monocrotaline is of interest because of its role as an environmental toxin (Mattocks, 1986) and as a precursor in the development of semisynthetic pyrrolizidine alkaloids (Gelbaum et al., 1982) for the treatment of cancer. The conventional preparative separation of monocrotaline from *Crotalaria spectabilis* is quite difficult and expensive. In our de-

velopment of a supercritical fluid based extraction alternative, we found that extraction selectivities toward monocrotaline as high as 24% could be achieved prior to the noticeable depletion of the seed components and as high as 40% after this depletion. The balance of the extracts consisted of lipid components normally found in seeds. Monocrotaline purities as high as 49% by mass were achieved by using a two-stage process in the temperature-solubility crossover region (Schaeffer et al., 1988b). While all of the monocrotaline could be removed using this process, a great deal of postprocessing is still required to isolate pure monocrotaline. In this work, we have investigated an alternative designed to improve the monocrotaline extraction purity. The new process is based on supercritical extraction of the seed material followed by adsorption of the monocrotaline on an ion-exchange resin. As such, it represents a novel approach to the isolation of alkaloids from plant materials.

II. Experimental Section

The apparatus used in our investigation has been discussed in detail in a previous paper (Schaeffer et al., 1988a) and is shown schematically in Figure 1.

Pressurized carbon dioxide (B) was filtered, liquified in an ice bath (C), and fed into one head of an Eldex dual-head metering pump (E). The cosolvent from a graduated cylinder (D) was filtered and fed into the other head of the metering pump. The solvent and cosolvent were pumped to the system pressure before entering the constant-temperature bath (F). The mixture was homogenized in a Kenics static mixer (I) and fed into the equilibrium cell (K) (a Jergeson level gauge). The equilibrium

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