Application of Smoothing Methods to Flash Problems

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Complementarity conditions are fundamental to optimization problems. They arise as the Karush-Kuhn-Tucker (KKT) conditions of a constrained nonlinear optimization and enforce a requirement that two sign-constrained vectors be orthogonal

$$x_k\, y_k = 0, \quad x_k,\, y_k \geq 0, \quad k = 1, 2, \ldots, n$$

Thus, either x_k or y_k must be zero for each $k = 1, 2, \ldots n$. For example, Ferris and Pang (1997) give an overview of the applications of complementarity to a wide variety of subjects. In chemical process modeling, complementarity is most commonly associated with the equilibrium flash.

The difficulty with solving equations of this form is their nondifferentiability. To overcome this, smoothing functions may be applied. Gopal and Biegler (1999) presented a method for solving the two- and three-phase flash problem with smoothing functions. This work offers several modifications that simplify their flash formulation. The complementarity conditions may be approximated as

$$x_k - \max(0, x_k - y_k) = 0$$

where max is a smoothing function. Differentiability is maintained by implicitly preventing x_k and y_k from being identically zero.

Gopal and Biegler (1999) presented two potential smoothing functions, their Eqs. 15 and 18, as follows

$$\max(0, X) = 1/2[X + (X^2 + \varepsilon^2)^{1/2}] \tag{1}$$

$$\max(0, X) = X + \varepsilon \ln[1 + e^{-X/\varepsilon}] \tag{2}$$

where ϵ is some appropriately chosen tolerance – the smaller the value, the greater the accuracy of the solution, but the greater the nonlinearity. This formulation has the advantage of implicitly enforcing the lower bound of zero.

Complementarity conditions may be used in the flash formulation to relax the equilibrium conditions when the phase boundary is crossed. As shall be shown, one complementarity condition is required for each phase.

Two-Phase Flash Formulation

The two-phase flash formulation may be written as follows

$$V - \alpha F = 0 \tag{3}$$

$$F - V - L = 0 \tag{4}$$

$$H_F - \alpha H_V - (1 - \alpha) H_L = 0 \tag{5}$$

$$z_i - \alpha\, y_i - (1 - \alpha) x_i = 0 \quad i = 1, n \tag{6}$$

$$y_i - \gamma\, K_i\, x_i = 0 \quad i = 1, n \tag{7}$$

$$\Sigma y_i - \Sigma x_i = 0 \tag{8}$$

$$\gamma - 1 + s_L - s_V = 0 \tag{9}$$

$$s_V\, \alpha = 0 \tag{10}$$

$$s_L(1 - \alpha) = 0 \tag{11}$$

In this formulation, the vapor fraction is used in the complementarity conditions rather than the vapor and liquid flows, as chosen by Gopal and Biegler (1999). This avoids potential scaling problems when selecting the smoothing tolerance because the vapor fraction is always bounded between zero and

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one. This could be a concern in process simulation where the flows may vary significantly during the course of the solution. In these situations, placing the complementarity conditions on the flows could compromise solution accuracy if the flows were to decrease significantly. Moreover, this formulation has been found to be more computationally efficient, as will be demonstrated. The complementarity conditions may be written as

$$s_V - \max0[s_V - \alpha] = 0 \tag{12}$$

$$s_L - \max0[s_L - (1 - \alpha)] = 0 \tag{13}$$

where max0 is a suitable smoothing function as discussed previously.

In the two-phase region, the correction factor, γ, is unity and both slacks are zero. As the phase boundary is crossed, the appropriate slack becomes nonzero and the vapor fraction approaches zero or unity as determined by the smoothing function. This drives the correction factor to the value required to maintain the equilibrium condition.

To specify saturated systems, it is not possible to simply fix the vapor fraction at zero or one, or set the phase flow to zero because this is prevented by the smoothing function. In this case, the complementarity conditions could be disabled. An alternative approach is to define an extended vapor fraction as

$$\alpha_X = \alpha + s_L - s_V \tag{14}$$

In the two-phase region, α_X is approximately equal to α because the slacks are near zero. At the dew point, α_X is equal to one, and becomes greater than one as the system becomes superheated. The larger the value, the farther the system is from the dew point. Similarly, in the subcooled region, α_X is less than zero becoming more negative as the system moves from the bubble point.

Thus, to create a saturated system, the extended vapor fraction could be fixed at zero or one to create the desired conditions. Although simple to implement, this could create an accuracy issue at the phase boundary. This will be investigated in the examples.

Three-Phase Flash Formulation

The three-phase flash formulation may be written as follows

$$\alpha + \beta_{L1} + \beta_{L2} - 1.0 = 0 \tag{15}$$

$$H - \alpha\, H_V - \beta_{L1}\, H_{L1} - \beta_{L2}\, H_{L2} = 0 \tag{16}$$

$$z_i - \alpha\, y_i - \beta_{L1}\, x_{L1,i} - \beta_{L2}\, x_{L2,i} = 0 \quad i = 1, n \tag{17}$$

$$y_i - \gamma_1\, K_{L1,i}\, x_{L1,i} = 0 \quad i = 1, n \tag{18}$$

$$y_i - \gamma_2\, K_{L2,i}\, x_{L2,i} = 0 \quad i = 1, n \tag{19}$$

$$\Sigma y_i - \Sigma x_{L1,i} = 0 \tag{20}$$

$$\Sigma y_i - \Sigma x_{L2,i} = 0 \tag{21}$$

$$\gamma_1 - 1 + s_{L1} - s_V = 0 \tag{22}$$

$$\gamma_2 - 1 + s_{L2} - s_V = 0 \tag{23}$$

$$s_V\, \alpha = 0 \tag{24}$$

$$s_{L1}\, \beta_{L1} = 0 \tag{25}$$

$$s_{L2}\, \beta_{L2} = 0 \tag{26}$$

Again, the phase fractions are used in the complementarity conditions, which may be written as

$$s_V - \max0[s_V - \alpha] = 0 \tag{27}$$

$$s_{L1} - \max0[s_{L1} - \beta_{L1}] = 0 \tag{28}$$

$$s_{L2} - \max0[s_{L2} - \beta_{L2}] = 0 \tag{29}$$

Gopal and Biegler (1999) defined six complementarity conditions and presented a formulation that was nonsquare, having one additional equation. This over-specification was the most serious drawback with their formulation because it limited the choice of solvers (the authors used GAMS; Biegler, 2001). Here, only three complementarity conditions are required, and the formulation is square. Thus, any Newton- or SQP-based solver is appropriate.

As with the two-phase flash, the vapor fraction cannot be specified at zero or one to create a saturated mixture. Unlike the two-phase system, however, the complementarity cannot be dropped at the dew or bubble points without knowing the phases present *a priori*. An extended vapor fraction must, therefore, be defined

$$\alpha_X = \alpha - s_V + \min(s_{L1}, s_{L2}) \tag{30}$$

As before, an extended vapor fraction greater than one indicates a superheated vapor; a value equal to one, a saturated vapor; a value of zero, a saturated liquid(s); and less than zero, a subcooled system. A smoothing function may be used in place of the min function, such as the following modification of Eq. 1

$$\min(s_{L1}, s_{L2}) = 1/2[(s_L + s_{L2}) + ((s_{L1} - s_{L2})^2 + \varepsilon^2)^{1/2}] \tag{31}$$

Examples

Three examples are presented to demonstrate the applicability of these flash formulations, taken from Gopal and Biegler (1999). For the smoothing algorithm, Eq. 1 is chosen with a smoothing tolerance, ϵ, of 10^{-4}. The formulations were implemented in Aspen Custom Modeler, which uses a Newton algorithm. As such, Gopal and Biegler's (1999) three-phase flash formulation could not be tested, because it is nonsquare.

Example 1:Ideal binary flash

This example consists of an equimolar ideal mixture of benzene and toluene at a pressure of 1 bar. Equations 3 – 13 are

Table 1. Solution of Example 1: Ideal Binary Flash

T (K)	Iterations	Vapor Fraction	Extended Vapor Fraction	x_B
378	—	1.0	1.1762	0.295
376	3	1.0	1.1227	0.293
374	3	1.0	1.0701	0.292
372	3	1.0	1.0137	0.291
370	5	0.7559	0.7562	0.335
368	3	0.4658	0.4658	0.396
366	3	0.1774	0.1768	0.461
364	4	0.0	−0.0257	0.500
362	2	0.0	−0.0889	0.500
360	2	0.0	−0.1568	0.500
358	2	0.0	−0.2300	0.500

used to solve the flash problem at temperatures descending from 378 to 358 K. The results are given in Table 1, which shows the temperature, number of iterations from the preceding solution, the vapor fraction, the extended vapor fraction, and the benzene mole fraction. The extended vapor fraction clearly shows the crossing of the phase boundary near 372 K and 364 K, becoming more positive as the system is superheated and more negative as the system becomes further subcooled.

The numerical results are nearly identical to Gopal and Biegler (1999). They exhibited a wider range of iteration counts (from 2 to 10, especially near the phase boundary), which may be attributed to their implementation platform, GAMS, because with the feed flow at 100 mol/s and a smoothing tolerance of 10^{-4} there is very little difference in the two formulations for this system.

Example 2: Nonideal five-component flash

This example consists of methanol, acetone, methyl acetate, benzene, and chloroform with mole fractions of 0.15, 0.40, 0.05, 0.20, and 0.20, respectively, at a pressure of 1 bar. Equations 3 – 13 are used to solve the flash problem at temperatures ascending from 331 to 340 K. The system used the UNIQUAC model. The results are given in Table 2, which shows the temperature, number of iterations from the preceding solution, the vapor fraction, the extended vapor fraction, and the acetone mole fraction. Again, the extended vapor fraction clearly shows the crossing of the phase boundary near 331 K and again at 338 K. To demonstrate the robustness of this formulation, the last case at 331.5 K is solved starting from the solution at 340 K.

Table 2. Solution of Example 2: Nonideal Five-Component Flash

T (K)	Iterations	Vapor Fraction	Extended Vapor Fraction	x_a
331	—	0.0	−0.0269	0.400
332	5	0.0947	0.0947	0.396
333	4	0.3667	0.3667	0.378
334	4	0.5634	0.5634	0.357
335	4	0.7238	0.7238	0.333
336	4	0.8645	0.8645	0.308
337	5	0.9946	0.9946	0.284
338	5	1.0	1.0323	0.283
340	3	1.0	1.0957	0.285
331.5	7	0.0	−0.0086	0.400

Table 3. Solution of Example 2: Nonideal Five-Component Flash Dew Point Temperature, Effects of the Smoothing Tolerance

ε	Iterations	T (K)
10^{-2}	5	337.15
10^{-4}	5	337.04
10^{-6}	7	337.04

In this example, there is some difference in the prediction of the dew point from Gopal and Biegler (1999), which may be attributed to differences in the physical properties. Again, they exhibited a wider range of iteration counts (from 2 to 18), although the higher iterations were within the two-phase region.

To demonstrate the effectiveness of the extended vapor fraction, it is used to compute the exact value of the dew point temperature by fixing its value at unity and releasing the specification of the temperature. Table 3 shows the results for different values of the smoothing tolerance starting from the solution at 331 K. The accuracy of the solution increases as the smoothing tolerance is lowered with little effect on the iteration count. The computation yields a temperature of 337.04 K.

Table 4 shows the results of the dew point calculation when the phase flows are used in the complementarity conditions, rather than vapor fraction, as done in Gopal and Biegler (1999). The table shows the effects of the feed flow on the results when the smoothing tolerance, ϵ, is 10^{-2}. The accuracy of the solution is reduced as the feed flow is lowered. The proposed formulation exhibits no loss in accuracy as the feed flow is changed. Moreover, the proposed formulation takes fewer iterations for the same degree of accuracy.

Example 3: Three-phase flash

This is a water-acrylonitrile-acetonitrile system at a temperature of 333 K and a feed composition of 0.60, 0.35, and 0.05. Equations 15 – 29 were used to solve the flash at pressures ascending from 0.64 to 0.66 bar where the flash exhibits three different phase combinations. The system used the UNIQUAC model. The results are given in Table 5, which shows the pressure, the number of iterations from the previous solution, the three-phase fractions, and the extended vapor fraction. The model predicts the formation of a second liquid phase at a pressure of 0.656 bar, and the loss of the vapor phase at about 0.66 bar. These pressures are slightly different than Gopal and Biegler (1999) and may be attributed to the physical properties. Again, they exhibited a much wider range of iteration counts (from 3 to 58), the higher values near the phase boundaries, which may indicate difficulties with their complementarity conditions.

As another demonstration of the extended vapor fraction, the bubble point pressure may be found by fixing the extended

Table 4. Solution of Example 2: Nonideal Five-Component Flash Dew Point Temperature, Formulation of Gopal and Biegler, Effects of the Feed Flow

F (mol/s)	Iterations	T (K)
10^{-1}	7	337.38
10^{2}	9	337.05
10^{5}	17	337.04

Table 5. Solution of Example 3: Three-Phase Flash

P (bar)	Iterations	Vapor Fraction	Extended Vapor Fraction	L1 Fraction	L2 Fraction
0.64	—	0.5424	0.5424	0.4576	0.0
0.65	4	0.5371	0.5371	0.4629	0.0
0.656	6	0.4775	0.4775	0.4700	0.0526
0.657	3	0.0753	0.0752	0.4989	0.4258
0.66	4	0.0	−0.0044	0.5045	0.4955
0.68	3	0.0	−0.0348	0.5045	0.4955
0.70	2	0.0	−0.0652	0.5045	0.4955
0.75	2	0.0	−0.1413	0.5045	0.4955
0.80	2	0.0	−0.2174	0.5045	0.4955
0.90	2	0.0	−0.3700	0.5045	0.4955
1.00	2	0.0	−0.5217	0.5045	0.4955

vapor fraction at zero and releasing the specification of the pressure. Table 6 shows the results for different values of the smoothing tolerance starting from the solution at 1.0 bar. As before, the accuracy of the solution increases as the smoothing tolerance is lowered with little effect on the iteration count. The computation yields a pressure of 0.657 bar.

Conclusions

Smoothing methods can be successfully applied to the solution of complementarity conditions for simulating phase changes in equilibrium flash calculations. The formulations offered are simple and easy to implement, yet effective in modeling phase changes. Compared with Gopal and Biegler (1999), the formulations are less prone to scaling issues because the complementarity is associated with the vapor fraction rather than phase flows, and provide a clear indication of the phase condition through the extended vapor fraction, which also provides a convenient variable for specifying saturated systems. Most importantly, the three-phase formulation is square allowing solution with common Newton-based algorithms.

Table 6. Solution of Example 3: Three-Phase Flash Bubble Point Pressure

ε	Iterations	P (bar)
10^{-2}	5	0.659154
10^{-4}	3	0.657185
10^{-6}	3	0.657165

Notation

F = feed flow
H = enthalpy
K = phase equilibrium ratio
L = liquid flow
n = size of variable vectors $\mathbf{x}$ and $\mathbf{y}$
s = slack variable
V = vapor flow
X = real valued argument of smoothing function
x = vector of liquid mole fractions
$\mathbf{x}$ = variable vector
y = vector of vapor mole fractions
$\mathbf{y}$ = variable vector
z = vector of feed mole fractions
α = vapor fraction
β = liquid fraction
ϵ = smoothing tolerance
γ = correction factor

Subscripts

i = component number
k = variable vector element number
L = liquid
$L1$ = first liquid
$L2$ = second liquid
V = vapor
X = extended

Literature Cited

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