Iterated Linear Programming Strategies for Nonsmooth Simulation: A Penalty Based Method for Vapor-Liquid Equilibrium Applications

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ABSTRACT

We extend our iterated linear programming (LP) approach (Bullard and Biegler, 1991) to two-phase vapor-liquid equilibrium problems, which are characterized by regions of continuous operation with nonsmooth boundaries. Here we show that a simple reformulation allows us to handle the disappearance or reappearance of phases and thus allows us to solve a wider class of process problems. The proposed strategy uses a penalty function approach, called Penalty Simulation of Nonsmooth Algebraic Terms and Attributes (P-SONATA), to accommodate the nonsmooth nature of the system. To solve the vapor-liquid equilibrium problem, we also extend the theoretical results of the approach of Bullard and Biegler (1991) to characterize descent and convergence properties for P-SONATA. The performance of this formulation is demonstrated for process models involving phase equilibrium, such as transitions from one and two phases in flash and distillation problems, where mass and energy balances must be satisfied but the phase equilibrium expression can be relaxed. Isothermal flash problems with ideal and nonideal phase equilibrium relations are considered as well as a case which exhibits retrograde condensation behavior near the critical point Finally, we examine limiting distillation cases including columns operating below the minimum reflux ratio (resulting in dry trays) and below the minimum reboiler heat duty (resulting in vaporless trays).

Finally, we develop convergence properties for P-SONATA and discuss additional classes for nonsmooth problems. The results demonstrate that this approach is straightforward to implement, captures a wider range of phase equilibrium behavior, and otherwise performs competitively with conventional Newton-based approaches.

1. INTRODUCTION

In a previous paper (Bullard and Biegler, 1991) we develop an iterated linear programming (LP) strategy for constrained simulation problems. The motivation for this type of method is evident when failure to consider physical constraints and bounds on variables can cause convergence problems with existing methods. This simple, straightforward algorithm converges quadratically to the solution and has global convergence properties for nonzero solutions of the linear program.

Using this constrained simulation approach we can also consider other classes of simulation problems for which iterated LP's are efficient and robust. In a related study (Bullard and Biegler, 1992) we consider the nonsmooth simulation problem where *equality constraints* are not everywhere differentiate. These problems have received little attention in the literature. Problems such as pipeline networks containing check valves and transitions from laminar to turbulent flow include functions of this form and we extend our iterated LP approach to address this type of nonsmooth problem.

In this paper we consider nonsmooth problems that arise from process models involving phase equilibrium. These problems are less straightforward to solve than problems which contain explicit nonsmooth operators. For example, consider an isothermal flash unit, where different sets of equations are valid depending on the number of phases present at equilibrium. The combined set of equations is a nonsmooth problem with well-defined smooth regions. Usually, however, the number of phases is not known *a priori.* Typically, procedures have been proposed to address this nonsmooth problem (Boston and Britt, 1978; Fournier and Boston, 1981; Kinoshita and Takamatsu, 1986; and Nelson, 1987). A more systematic approach, involving the minimization of Gibbs free energy, has been implemented in the form of nonlinear programs (Gautam and Seider, 1979; Castillo and Grossmann, 1981; and Soares *et al.,* 1982) and mixed integer nonlinear programs (Paules and Floudas, 1989).

In this study we identify and formulate a class of problems related to vapor-liquid equilibrium (VLE) which can be treated directly using a penalty function extension of our iterated LP constrained simulation approach. The resulting algorithm, termed Penalty Simulation of Nonsmooth Algebraic Terms and Attributes (P-SONATA), is easier to apply than a direct nonlinear programming strategy and can be extended beyond simple flash calculations to include distillation cases with dry or vaporless trays. In the next section we develop this formulation and algorithm for flash problems with one or two phases. Next we consider a number of flash examples with ideal and nonideal equilibrium. Section 4 extends the P-SONATA formulation to distillation simulations as well. Here cases are described below the minimum reflux ratio or below the minimum required heat duty. In section 5 we then describe the convergence properties of P-SONATA and provide guidelines for tuning parameters and for addressing other classes of nonsmooth problems. Details of this analysis are provided in the appendices. Finally, section 6 concludes the paper and discusses topics for future research.

2. APPLICATIONS TO PHASE EQUILIBRIUM

Phase equilibrium problems, such as phase transitions for flash and distillation units, are an important class of problems which can be addressed with iterated linear programming. To introduce the application of the penalty function formulation to phase equilibrium problems, we first consider the isothermal flash problem shown in Figure 1.

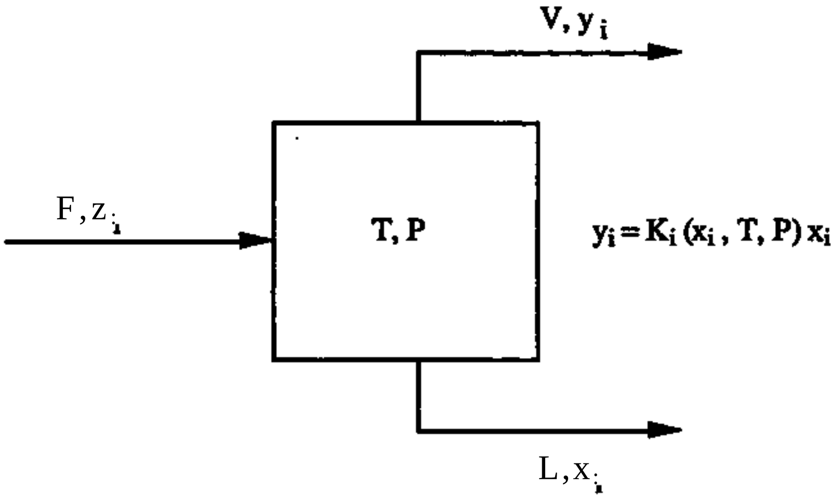

Figure 1. Isothermal flash operation.

Here a feed stream with flowrate F and composition Zi enters the flash operation with a specified temperature T and pressure P. The products are a vapor phase stream with flowrate V and composition yi and/or a liquid phase stream with flowrate L and composition x^. The isothermal flash contains equilibrium equations which are generally not valid in either of the one phase regions. A severe problem with flash calculations at isothermal and isobaric conditions is that the number of equilibrium phases is not known in advance; continuous regions (one or two phases) are defined by different active sets. Also, for the scope of this paper we restrict ourselves to a maximum of only two equilibrium phases.

Several different approaches have been suggested to circumvent this problem. Probably the most familiar is the classic "sequential modular" approach (Boston and Britt, 1978; Fournier and Boston, 1981; Kinoshita and Takamatsu, 1986; and Nelson, 1987). In general, these methods calculate bubble and dew points and then determine the number of phases present at equilibrium. The appropriate set of equations which describe the phase behavior of the flash is then solved. This procedure-based method may be difficult to extend to an equation-oriented simulation approach.

Another more recent approach involves minimizing the Gibbs free energy of the system subject to material balance constraints, since the stability of original mixture requires Gibbs free energy to be at its global minimum. Nonlinear programming (NLP) formulations for minimizing Gibbs free energy have been suggested by Gautam and Seider (1979), Castillo and Grossmann (1981), and Soares *et al.* (1982). Paules and Floudas (1989) have reformulated the Gibbs free energy minimization as a mixed integer nonlinear program (MINLP) in which discrete variables represent the existence/non-existence of phases at equilibrium. However, the highly nonlinear, nonconvex form of the objective function gives no guarantee that a global minimum will be found.

Finally, many of the methods mentioned above use stability criteria for phase determination. In both the sequential modular and Gibbs minimization approaches, various numerical methods exist for determining whether a phase is thermodynamically stable, as discussed by Gautam and Seider (1979). When phase distribution is uncertain at equilibrium, Gautam, Seider, and White (1980) recommend minimization of Gibbs free energy using an algorithm for NLP and phase splitting. Michelsen (1982a, 1982b) suggests stability analysis as a preliminary step in isothermal flash calculations. He applies a tangent plane criterion to determine whether a given phase distribution is stable.

In this study we wish to simulate vapor-liquid equilibrium for a specified temperature and pressure without having to specify in advance the number of phases present. In the one phase regions, the mass and energy balance equations must be satisfied, but we can relax the phase equilibrium expression by introducing a "pseudo" pressure Pp which differs from the specified pressure Ps outside the bounds of the dew and bubble points. In this way we can obtain a consistent set of equations in both the one and two phase regions which yields a physically realistic solution.

As an alternative to the sequential modular and Gibbs minimization approaches, we apply the extension of our LP formulation, P-SONATA. Here we pose the flash problem within the limitations of a penalty function formulation. This allows us to obtain a consistent system of equations in both the one and two phase regions by adding a penalty term to the objective to account for differences from equilibrium. The development of this approach is simple but can be generalized to complex equilibrium separations as well. In addition, after demonstrating this approach on numerous examples, we also provide a convergence analysis to show that P-SONATA is an appropriate way to solve these systems.

We begin with the equations for a simple n-component, two-phase flash:

$$
\begin{aligned}
&z_i F - (x_i L + y_i V) = 0, \qquad i = 1,\ldots n\\
&F - (L + V) = 0 \qquad\qquad\qquad\qquad (1)\\
&y_i - K_i(P,T,x)\,x_i = 0, \qquad i = 1,\ldots n\\
&\sum^{n} x_i - \sum^{n} y_i = 0
\end{aligned}
$$

and introduce new variables δ and Pp. along with the following relations:

$$
\begin{aligned}
&\delta \geq P_P - P_S \qquad\qquad (2)\\
&\delta \leq 0\\
&y_i - K_i(P_p,T,x)\,x_i = 0
\end{aligned}
$$

Here, Ps is the specified pressure of the flash and Pp is a "pseudo" pressure, which is allowed to differ from the specified pressure in the single phase regions if P_s goes above the bubble or below the dew point pressures. In the two phase region, (1) and (2) reduce to the square system

$$
\begin{aligned}
&\delta = 0\\
&P_S = P_P\\
&z_i F = x_i L + y_i V, \qquad i = 1,\ldots n\\
&F = L + V \qquad\qquad\qquad (3)\\
&y_i = K_i(P_P,T,x)\,x_i \qquad i = 1,\ldots n\\
&\sum_{i=1}^{n} x_i - \sum_{i=1}^{n} y_i = 0
\end{aligned}
$$

For the single phase liquid region, this formulation reduces to:

$$
\begin{aligned}
&V = 0\\
&\delta = P_S - P_p\\
&z_i = x_i
\end{aligned}
$$

$$F = L \tag{4}$$
$$y_i = K_i(P_P, T, x_i)\, x_i$$
$$\sum_{i=1}^{n} x_i - \sum_{i=1}^{n} y_i = 0$$

and Pp is the bubble point pressure. Finally, for the one phase vapor region the system of equations becomes:

$$L = 0$$
$$5 = P_P - P_s$$
$$Zj = yi$$
$$F = V \tag{5}$$
$$y_i = K_i(P_P, T, x_i)\, x_i$$
$$\sum_{i=1}^{n} x_i - \sum_{i=1}^{n} y_i = 0$$

and Pp is the dew point pressure. We consider the following optimization problem to obtain these solutions:

$$\begin{array}{ll} \min & 8 \\ \text{st} & h(x,y,L,V,P_P) = O \\ & \delta \geq P_S - Pp \\ & \delta \geq P_P - P_S \\ & \delta \geq 0 \\ & 0 \leq L, V \leq F \\ & 0 \leq Xi,\ yi \leq 1 \end{array} \tag{6}$$

where h(x, y, L, V, Pp) = 0 are the flash equations given in (1), Note that the objective, 8, must be constrained at the optimum and we show in section 5 and Appendix B that (6) has solutions that satisfy (3), (4) or (5). To solve problem (6) we apply a version of Successive Linear Programming (SLP). SLP requires little work at each iteration and as noted by Zhang et al. (1985), SLP is quadratically convergent and quite efficient when the optimum solution is a vertex optimum (i.e., the number of active constraints equals the number of variables). In section 5 of this paper we show that problem (6) satisfies this requirement and can therefore be solved inexpensively.

Moreover, the SLP approach is also closely related to the use of iterated linear programming for constrained simulation (BuUard and Biegler, 1991). Here we extend our previous formulation to consider (6). To ensure that each linear program has a solution at each iteration *i* we also add artificial variables pj and nj

$$\min \quad]^{\wedge}_{j} (Pj+nj) + co\ 8$$

$$\text{st} \quad h_j + \nabla h_j^T d = p_j - n_j$$
$$8 \wedge P_S - P_p \qquad (7)$$
$$8 \pounds P_p - P_s$$
$$8, p_j, n_j \pounds 0$$
$$0 \leq L, V \leq F$$
$$0 \leq x_i, y_i \leq 1$$

Here we note the close similarity of the SLP approach to the iterated linear programming approach of Bullard and Biegler (1991). In particular, solution of (7) provides a descent direction for problem (6) provided that the parameter co is chosen appropriately. Guidelines for choosing co are derived in section 5. Finally, note that (7) always has a bounded solution that is unaffected by singularities in h.

The P-SONATA algorithm for solving flash problems can now be stated as follows:

0. Initialize die problem at w°. where the vector w includes all of the variables in (6). Here w and h are of the same dimension.

1. Evaluate hj (w*), V hj (w^1), and $\mu^i = \omega\delta^i + \sum_j |h_j^i|$

   If DD £ e, stop. (Here, e.g., e = 10^{6}). Else, go to 2.

2. Generate the search direction d by solving the linear program (7).

$$\min \quad \wedge_j (p_j + fl_j) + co\ 8$$
$$\text{st} \quad h_j(w^*) + \nabla h_j(w^*)\, d = p_j - n_j$$
$$82 > P_S - P_p$$
$$\delta \geq P_P - P_S$$
$$\delta, p_j, n_j \geq 0$$
$$O \pounds L, V \leq F$$
$$0 \leq x_i, y_i \wedge 1$$

   If $||d|| \leq e$, stop. Else, go to 3.

3. From the solution of (7), evaluate an upper bound on the directional derivative, DD (see Appendix B for derivation) at w*:

$$DD \pounds\ \omega\delta^{i,1} + \sum_j p_j + n_j - \sum_j |h_j^i|.$$

4. Set the stepsize a = 1.

5. Evaluate $w^N = w^i + ad,h(wN)and\wedge^N = co8^N + £ \sum_j |hj(w^N)|$

6. If |J,N - M-Cw^1)_< 0.1 a DD, then go to 7.

   Else, set a = max /o.Ol a,———-O^~~DD~~ff^2-———.\.
   \ (^^{N}-^(wi).DDa)/

   i.e., by quadratic interpolation. Go to 5.

7. Setw^{i+1} = w^i + adandi = i + L Gotol.

There are two important properties associated with this algorithm:

(1) The Karush-Kuhn-Tucker conditions of (6) ensure a vertex optimum (See Appendix B.2).

(2) An upper bound on CD can be derived or calculated from the Kuhn-Tucker multipliers of (7). A discussion of this bound is deferred to Section 5. Because of the importance of forcing pj and nj to zero upon convergence of P-SONATA, co should be made small. In practice we generally set co between 0.001 and 10"^{6} althoughjerformance was largely insensitive to this value.

Thus, upon convergence, we have Ps = Pp and 8 = 0 for solutions in the two phase regions. For regions where the equilibrium equation does not hold, such as the one phase regions in the flash problem, 5 > 0. In fact, the approach which we propose here is related to a particular Gibbs minimization formulation. In Appendix A we show that the Kuhn Tucker conditions of the Gibbs minimization are related to those of (6). Thus our approach can be viewed as an efficient Successive Linear Programming (SLP) method for a special class of Gibbs minimizations.

3. EXAMPLE PROBLEMS

To examine the performance of this formulation, we consider seven example problems. The first three involve two ideal flash units and one nonideal flash operating in the one and two phase regions, and the fourth is a flash example which exhibits more complex retrograde condensation behavior. Examples 5, 6, and 7 in section 4 illustrate the extension of the penalty function formulation to the cases of ideal and nonideal distillation columns. In the distillation examples we consider "one phase" regions where the column is operating below "minimum reflux" conditions in Examples 5 and 7 and below "minimum reboiler heat duty" in Example 6.

Examples 1-3: Isothermal Ideal and Nonideal Flash

The ideal flash units in Examples 1 and 2 are modeled using the simple Antoine equation for phase equilibrium. For the nonideal flash in Example 3, the liquid phase is modelled by UNIQUAC equations (Prausnitz *et al.*$_y$ 1980). The generalized method of Hayden-O'Connell is used to compute the pure component and second virial coefficients are used to evaluate the vapor phase fugacity coefficient All cases for these three flash examples were initialized in the two phase region with V = L = 50. In the first two examples both liquid and vapor mole fractions were initialized to 0.3. In the third example, the vapor and liquid mole fractions were initialized to the feed compositions.

Here we characterize the flash problem as a nonsmooth system having well-defined smooth regions. Nondifferentiabilities or "kinks" occur at the vapor-liquid transitions, or bubble and dew points. For Example 3, shown in Figure 2, $T_{bu}b$ = 329.7°K and Tdew = 332.7°K.

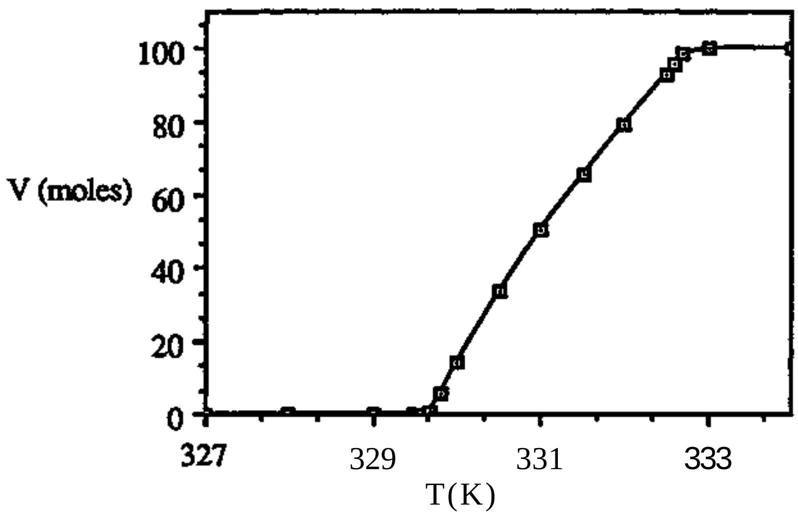

Figure 2. Vapor flowrate versus temperature for Example 3.

We also compare this approach to one where 8 was minimized as an NLP with MINOS in the formulation shown in (8),

$$
\begin{array}{ll}
\min & 8 \\
\text{st} & h(w) = 0 \\
 & \delta \geq P_P - P_S \\
 & 8 \geq P_S - P_p \\
 & 8 \geq 0
\end{array}
\tag{8}
$$

As shown in Tables 1-3, the number of function evaluations required by MINOS is significantly greater, and in a few cases MINOS terminated without finding a feasible solution, indicated by (*•). Here the robustness of our method in these cases is most likely due to the effect of the slack variables pj and nj in handling inconsistent linearizations.

Example 4: Retrograde Condensation

In the first three examples, we solved both ideal and nonideal flash problems to demonstrate the potential of the penalty function formulation to handle simple problems. We can also simulate the behavior of more complex phase equilibria systems near the critical point Consider the retrograde condensation phenomena described in Smith and Van Ness (1987) for which, under certain conditions, a condensation process occurs as the result of a pressure reduction. The pressure-temperature diagram for this type of system is depicted in Figure 3.

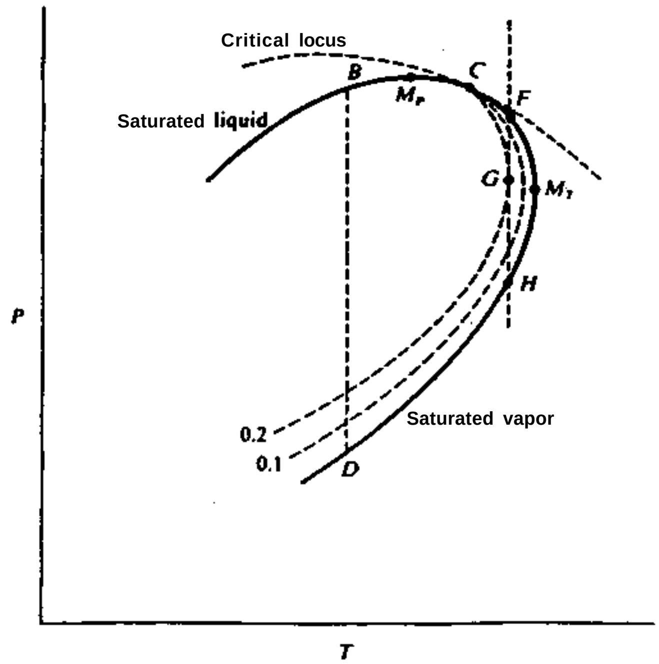

Figure 3. Portion of a PT diagram showing phase behavior in the critical region (taken from Smith and Van Ness, 1987).

Here the critical point is at C, and Mp and Mr identify the points of maximum pressure and maximum temperature. The dashed curves indicate the liquid fraction in a two-phase liquid and vapor mixture. Inside the two phase envelope and to the left of the critical point C, we expect that a reduction in pressure along line BD will result in vaporization from the bubble point to the dew point However, if we consider point F, a state of saturated vapor located to the right of the critical point C, liquefaction occurs when the pressure is reduced and reaches a maximum at G, after which vaporization takes place until the dew point is reached atH.

In order to model this type of system, we cannot use the UNIQUAC relations as in Example 3, since they are not accurate near this critical region. Instead, we use the Soave-Redlich-Kwong cubic equation of state (Soave, 1972), where the compressibility factor Z is obtained by solving the cubic equation of state

$$f = Z^3 - Z^2 + Z\,(A - B - B^2) = 0 \qquad (9)$$

and

$$A = 0.42747\ \frac{P}{T^2}\left\{\sum_i x_i \frac{T_{ci}\,\alpha_i^{0.5}}{P_{ci}^{0.5}}\right\}^2 \qquad (10)$$

$$B = 0.08664\ \frac{P}{T}\left\{\sum_i x_i \frac{T_{ci}}{P_{ci}}\right\} \qquad (11)$$

$$a_i{}^{\circ}\text{-}^{5} = l + (0.480 + 1.574\ \mathit{an} - 0.176\ \text{eo?})(l\text{-}T\&^{5}) \qquad (12)$$

One or three Teal roots will be obtained from the solution of equation (9); in the latter case, the smallest root (ZL) will be taken for a liquid phase and the highest one (Zy) for a vapor phase, as shown in Figure 4.

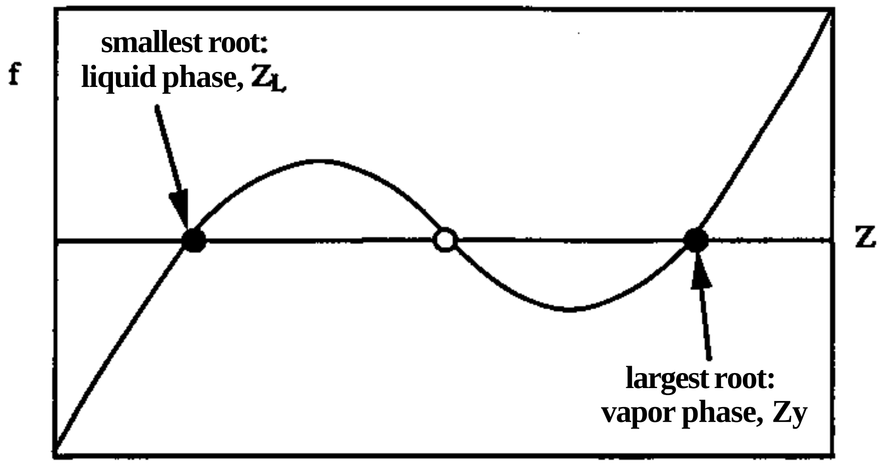

Figure 4. Plot of f versus Z, showing the location of Z corresponding to liquid (ZL) and vapor (Zv) phases.

At the critical point we would expect "one phase" behavior in which the liquid and vapor roots of equation (9), ZL and Zv, would converge into one root In addition to the flash equations and equation of state relations, we can enforce inequality constraints which ensure that the first derivatives of equation (9) will be positive at ZL and Zy. In addition, given the second derivative of equation (9), $f^f = 6Z - 2$, we can enforce an upper bound of 1/3 on ZL and a lower bound of 1/3 on Zy.

To demonstrate this approach, we consider an isothermal flash having a feed stream of 58.7 mole% ethane and 41.3 mole% n-heptane. The physical property data for this system are taken from Reid, Prausnitz, and Sherwood (1977). We compare operation at 400°F and 39£°F where the pressure is decreased from 38000 mm Hg to 25000 mm Hg. Both isotherms illustrate retrograde condensation behavior for the ethane/n-heptane system. Table 4 reports the vapor and liquid flowrates obtained by P-SONATA in solving the penalty function formulation with co = 10^6. The iterations and function evaluations required are shown in Table 5.

The starting point for all of the problems is in the two phase region, with L = 16.09 moles and V = 83.91 moles and Ps = Pp. Starting as a saturated vapor at T = 395°F, the system exhibits maximum condensation at around 35000 mm Hg, and then reaches the dew point at around 26000 mm Hg. Similarly for T = 400°F, the system exhibits maximum condensation at around 36000 mm Hg, and then reaches the dew point at around 29000 mm Hg. Also using formulation (8), MINOS fails to find a feasible solution for 19 of the 22 cases.

4. DISTILLATION EXAMPLES: HANDLING LARGER SYSTEMS

The same approach applied to Examples 1 through 4 can be extended to larger systems such as distillation. In the flash examples the mass and energy balances were enforced while the phase equilibrium equations were relaxed when necessary to allow for convergence to a physically realistic solution. For the distillation case, we consider two limiting cases, that of columns operating with dry and vaporless trays. The first limiting case, with dry trays, occurs as a result of a high boilup rate and low reflux (for saturated liquid feed); the second case, with vaporless trays, occurs with low boilup rate and high reflux (for saturated vapor feed). These are limiting cases in which the column is operating below the minimum reflux or minimum reboiler heat duty, respectively, where a feasible solution cannot be found using traditional simulation techniques.

The calculation of minimum reflux ratios is an essential and difficult task in the design and simulation of distillation columns. As defined by Underwood (1946), the minimum reflux ratio r_m is the ratio which will require an *infinite* number of trays for the desired separation. In addition, Levy and Doherty (1985) as well as Koehler *et al.* (1991) have extended his approach for determining r_m to nonideal systems, including those with azeotropes. Here we consider limiting cases for columns with a *specified* number of trays. Thus, the minimum reflux is found at which the column can still operate with a specified overhead product rate (D/F); the minimum reboiler heat duty has an analogous interpretation with bottom product rate (B/F). We wish to obtain a solution to the simulation problem for which the mass balances are enforced and the relaxed phase equilibrium expression is satisfied both above and below the minimum ieflux and reboiler heat duty rates, analogous to the flash examples of Section 3. The McCabe-Thiele diagrams in Figures 5 and 6 illustrate the modes of operation below the minimum rates, where, in each case, the stripping and rectifying operating lines do not intersect.

If the specified reflux for the simulation problem is indeed below the minimum, the liquid flowrate on the trays above the feed becomes zero and the phase equilibrium expression can no longer be satisfied in an equation-oriented approach. Here, the penalty function formulation allows the liquid flowrates on the trays above the feed tray to become zero while the pseudo pressure Ppon those trays differs from the specified column pressure Ps and allows the phase equilibrium relation to be satisfied. Thus the penalty function formulation ensures that the mass and energy balances are satisfied with a relaxed phase equilibrium expression and a feasible solution exists for both two phase and one phase (dry tray) regions. The penalty function formulation for the distillation case (13), below,

is very similar to the general flash formulation (7) with the difference that there are variables 6_m and Ppm^s well as an associated set of inequality constraints similar to (2) for each stage in the column, m = 1,..., NS.

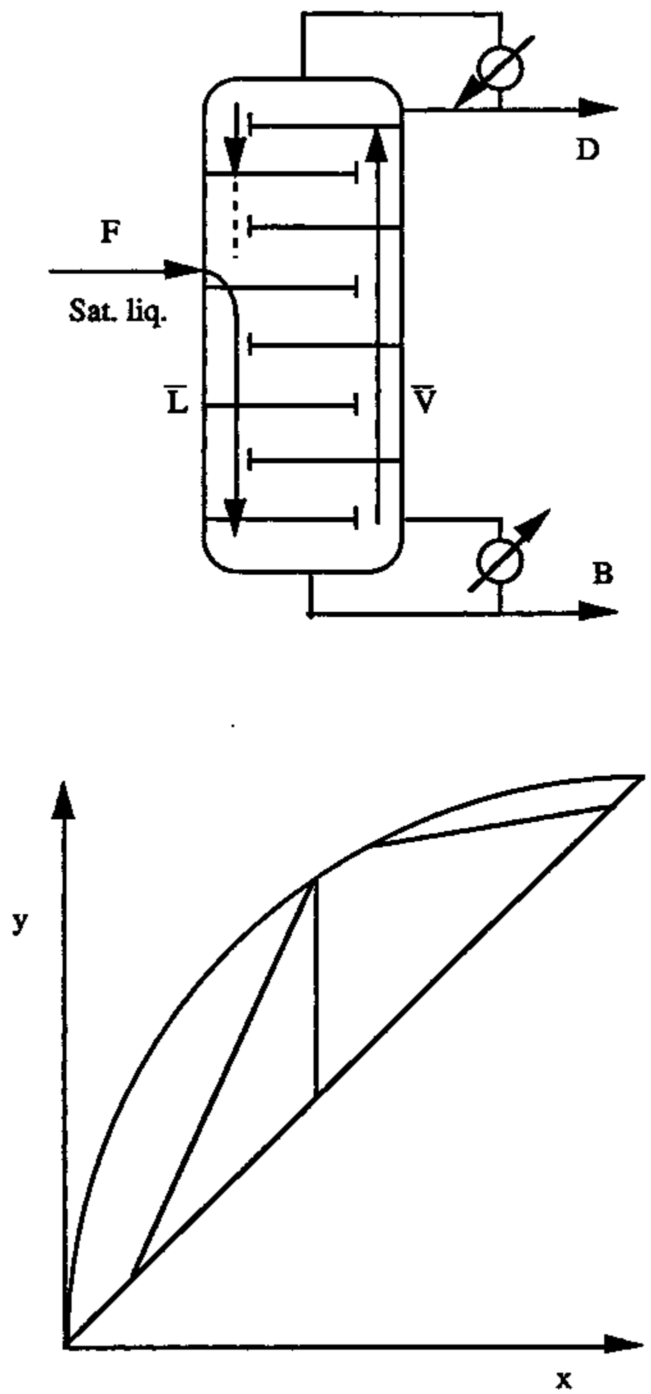

Figure 5. The McCabe-Thiele diagram (lower) illustrates the distillation case (upper) having low reflux and high boilup rate with saturated liquid feed- When reflux ratio is below its minimum operational value, liquid flow becomes zero on trays above the feed

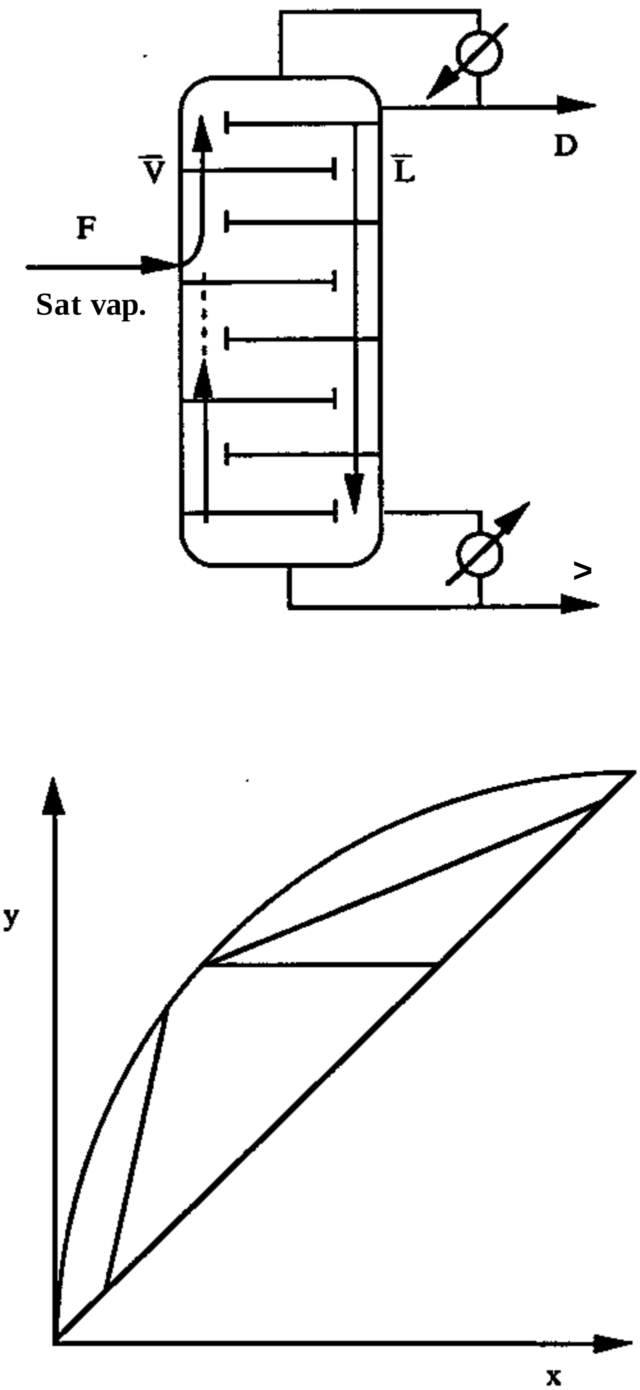

Figure 6. The McCabe-Thiele diagram (lower) illustrates the distillation case (upper) of high reflux, low boilup rate with saturated vapor feed When $Q_{r,b}$ is below its minimum operational rate, vapor flow becomes zero on trays below the feed, resulting in a vaporless tray.

$$\min \quad \sum_{j} (p_j + n_j) + \sum_{m}^{NS} \omega \, \delta_m$$

st hj + V hj d = pj - nj

5m^Ppm-Psm m = 1, ..., NS (13)

8_m ^ Psm - P_{Pm}

8_m, pj, nj £ 0

$L_m, V_m \geq 0$

D/F or B/F specified

where hj includes the relaxed equilibrium expression

$$yi = Ki\ (x_b\ T,\ P_P)$$

as well as the remaining MESH (Material balance, Equilibrium, Summation of mole fractions, and Heat balance) equations for distillation.

Example 5: Ideal Distillation Operating Below Minimum Reflux

Example 5 is an 25-tray ideal distillation column with a saturated liquid feed of 70% benzene - 30% toluene to stage 7. This 228 variable problem was addressed in Bullard and Biegler (1991) as a simulation case in which the reflux ratio was fixed and the square system was solved using an iterated LP approach. Starting points for this column are same as used in Bullard and Biegler (1991) and Vasantharajan et aL (1990), and are reasonable far from the solution. Because the recovery is not specified, we fix D/F = 0.30 and decrease the reflux ratio to see the effect on liquid flowrate in the column.

In order to have a basis of comparison for the distillation cases, we also used the FRAKB block in FLOWTRAN to solve the problem. There is close agreement between the liquid mole fractions predicted by the equation-oriented formulation and the simulation program, with small differences resulting from different physical property data being used. We note, however, that FLOWTRAN is unable to converge for small reflux ratio near or below the minimum. Table 6 lists the dry tray location predicted by MINOS, P-SONATA, and FLOWTRAN. As expected, the tray above the feed (at stage 7) is the first to become dry. A comparison of iterations and function evaluations for MINOS and P-SONATA is listed in Table 7. The penalty weight for both MINOS and P-SONATA for this example is co = 0.5. The solution from each case was used as the starting point for the next case for both MINOS and P-SONATA. Here, the minimum operating reflux ratio is close to 0.005.

In addition, solving an NLP with MINOS to minimize the reflux ratio subject to the operating equations gives a minimum operating reflux of r = 0.005, which is consistent with our results where the reflux is fixed. Both MINOS and P-SONATA predict the same overhead and bottoms composition using (13) and indicate that tray 8 becomes dry near r = 0.005.

Example 6: Ideal Distillation Operating Below Minimum Reboiler Heat Duty

Example 6 illustrates another limiting case of minimum operational reboiler heat duty. The physical description and initialization of the column is the same as in Example 5. The feed temperature is changed to 372°K to provide a saturated vapor feed and the overhead ratio D/F is specified as 0.921. For a 100 kmol/h feed with 70% benzene, we begin with the reboiler heat duty fixed at 6.33 MJ/h and gradually decrease the heat duty to see the effect on vapor flowrate in the column.

Both MINOS and P-SONATA predict that vapor disappearance on tray 6, directly below the feed tray (stage 7), occurs with $Q_{reb} < 0.316$ MJ/h. Both approaches obtain the same bottom and overhead mole fractions. A comparison of iterations and function evaluations required by MINOS and P-SONATA for Example 6 is listed in Table 8. The penalty weight for both MINOS and P-SONATA for this example is co = 0.5. As in Example 5, the solution from each case was used as the starting point for the next case for both MINOS and P-SONATA.

Example 7: Nonideal Distillation Operating Below Minimum Reflux

Finally, Example 7 is a case of a nonideal 17-tray distillation column described by 997 equations. The problem was originally formulated by Vasantharajan et al. (1990) and was solved as a simulation problem in Bullard and Biegler (1991) with fixed reflux. The starting points are far from the solution and are the same as specified in these references. As in Example 5, we consider the case of minimum operational reflux for this large scale example. The saturated liquid feed to tray 12 consists of 15% methanol, 40% acetone, 5% methylacetate, 20% benzene, and 20% chloroform. We expect the liquid flowrates on the trays above the feed to go to zero when below the minimum reflux, $r_m \leq 0.00005$. As in the nonideal flash in Example 3, the liquid phase is modelled by UNIQUAC equations.

The generalized method of Hayden-O'Connell is used to compute the pure component and cross second virial coefficients are used to evaluate the vapor phase fugacity coefficient

P-SONATA predicts the liquid top and bottom compositions shown in Table 9. Table 10 reports the number of iterations and function evaluations required as well as the number of dry trays predicted. We note that MINOS is unable to obtain a feasible solution for any of the simulation cases. Because of the size and nonlinearity of Example 7, it was also useful to slowly decrease the reflux while using the previous solution as the starting point for the next case.

5. PROPERTIES OF P-SONATA AND OTHER NONSMOOTH PROBLEMS

In this section we evaluate the convergence properties of P-SONATA for the vapor-liquid equilibrium problems that were solved in the previous two sections. Also, we are interested in examining the generality of the P-SONATA approach for other nonsmooth problems. Thus, we now consider the conditions on nonsmooth problems for which P-SONATA will yield valid solutions. In addition to problem (6), we consider the nonsmooth problem with n equations and Mg piecewise linear terms given by:

$$h(x, \Delta) = 0$$

$$\delta_m = \max_{k \in K_m} \{ f_{k,m} + a_{k,m}^T x \}, \quad m = 1, \ldots M_g \qquad (14)$$

Note that each piecewise linear term is made up of K_m linear segments. Here x is the n-vector of variables and Δ is a vector of length Mg with elements δ_m. We choose only piecewise linear terms in the (14) in order to simplify the analysis, although terms such as $\delta_m = \max \{ f_{k,m}(x)\}$ have also been treated in practice.

An appealing way to handle this problem is to generalize the P-SONATA algorithm above. As with equation (6) we can formulate the following NLP to solve (14):

$$\begin{aligned} &\min \sum_m \omega\, \delta_m \\ &\text{st} \quad h(x,\Delta) = 0 \\ &\qquad \delta_m \geq a_{k,m}^T x + f_{k,m} \qquad m = 1, \ldots, M_g, \; k \in K_m \\ &\qquad x^L \leq x \leq x^u \end{aligned} \qquad (15)$$

Note that problem (6) is a special case of (15). If we linearize the equalities and apply the iterated linear programming strategy, the following subproblem can be solved at each iteration:

$$\min \sum_m \omega\, \delta_m + \sum_j (p_j + n_j)$$

st $\quad h_j(x^J, A^1) + \nabla h_j(x^j, A^1)^T d = p_j - n_j$ (16)

– rp ^ ^ mmm -I Tky|

m — – k,m ·· · -k,u σ

$k \in K_m$

$x^L \leq x^\wedge + d^\wedge \leq x^\wedge$

$p_j, n_j \geq 0$

where $d = \begin{bmatrix} x - x^j \\ A - A^1 \end{bmatrix}$.

Note that both (7) and (13) are special cases of (16). However, not all nonsmooth problems can be handled using the penalty function formulation (16). Generally, the NLP (15) may not converge to a vertex optimum (e.g. to satisfy (14) or (2)) and this will cause difficulties for the SLP approach. A simple example of this problem is illustrated by the two dimensional problem illustrated in Figure 7 and described by:

$$\begin{array}{ll} \min & \delta \\ \text{st} & h(x,\delta) = 0 \\ & \delta \geq x \\ & \delta \geq -x \end{array} \qquad (17)$$

Here the constraints $\delta \geq x$ and $\delta \geq -x$ account for the nonsmooth function $\delta = |x|$. In Figure 7 two alternative equations, h_1 and h_2, are shown along with the absolute value constraint $\delta = |x|$.

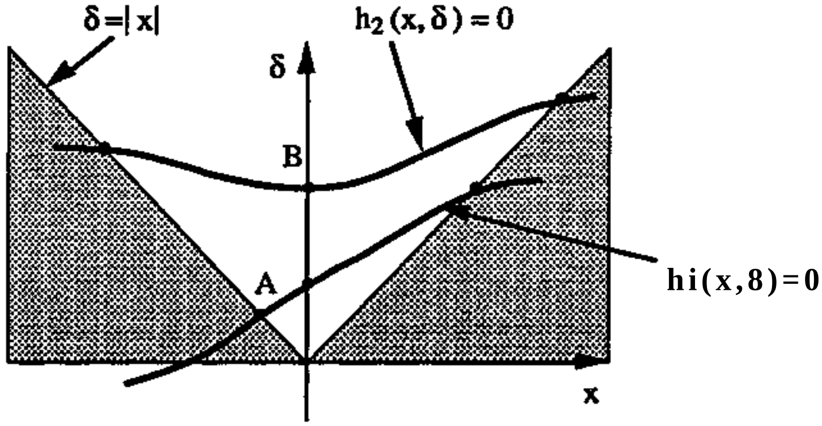

Figure *1.* Example of limitation of application of the penalty function formulation with nonsmooth function 5 = | x|.

For a function of the form hi, where the equality constraint h is monotonic in 8, the penalty function formulation (IS) will converge to point A, where the constraint 5 = -x is satisfied However, application of (15) to equality constraint I12 will minimize the objective (8) by converging to point B, where $\frac{dh_2}{3x}$ =- 0, and neither part of the absolute value constraint is satisfied. Thus, there is no vertex solution to the problem, and the nonsmooth constraint is not satisfied with an equality constraint of the form h_2 (see Appendix B.2 for an extended discussion).

Figure 7 gives us an intuitive geometric description of the application of the penalty function approach. We therefore need to consider the theoretical limitations of the approach in Order to more clearly define the class of problems for which P-SONATA is applicable.

To relate problems (15) and (16) note that solving (16) is equivalent to solving the unconstrained nonsmooth problem

$$\min_d \sum_m \omega \delta_m + \sum_j \left| h_j + \nabla h_j^T d \right| + M \sum_m \sum_k \left[\max \left(0, a^T_{k,m} x + f_{k,m} - \delta_m \right) \right]. \quad (18)$$

where M is a sufficiently large constant. A natural exact penalty function follows from (18) for (15):

$$\mu(x) = \sum_m \omega \, \delta_m + \sum_j |h_j| + M \sum_m \sum_k \left[\max \left(0, a^T_{k,m} x + f_{k,m} - \delta_m \right) \right] \quad (19)$$

The following three properties are derived in Appendix B which allow (16) to solve problem (15):

(a) To guarantee activity of the inequality constraints for each 5m at convergence, we require that

$$\omega > -\sum_j \gamma_j \nabla_{\delta_m} h_j \text{ (see Appendix B. 1).}$$

where yis the Lagrange multiplier on h from (16).

An upper bound on this quantity is:

$$\omega > \sum_j \left| \nabla_{\delta_m} h_j \right| .$$

Fortunately, for the phase equilibrium problem, the quantity on the right hand side is zero. (5 does not appear in the flash equations)

(b) To ensure that repeated solution of LP (16) will lead to the solution of NLP (15), we require that

$$1 > \left\| (\nabla_x h)^{-1} \sum_m a_{\bar{k},m} \right\| \omega > \wedge \| [Y_j \|| \qquad (20)$$

where $\bar{k}$ is the active constraint for each 5m in (16). Note that

if $\left\| (\nabla_x h)^{-1} \sum_m \wedge m \right\|$ is large, co may need to become very small and this leads to precision problems. We can easily extend the derivation to the case where the slacks in the objective function of (16) are weighted by a large number N:

$$\min \sum_m \omega\, \delta_m + N \sum_j P_j + {}^n j$$

with the corresponding restriction that

$$N > \left\| (\nabla_x h)^{-1} \sum_m a_{\bar{k},m} \right\| \omega \qquad (21)$$

(c) The solution of (16) is a descent direction for (15) (see Appendix B.3).

Thus, with appropriate selection of the parameter co, the application of the P-SONATA approach is an effective method for a subclass of nonsmooth problems which have a vertex optimum. In particular, for the phase equilibrium problems, we have (V_x h) nonsingular and the nonzero elements of a$£_m$ are +/-1 from (6). Consequently, the upper bound on co is bounded away from zero and an appropriately small value of co can be used. On the other hand, the counterexample shown in Figure! does not yield a vertex solution and, in fact, (b) cannot be satisfied because $\frac{\partial h_2}{3x}$ = (X

From the analysis in Appendix B, we therefore see that P-SONATA is appropriate for a restricted problem class given by the properties described above. Fortunately, because of features of the VLE problem, using the penalty function approach allows us to effectively simulate the transition between one and two phase regions. For problems that do not satisfy these conditions, a different approach must be used. For this reason we develop an alternate SONATA formulation in a separate study (Bullard and Biegler, 1992). Here the nonsmooth terms in (14) are replaced by the constraints:

5m ^ fkan + *\m <* m = 1, ..., M5

keKm

$$\sum_k \lambda_k (f_{k,m} + a_{£8} d) \geq \ _m$$

$$\sum_{k=1} \lambda_k \tag{22}$$

$$0 £ X_k \leq 1$$

Note that at least one of the linear segments must equal 5_m and thus the max operator is satisfied. The constraints in (22) are then linearized and an iterated linear programming strategy is applied. While this approach does not apply directly to phase equilibrium problems, it has been applied effectively to numerous problems with explicit nonsmooth terms such as pipe networks with checkvalves and flow transition problems. A description of this approach along with its convergence properties is given in Bullard and Biegler (1992).

6. CONCLUSIONS

In this paper we extend the constrained simulation algorithm introduced in BuUaid and Biegler (1991) to handle nonsmooth relations that arise in two-phase vapor-liquid equilibrium problems. The performance of this formulation is demonstrated for process models involving phase equilibrium, such as transitions from one and two phases in flash and distillation problems, where mass and energy balances must be satisfied but the phase

equilibrium expression can be relaxed outside the two phase region. Isothermal flash problems with ideal and nonideal phase equilibrium relations are considered as well as a case which exhibits retrograde condensation behavior near the critical point. We also examine limiting distillation cases including columns operating below minimum reflux ratio (resulting in dry trays) and below minimum reboiler heat duty (resulting in vaporless trays). In all of these examples, we demonstrate that P-SONATA yields a consistent set of equations in both the one and two phase regions of operation. Thus, by applying this formulation, we can effectively simulate these types of nonsmooth systems to obtain physically realistic solutions.

These types of phase equilibrium problems could also be extended to any equilibrium-based separation where the mass and energy balances must be satisfied but the phase equilibrium expression can be relaxed outside the two phase region. We have not yet considered a system with more than two phases; examples such as liquid-liquid equilibrium have not been investigated, and the extension of this approach to those systems is an open question. However, based on the results shown in this paper, the penalty function formulation, P-SONATA, appears to be a promising approach for handling VLE systems of one or two phases.

Finally, by extending the convergence results of Bullard and Biegler (1991), we analyze the P-SONATA algorithm in order to demonstrate its convergence properties for vapor-liquid equilibrium as well as a subclass of other nonsmooth problems which can be solved by incorporating penalty functions in the objective.

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APPENDIX A: Relation Between Gibbs Free Energy Minimization and P-SONATA

The objective is to establish a relationship between the Gibbs minimization formulation and the proposed formulation involving P_p, Le. the solution of the reformulated P_p problems satisfies the Kuhn Tucker conditions of the original Gibbs minimization.

$$\min G^T = \sum_{i=1}^{n} n_i^L(\Delta G_i^f + RT\ln f_i^L) + \sum_{i=1}^{n} n_i^V(\Delta G_i^f + RT\ln f_i^V)$$

$$\text{st} \quad n_i^L + n_i^V = n_i^T \quad i = 1,\ldots n \qquad \text{(A.I)}$$

$$n_i^L \geq 0,\ n_i^V \geq 0 \quad i = 1,\ldots n$$

where ni denotes the moles of component i in each phase. Here we show an equivalence under the following assumptions:

1) Vapor/liquid systems are considered with only a maximum of two phases.
2) Vapor and liquid fugacities are defined using vapor and liquid fugacity coefficients (O{ and 7i, respectively) which are *not* functions of pressure.
3) K{ = (7i PiO / P Oi) > 0 always for i = l,n. In this case,

$$n_i^L = \frac{n_i^T}{(1 + K_iV/L)}, \qquad n_i^V = \frac{n_i^T}{(1 + L/VK_i)}$$

and neither nj* nor n^ can become zero unless the entire phase disappears. Under these assumptions, the nonnegativity conditions in (A.1) can be simplified to give the following problem:

$$\min G^T = \sum_{i=1}^{n} n_i^L(\Delta G_i^f + RT\ln f_i^L) + \sum_{i=1}^{n} n_i^V(\Delta G_i^f + RT\ln f_i^V)$$

$$\text{st} \quad n_i^L + n_i^V = n_i^T \quad i = 1,\ldots n \qquad \text{(A.2)}$$

$$\sum_{i=1}^{n} n_i^L \geq 0,\ \sum_{i=1}^{n} n_i^V \geq 0$$

Expanding,

$$\min G^T = \sum_i (n_i^T\, \Delta G_i^f + n_i^L\, RT\ln f_i^L + n_i^V\, RT\ln f_i^V)$$

$$\text{st} \quad n_i^L + n_i^V = n_i^T \quad i = 1,\ldots n \qquad \text{(A3)}$$

$$\sum_{i=1}^{n} n_i^L \geq 0,\ \sum_{i=1}^{n} n_i^V \geq 0$$

The Kuhn Tucker conditions of this problem are now

$\bar{\partial}$nf L i=i J

$$\frac{\partial}{\partial n_i^L}\left[\sum_{i=1}^{n} n_i^L RT \ln\left(f_i^L\right)\right] + \alpha_i - \beta^L = 0 \qquad \text{(A.4)}$$

$$\beta^L \sum_{i=1}^{n} n_i{}^L = 0$$

$$\beta^V \sum_{i=1}^{n} n_i{}^V = 0$$

where oq are the multipliers for the equality constraints.

Now (A.4) reduces to

$$RT \ln\left(f_i^V\right) + RT \sum_{j-i}^{n} n_j^V \frac{\partial \ln\left(f_j^V\right)}{\partial n_i^V} + \alpha_i - \beta^V = 0$$

$$\text{RTln(fB} + \text{R} \overset{n}{\underset{j=1}{\text{T}}} \text{X n} \wedge \underset{3n_I}{\text{M}} {}_{+}\text{Oi-p}^L = 0 \qquad \text{(A.5)}$$

where the second terms go to zero from the Gibbs-Duhem relation:

$$\sum_{j=1}^{n} n_j \frac{\partial \ln\left(f_j\right)}{\partial n_i} = 0 \qquad \text{(A.6)}$$

Alternatively, for n* = RT In f,, we have

$$\text{Hi}^L + \text{ai} - \text{p}^L = 0$$

$$\mu_i{}^V + \alpha_i - \beta^V = 0 \qquad \text{(A.7)}$$

$$\beta^L \sum_{i=1}^{n} n_i{}^L = 0$$

$$\beta^V \sum_{i=1}^{n} n_i{}^V = 0$$

These conditions allow three cases:

<u>CASE 1(2 phase):</u>

$$\text{Both} \sum_{i=1}^{n} n_i^{L} \text{ and } \sum_{i=1}^{n} n_i^{V} > 0$$
$$\beta^L = \beta^V = 0 \tag{A.8}$$
$$Mi^L = W^V \text{ (equilibrium)}$$

CASE 2 (1 liquid phase):

$$\sum_{i=1}^{n} n_i^{L} > 0 \text{ and } \sum_{i=1}^{n} n_i^{V} = 0 \tag{A.9}$$
$$\beta^V = \mu_i^{V} - \mu_i^{L} > 0$$

CASE 3 (1 vapor phase):

$$\sum_{i=1}^{n} n_i^{V} > 0 \text{ and } \sum_{i=1}^{n} n_i^{L} = 0 \tag{A.10}$$
$$\beta^L = \mu_i^{L} - \mu_i^{V} > 0$$

Substituting fugacity and activity coefficient expressions for vapor and liquid fugacities leads to:

$$RT\ln\left(\frac{P\,\Phi_i\, n_i^V}{\sum_j n_j^V}\right) - RT\ln\left(\frac{P\,\gamma_i\, n_i^L}{\sum_j n_j^L}\right) =: \text{constant } (P^V \text{ or } -\beta^L) \tag{AM}$$

$$\frac{y_i}{K_i x_i} = \left(\frac{P\,\Phi_i \dfrac{n_i^V}{\sum_j n_j^V}}{P_i^o\,\gamma_i \dfrac{n_i^L}{\sum_j n_j^L}}\right) = \exp\left(\frac{\text{constant}}{RT}\right) = \Lambda \tag{A.12}$$

$$P_i^o\,\gamma_i\, x_i = P\,\Phi_i\, y_i/\Lambda = \Phi_i\left(P/\Lambda\right) y_i = \Phi_i\, P_P\, y_i \tag{A.13}$$

where Pp = P / A, the "pseudopressure" in (6).

Now for the flash operation,

$$n_i^L = L\, x_i$$
$$n_i^V = V\, y_i \tag{A.14}$$
$$n_i^T = F\, z_i$$

So we can express the flash problem in the penalty formulation as

mincoS

st $\underset{i}{X}\ Xi - \underset{i}{X}\ yi = 0$

$L + V = F$

$yi = Ki(x, T, Pp)_{Xi} = (71\ PiO / P_P <Þi)xi$

$Lxi + Vyi = Fzi$ **(A.15)**

$8 \wedge P_s - P_P$

$8\ £\ P_P - P_s$

$0 \leq (xi, {}_{yi}) \wedge l$

$0 \leq (L, V) \leq F$

Thus, we can show that the solution of (A.IS) satisfies the Kuhn Tucker conditions of the original Gibbs minimization. Finally, we note that the second assumption is necessary in (A.13); otherwise 71 and Oj would be functions of Ps (not Pp) and the definition for Kj would not hold in (A.15). Note, however, that even under these conditions P-SONATA would agree with the Gibbs minimization in the two-phase region (Pp = Ps). Moreover, P-SONATA would still identify the correct phases when V or L are zero but the *compositions for the missing phase* would not be the same as with Gibbs minimization.

APPENDIX B: BOUNDS FOR co TO ENSURE CONSTRAINT ACTIVITY

From the problem

$$h(x, max_k(a^T_{km} x + f_{km})) = 0 \qquad \text{(B.I)}$$

or the phase equilibrium problem (1),(2) we pose the NLP (B,2):

$$\min \sum_m \omega \, \delta_m \qquad \text{(B.2)}$$
$$\text{st} \quad h(x, A) = 0$$
$$\delta_m \geq a^T_{k,m} x + f_{k,m}$$

Here x and h are of the same dimension n. Now we consider bounds for co when applied with an iterated LP method

B.I. Lower bound to establish constraint activity of the LP.

Problem (B.2) is solved by repeated solution of the following subproblem (B.3) at iteration i:

$$\min \sum_m ttSm + \sum_j JLPj + nj$$

st hj (xi, A^1) + V hj (xi, A ^ d = Pj - nj (B3)

6m £ $a\backslash_m$ x + f_{km} m = 1,..., M_5

kelQn

Pj, nj £ 0

where d = $\begin{bmatrix} x \text{ " } x * \\ A - A^1 \end{bmatrix}$.

Here we require a bound on co which ensures activity of the equality constraints for each 5m. Taking the Kuhn-Tucker conditions for (B.3) gives the following Lagrange function:

L= $\sum_m$ G>8_m + $\sum_j$ Pj + nj - $\sum_j$ (ct]"Pj+aj iij)

$$+ \sum_j \gamma_j \left(h_j + \nabla_\delta h^T (\Delta - \Delta^i) + \nabla_x h^T (x - x^i) - p_j + n_j \right) \qquad \text{(B.4)}$$

$$+ \sum_{m} \sum_{k} \beta_{k,m} \left(a_{k,m}^T x + f_{k,m} - \delta_m \right)$$

with optimality conditions given by:

$$1 - \gamma_j - \alpha_j^+ = 0$$

$$1 + \gamma_j - \alpha_j^- = 0$$

$$\omega + \sum_j \gamma_j \nabla_{\delta} h_j - \sum_k \beta_{k,m} = 0 \qquad \textbf{(B.5)}$$

$$\sum_j \gamma_j \nabla_x h_j + \sum_m \sum_k \beta_{k,m} a_{k,m} = 0$$

$$\alpha_j^+ p_j = 0, \qquad \alpha_j^- n_j = 0$$

$$\beta_{k,m} \left(a_{k,m}^T x + f_{k,m} - \delta_m \right) = 0$$

and from these expressions we have

$$p_j n_j = 0, \qquad -1 \le \gamma_j \le 1$$

$$\text{and } 0 \le \{\alpha_j^+, \alpha_j^-\} \le 2 \qquad \text{(B.6)}$$

Now to guarantee activity for the inequalities, we require:

$\sum_k \beta_{k,m} > 0$ for $m = 1, \ldots, n_\delta$ which is implied by *(B.5)* and (B.6) when

$\omega > -\sum_j \gamma_j \nabla_{\delta_m} h_j$. An upper bound on the right hand side is given by

$\omega > \sum_j |\nabla_{\delta} h_j|$. For the formulation for the flash problem (7), $\omega > 0$.

B.2. **Requirements on ω so that repeated solution of (B.3) will lead to solution of (B.2).**

As seen in the counterexample (Section 5), conditions on ω cannot always be imposed so that the iterated LP solves (B. 1). To derive sufficient conditions for this we note that (B.3) is equivalent to solving the following nonsmooth problem:

$$\min_d \sum \omega \delta_m + \sum_j |h_j + \nabla h_j^T d| + M \sum_k \left[\max\left(0, a_{k,m}^T x + f_{k,m} - \delta_m\right) \right] \qquad \textbf{(B.7)}$$

where M is sufficiently large to ensure satisfaction of the inequalities. A natural exact penalty function follows from (B.7):

$$\mu(x) = \sum_m \omega\, \delta_m + \sum_j |h_j| + M \sum_m \sum_k \left[\max\left(0, a^T_{k,m}\, x + f_{k,m} - \delta_m \right) \right] \qquad \text{(B.8)}$$

In Appendix B.3 we show that the solution to (B.3) gives a descent direction for (B.8). To relate (B.7) to (B.2) we note that the solution of (B.2) is given by minimization of

$$\bar{\mu}(x) = \sum_m \omega\, \delta_m + \bar{C} \sum_j |h_j| + \bar{M} \sum_m \sum_k \left[\max\left(0, a^T_{k,m}\, x + f_{k,m} - \delta_m \right) \right] \qquad \text{(B.9)}$$

as long as:

$$\bar{C} > \max_j |\gamma_j| \qquad \text{and} \qquad \bar{M} > \max_{k,m} (\beta_{k,m})$$

(see Han and Mangasarian, 1979), and we need to show that $\bar{C} \leq 1$ and $\bar{M} \leq M$ in (B.8).

From the Kuhn-Tucker conditions of (B.2) we have:

$$\begin{aligned} &\omega + \sum_j \gamma_j \nabla_{\delta_m} h_j - \sum_k \beta_{k,m} = 0\,; \qquad m = 1, \ldots, M_S \\ &\sum_j \gamma_j \nabla_x h_j + \sum_m \sum_k \beta_{k,m}\, a_{k,m} = 0 \\ &\beta_{k,m} \left(a^T_{k,m}\, x + f_{k,m} - \delta_m \right) = 0 \end{aligned} \qquad \textit{(BAG)}$$

Now, if at least one inequality, $\bar{k}$, is active for each δ_m, we have $\beta_{\bar{k},m} > 0$ and a vertex optimum. Multipliers are then given by:

$$\begin{bmatrix} \gamma \\ \beta_{\bar{k}} \end{bmatrix} = - \begin{bmatrix} \nabla_x h & A_{\bar{k}} \\ \nabla_\delta h & -I \end{bmatrix}^{-1} \begin{bmatrix} 0 \\ \omega e \end{bmatrix} \qquad \text{(B.11)}$$

where $e^T = [\ 1, 1, \ldots, 1\ ]$ (M_S vector)

$A_{\bar{k}} = [\ a_{\bar{k},1}\ a_{\bar{k},2} \ldots a_{\bar{k},M_S}\ ]$ ($n \times M_S$ matrix)

and $\beta_{\bar{k},m} > 0$.

By Motzkin's theorem of the alternative, it can be shown that these (B.11) has a solution if and only if the following system has no solution (Mangasarian, 1969):

$$\nabla_\delta h^T \Delta \delta + \nabla_x h^T \Delta x = 0$$

$$\begin{bmatrix} A_{\bar{k}} - I \\ 0 \quad e \end{bmatrix} \begin{bmatrix} Ax \\ AS \end{bmatrix} \geq 0, \qquad \begin{bmatrix} Ax \\ A8 \end{bmatrix} \neq 0 \tag{B.12}$$

We now consider three special cases:

(a) In the counterexample of Figure () in Section 5, V_x h2 = 0, Ak = ± 1 and (B.12) <u>does</u> have a solution at point B. Hence, (B.I 1) has no solution.

(b) If A£ = 0 it is clear that (B.12) has no solution (and any positive value of co can be used). Moreover, if V_x h is nonsingular we have $pk_{\bar{m}}$ = CD and 75 = 0. Finally, from (B.I 1) we see that (B.2) has a vertex solution.

(c) If V5 h = 0 and V_x h is nonsingular (the case for VLE systems), then Ax = 0 and it is easily seen that (B.12) has no solution. Here Pk̄m = ≮ and y= - $(V_x h)^{-1}$ A£e co. Also, it is clear from (B.1l) that (B.2) has a vertex solution.

Finally, to use (B.8) we need to find co which satisfies

$$\text{co>O and } 1 > \left\| (\nabla_x h)^{-1} A_{\bar{k}} e \right\| \omega \geq \|\gamma\|.$$

Here co must therefore be suitably small.

B.3 Descent property for exact penalty function.

Consider the exact penalty function for (B.2):

$$\mu(x) = \sum_m \omega \delta_m + \sum_j |h_j| + M \sum_m \sum_k (a_{km}^T x + f_{km} - \delta_m)_+$$

with the directional derivative given by

$$D_d n(x0= \sum_m <°(5_m-8_I>\sum_U \nabla h_j^T d - \sum_{J.} \nabla h_j d$$
$$+\sum_{J_o} \max (\pm \nabla h_j^T d) + M \sum_m \sum_{k \in K_+} (a_{km}^T dx - d\delta_m)$$

$$J_+ = \{j \mid h_j(x^i, \delta^i) > 0\}$$

where $$J_- = \{j \mid h_j(x^i, \delta^i) < 0\}$$

$$J_0 = \{j \mid h_j(x^i, \delta^i) = 0\}$$

$$K_+ = \{ k \mid a^T_{km} x^i + b_{km} - \delta^i_m > 0 \}$$

Assume that $b°_m$ 2: a^ x° + fkm, then because we solve linear programs this constraint is always satisfied. Thus, the last term always vanishes in \i(x). Also by making substitutions from (B.3) (see also Bullard and Biegler, 1991) we have:

$$D_d \mu = \sum_m \omega (\delta_m - \delta^i_m) + \sum_j p_j + n_j - \sum_j |h_j|$$

Now by setting d = 0 we have a feasible point for (B.3) since

$$\delta^i_m \geq a^T_{km} x^i + f_{km}$$

$$p_j = h_j(x^i, \Delta^i) \qquad j \in J_+$$

$$n_j = - h_j(x^i, \Delta^i) \qquad j \in J_-$$

$$p_j = n_j = h_j(x^i, \Delta^i) = 0 \qquad \text{otherwise}$$

then we would expect the objective function at the optimal solution to satisfy

$$\sum_m \omega \delta_m + \sum_j p_j + n_j \leq \sum_m \omega \delta^i_m + \sum_j \left| h_j (x^i, \Delta^i) \right|.$$

Subtracting the right hand side from the left shows that $D_d \mu \leq 0$.

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Example 1: Ideal Flash (N-Butane, N-Hexane, N-Pentane) (co = 10"^{6})

T(K)	MINOS rr	MINOS FE	P-SONATA rr	P-SONATA FE	
390	38	208	33	61	
392	42	226	30	57	one phase
394	41	220	27	51	liquid region
396	29	155	15	26	
398	27	237	7	10	
400	25	135	5	6	
402	16	83	5	6	two phase
404	13	63	5	6	region
406	15	82	6	8	
408	15	86	8	12	
410	15	83	15	27	
411	14	76	21	39	one phase
412	16	82	17	31	vapor region

Table 1. Comparison of iterations and function evaluations required by MINOS and P-SONATA for Example 1, where Tbub = 394.1°K and T_{de}w = 410.6°K, The feed composition is (0-20, 0-50, 0.30).

Example 2: Ideal Flash (N-Butane, Cis-2-Butane, N-Propane) (G> = 10^6)

T(K)	MINOS rr	MINOS FE	P-SONATA rr	P-SONATA FE	
298	41	314	8	12	**one phase**
300	**	**	6	8	**liquid region**
302	34	192	4	5	
304	12	64	5	7	**two phase**
306	17	90	7	11	**region**
308	35	204	13	23	
310	37	205	21	39	**one phase**
312	11	74	16	26	**vapor region**

**** terminated as infeasible**

Table 2. Comparison of iterations and function evaluations required by MINOS and P-SONATA for Example 2, where T_{bub} = 300°K and T_{dew}= 308.2°K. The feed composition is (0.35, 0.40, 0.25).

Example 3: Nonideal Flash (Methanol, Acetone, Methyl Acetate, Benzene, Chloroform) (0) = 10-[3])

T(K)	MINOS rr	MINOS FE	P-SONATA rr	P-SONATA FE	
329	8	17	5	6	one phase liquid region
329.8	10	29	6	7	
330	10	29	6	7	
331	12	34	6	7	two phase
332	12	39	12	15	region
332.7	12	41	6	7	
333	12	35	6	7	one phase vapor region

Table 3. Comparison of iterations and function evaluations required by MINOS and P-SONATA for Example 3, where Tbub = 329.7°K and Tdew = 332.7°K. The feed composition is ((U5, 0.40, 0.05, 0.20, 0.20).

P-SONATA P(mm Hg)	T = 395°F		T = 400°F	
	L(moles)	V(moles)	L(moles)	V(moles)
38000	0	100	0	100
37000	0	100	0	100
36000	0	100	12.22	87.77
35000	15.91	84.81	10.79	89.20
32000	10.58	89.42	6.14	93.86
30000	7.15	92.85	2.59	97.4
29000	5.28	94.70	0.653	99.35
28000	3.29	96.70	0	100
27000	1.17	98.83	0	100
26000	0	100	0	100
25000	0	100	0	100

Table 4. Liquid and vapor flowrates obtained by P-SONATA at T = 400°F and T = 395°F for Example 4.

P-SONATA P(mm Hg)	T=395°F Iterations	FE	T = 400°F Iterations	FE
38000	10	10	10	10
37000	10	10	84	144
36000	10	10	98	181
35000	90	168	58	101
32000	39	68	84	144
30000	73	132	49	83
29000	61	99	29	37
28000	13	15	17	24
27000	11	13	279	537
26000	105	179	13	18
25000	24	38	34	48

Table 5. Iterations and function evaluations required by P-SONATA at T = 400°F and T = 395°F for Example 4.

Reflux Ratio	MINOS	P-SONATA	FLOWTRAN
1.0	-	-	-
0.1	-	-	-
0.01	-	-	-
0.005	-	-	**
0.001	8	8	aleak
0.0005	8	8	*•

** failed to converge

Table 6. Location of dry tray predicted by MINOS, P-SONATA, and FLOWTRAN for Example 5. The feed tray is tray 7.

Reflux ratio r	MINOS		P-SONATA	
	Iterations	FE	Iterations	FE
1.0	13	49	36	78
0.1	10	306	6	7
0.01	5	10	3	3
0.005	3	6	2	2
0.001	4	8	4	6
0.0005	4	8	4	6

Table 7. Comparison of iterations and function evaluations required by MINOS and P-SONATA for Example 5.

Heat duty Qreb(MJ/h)	MINOS		P-SONATA		Vaporless trayloc.
	rr	FE	rr	FE	
6.33	15	81	5	5	-
5.06	4	8	4	5	-
3.79	4	8	3	4	-
2.53	4	8	3	3	-
1.26	4	8	4	5	-
0.633	4	8	3	4	-
0.316	4	8	3	4	6
0.0633	4	8	3	4	6
0.0317	4	8	3	4	6
0.00633	4	8	3	4	6

Table 8. Comparison of iterations, function evaluations, and cpu times required by MINOS and P-SONATA for Example 6. The location of vaporless trays is also identified. The feed tray is tray 7.

Reflux ratio	bottom product x_M	XA	XMA	XB	XC	top product XM	XA	XMA	XB	XC
8.5	0.013	0.350	0.053	0.283	0.301	0.373	0.482	0.044	0.065	0.035
7.0	0.010	0.356	0.055	0.281	0.298	0.377	0.472	0.042	0.068	0.041
6.0	0.009	0.340	0.055	0.280	0.296	0.379	0.465	0.041	0.070	0.044
5.5	0.008	0.362	0.056	0.279	0.294	0.380	0.461	0.041	0.071	0.047
4.5	0.007	0.367	0.056	0.278	0.291	0.382	0.453	0.040	0.073	0.052
4.0	0.006	0.373	0.057	0.276	0.287	0.384	0.443	0.039	0.076	0.058
3.0	0.006	0.391	0.057	0.275	0.284	0.384	0.437	0.038	0.078	0.063
2.5	0.007	0.385	0.058	0.274	0.281	0.383	0.431	0.038	0.080	0.068
2.0	0.008	0.389	0.058	0.272	0.277	0.380	0.424	0.037	0.083	0.076
1.5	0.013	0.389	0.058	0.269	0.271	0.372	0.418	0.037	0.088	0.085
1.0	0.025	0.391	0.058	0.264	0.262	0.353	0.415	0.038	0.096	0.099
0.75	0.036	0.391	0.057	0.260	0.256	0.335	0.415	0.038	0.103	0.108
0.10	0.075	0.393	0.055	0.240	0.236	0.271	0.411	0.042	0.135	0.141
0.001	0.075	0.393	0.055	0.240	0.236	0.271	0.411	0.042	0.135	0.141
5E-05	0.075	0.393	0.055	0.240	0.236	0.271	0.411	0.042	0.135	0.141
4E-05	0.075	0.393	0.055	0.240	0.236	0.271	0.411	0.042	0.135	0.141

Table 9. Top and bottom liquid mole fractions of methanol, acetone, methyl acetate, benzene, and chloroform obtained by P-SONATA for Example 7.

Reflux ratio	Iterations	Function evaluations	Dry tray location
8.5	3	3	-
7.0	6	6	-
6.0	3	3	-
5.5	3	3	-
4.5	3	3	-
4.0	2	2	-
3.0	11	20	-
2.5	13	26	-
2.0	5	5	-
1.5	4	4	-
1.0	15	27	-
0.75	4	5	-
0.10	9	29	-
0.001	5	5	-
5E-05	8	20	13
4E-05	10	15	13

Table 10. Iterations and function evaluations required by P-SONATA for Example 7. The location of the dry tray is also reported The feed tray is tray 12

Figure 1. Isothermal Flash Operation.

Figure 2. Vapor flowrate versus temperature for Example 3.

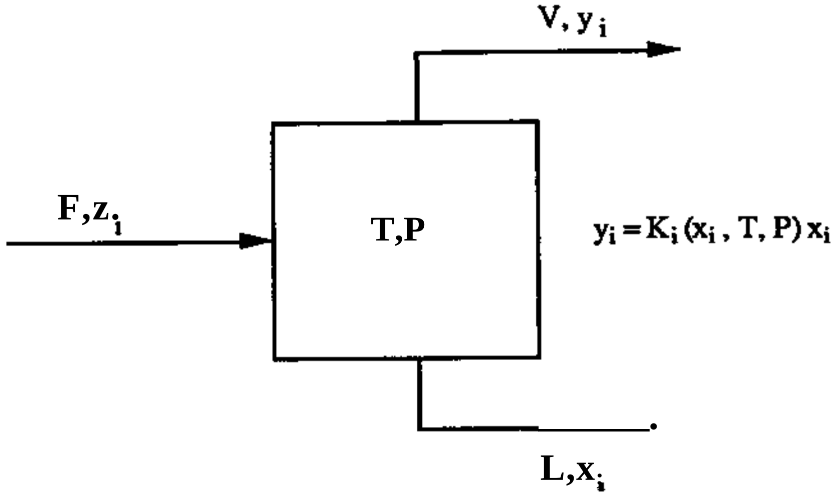
Figure 3. Portion of a PT diagram showing phase behavior in the critical region (taken from Smith and Van Ness, 1987).

Figure 4. Plot of f versus Z, showing the location of Z corresponding to liquid (Z_L) and vapor (Z_V) phases.

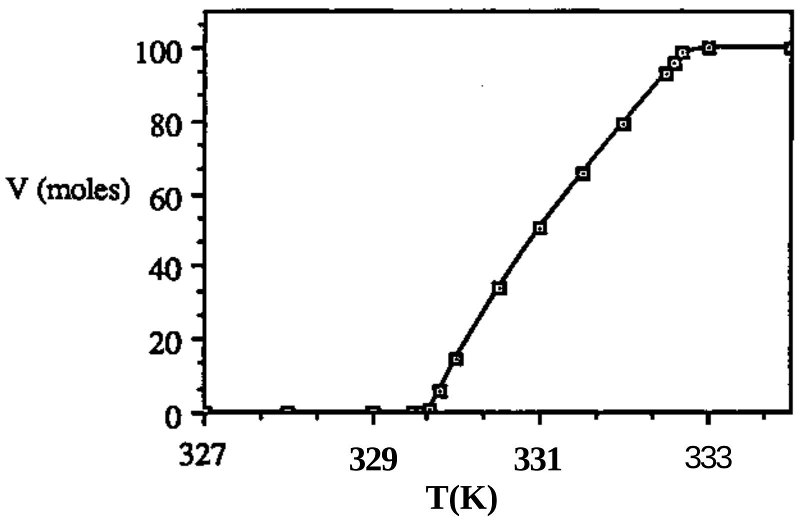
Figure 5. The McCabe-Thiele diagram (lower) illustrates the distillation case (upper) having low reflux and high boilup rate with saturated liquid feed. When reflux ratio is below its minimum operational value, liquid flow becomes zero on trays above the feed.

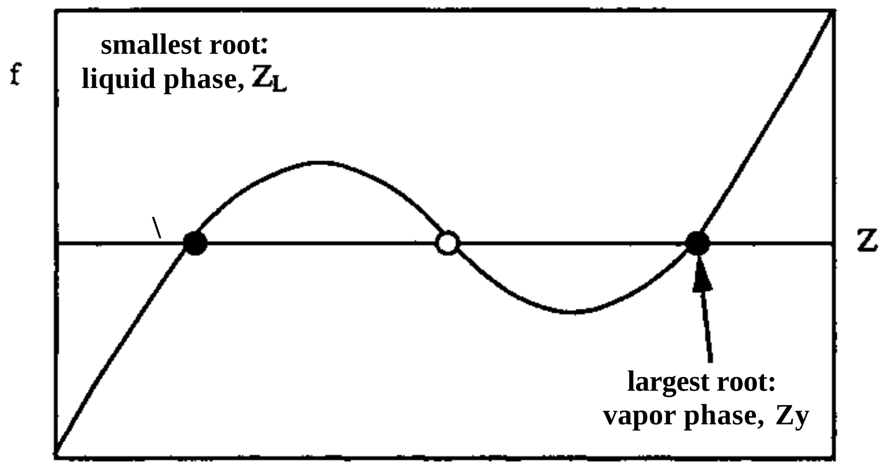
Figure 6. The McCabe-Thiele diagram (lower) illustrates the distillation case (upper) of high reflux, low boilup rate with saturated vapor feed. When Q_{reb} is below its minimum operational rate, vapor flow becomes zero on trays below the feed, resulting in a vaporless tray.

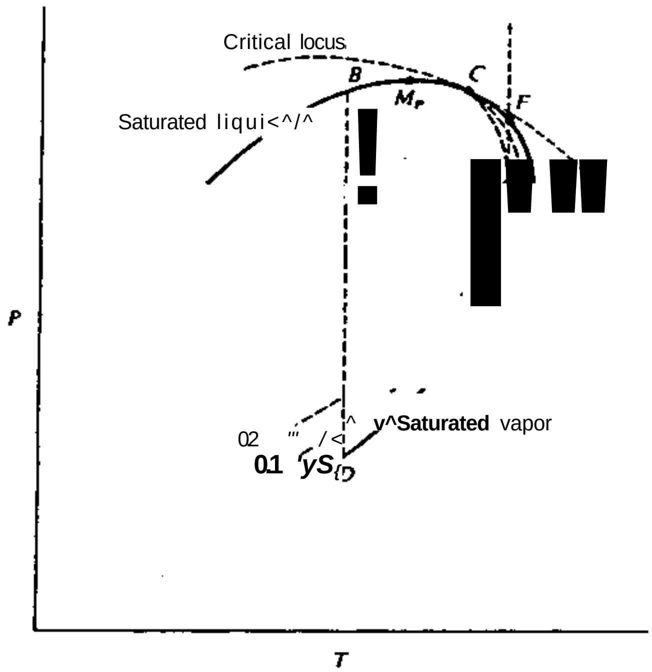
Figure 7. Example of limitation of application of the penalty function formulation with nonsmooth function 8 = | x|.

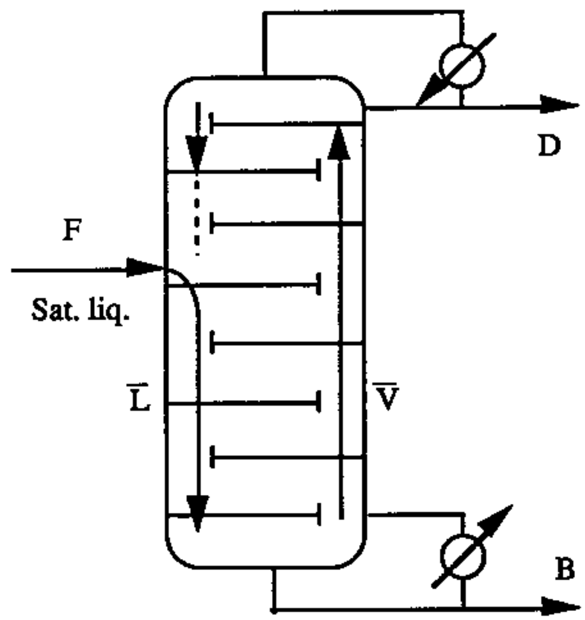


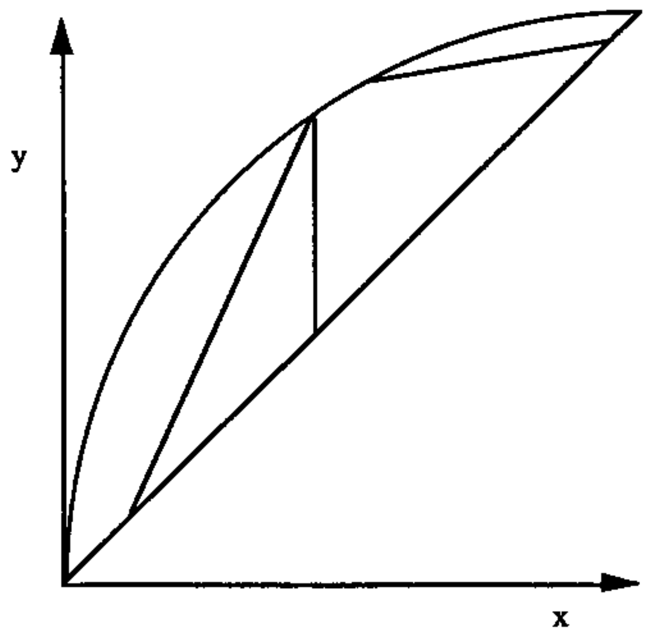
V, y_i
F,z_i
T,P
$y_i = K_i(x_i, T, P)\, x_i$
L,x_i

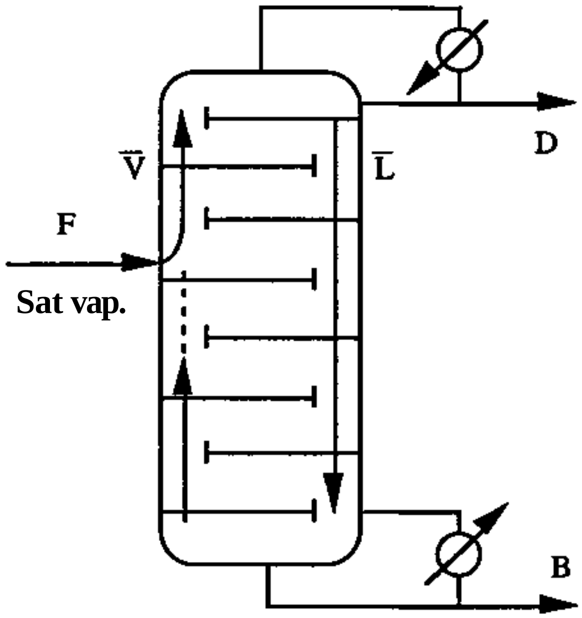

100
80
V (moles)
60
40
20
0
327
329
331
333
T(K)

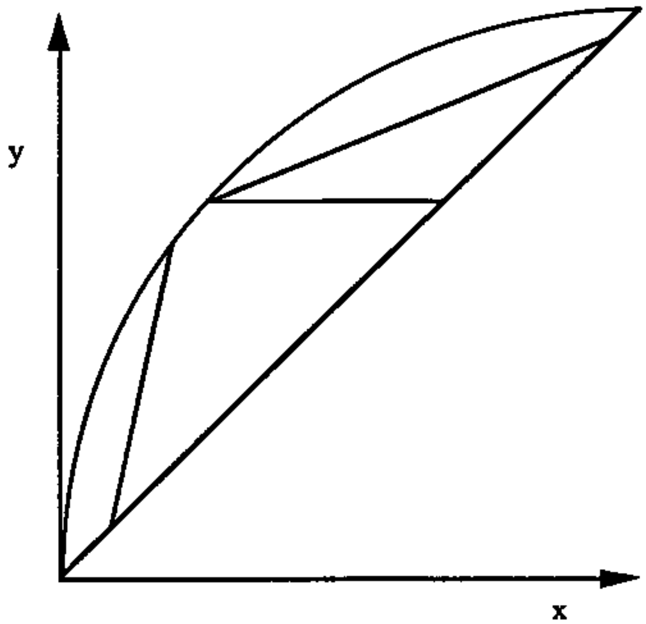

f
smallest root:
liquid phase, Z_L
Z
largest root:
vapor phase, Zy

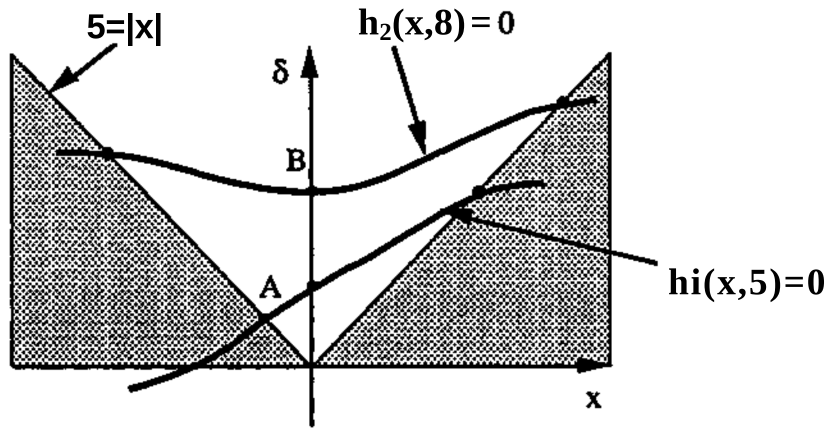

Critical locus
B
C
F
Saturated vapor
P
T


D
F
Sat. liq.
$\overline{L}$
$\overline{V}$
B


y
x


$\overline{V}$
$\overline{L}$
D
F
Sat vap.
B


y
x


5=|x|
h2(x,8) = 0
δ
B
A
hi(x,5)=0
x