NONLINEAR PROGRAMMING IN EQUATION OF STATE DEVELOPMENT

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A method for determination of parameters occurring nonlinearly in equations of state, using nonlinear programming techniques, is presented. The nonlinear programming method is compared with the Gauss-Newton nonlinear regression method.

It is well known that the equations of state which most accurately reproduce thermodynamic data over wide ranges of conditions are usually nonlinear functions of the equation of state parameters. The increasing use of computers in process design has made the task of using these complex equations of state much less formidable. Consequently, there exists a real need for a means to determine equation of state parameters which best represent the available thermodynamic data.

Starling (1) presented convincing evidence that the simultaneous use of multiproperty thermodynamic data, *i.e.*, not only pressure-volume-temperature (PVT) data, but also enthalpy, vapor pressure and vapor-liquid equilibrium data, allows determination of equation of state parameters which predict all properties well. Nonlinear regression methods have been applied in several multiproperty equation of state studies at the University of Oklahoma (2, 3, 4) with good success. The primary difficulty in using nonlinear regression methods in multiproperty equation of state development is that for each additional property considered, the number of required calculations is increased dramatically. Leung and Quon (5) and Clare (6) used dual linear programming to determine optimal equation of state parameters for a linear (Chebyshev) objective function with and without constraints upon the enthalpy departure. The purpose of this presentation is to demonstrate the utility of nonlinear programming for determination of equation of state parameters using multiproperty data. Example calculations using a program developed for this purpose are given to show the feasibility of the method.

The nonlinear programming method (INLP) used in this study is based upon the Method of Approximation Programming (MAP) technique presented by Griffith and Stewart (7) with certain modifications. In general terms, the problem may be stated as

minimize

$$g_1(\underline{x}) \qquad \text{Eq. 1}$$

subject to

$$g_i(\underline{x}) \le b_i, \quad i = 2, 3, \ldots, m \qquad \text{Eq. 2}$$

and

$$\underline{x} \ge \underline{0} \qquad \text{Eq. 3}$$

Assume an initial point $\underline{x}^\circ$ and expand the g_i in first order Taylor series about $\underline{x}^\circ$ to get

minimize

$$g_i(\underline{x}^\circ) + \sum_{j=1}^{k} \left[\frac{\partial g_i}{\partial x_j}\right]_o (x_j - x^\circ_j) \le b_i \qquad \text{Eq. 4}$$

subject to

$$g_1(\underline{x}^\circ) + \sum_{j=1}^{k} \left[\frac{\partial g_1}{\partial x_j}\right]_o (x_j - x^\circ_j) \qquad \text{Eq. 5}$$

and

$$\underline{x} > \underline{0} \qquad \text{Eq. 6}$$

Now define

$$v_i = g_i(\underline{x}^\circ), \quad i = 1, 2, \ldots, m. \qquad \text{Eq. 7}$$

$$d_1 = -v_1 \qquad \text{Eq. 8}$$

$$d_i = b_i - v_i, \quad i = 2, 3, \ldots, m. \qquad \text{Eq. 9}$$

$$w_{ij} = \left[\frac{\partial g_i}{\partial x_j}\right]_o, \quad i = 1, 2, \ldots, m; \quad j = 1, 2, \ldots, k. \qquad \text{Eq. 10}$$

$$y_j = x_j - x^\circ_j, \quad j = 1, 2, \ldots, k. \qquad \text{Eq. 11}$$

to obtain the linear problem (with slack variables added)

minimize

$$\sum_{j=1}^{k} w_{1j} y_j + v_1 \qquad \text{Eq. 12}$$

subject to

$$\sum_{j=1}^{k} w_{ij} y_j + y_{k+i-1} = d_i \qquad \text{Eq. 13}$$

The system of equations represented by Eq. 12 and 13 is then solved using any convenient linear programming algorithm. (The simplex method given by Kuo (8) was used in this study). The results of the linear programming algorithm, y_i^*, are the changes in the initial point $\underline{x}^\circ$ which minimize the objective function given in in Eq. 12.

In the INLP algorithm, these changes are further refined by using a formula suggested by Hartley (9)

$$\underline{x}^{i+1} = \underline{x}^i + v_{min}\, \underline{y}^* \qquad \text{Eq. 14}$$

where

$$v_{min} = 0.5 + 0.25 \frac{(g_1(\underline{x}^i) - g_1(\underline{x}^i + \underline{y}^*)}{(g_1(\underline{x}^i + \underline{y}^*) - 2g_1(\underline{x}^i + 0.5\underline{y}^*) + g_1(\underline{x}^i))} \qquad \text{Eq. 15}$$

This step effectively accelerates the movement toward the optimum $\underline{x}$. The new $\underline{x}$ are determined according to Eq. 14 and the process is repeated until a stationary point is reached. Although the acceleration towards the minimum aids greatly in convergence, the presence of the slack variables can cause the method to be somewhat insensitive in the vicinity of the minimum.

The INLP technique described here was compared with the MAP technique using an example problem given by Griffith and Stewart (7). The problem is

maximize

$$2x_1 + x_2 \qquad \text{Eq. 16}$$

subject to

$$x_1^2 + x_2^2 \leq 25 \qquad \text{Eq. 17}$$

$$x_1^2 - x_2^2 \leq 7 \qquad \text{Eq. 18}$$

$$\underline{x} \geq \underline{0} \qquad \text{Eq. 19}$$

The results on an iteration-by-iteration basis are shown in Table 1. It is evident that the INLP algorithm reaches the maximum somewhat more quickly than the MAP algorithm. This is due primarily to the use of Eq. 14.

TABLE 1. *Comparison of INLP and MAP algorithms for the Griffith and Stewart example.*

Iteration number	INLP objective function	MAP objective function	INLP x_1	MAP x_1	INLP x_2	MAP x_2
0	3	1	1	1	1	1
1	12.50	6	4.75	2	3	2
2	11.12	9	4.06	3	3	3
3	11.00	10.83	4	4	3	3.87
4	—	11.01	—	3.99	—	3.03
5	—	11.00	—	4	—	3

TABLE 2. *Methane pilot data calculation results.*

	No. of itn.	Obj. fcn.	Av. pct. Dv. Z	Av. pct. Dv. H	(C_0) initial x 10⁻⁹	(C_0) final x 10⁻⁹	(γ) initial	(γ) final
Bono[a]	4	—	1.37	2.69	.275763	.276608	1.53960	1.59056
INLP	2	0.0016	0.52	3.28	.275763	.283555	1.53960	1.53960

[a] Reference 2.

The INLP algorithm was then compared to the multiproperty nonlinear regression algorithm developed by Bono (2). Both programs were set up to handle PVT and enthalpy data simultaneously to determine values for C_0 and γ in the Benedict-Webb-Rubin (BWR) equation of state. The objective function used with the INLP was to minimize the sum of the square of the relative deviations in compressibility factor. The average absolute deviation in compressibility factor was constrained to be less than 0.005 and the average absolute deviation in enthalpy was constrained to be less than 0.5 Btu/lb. The results of these calculations using 20 PVT and 13 enthalpy values from the —100°F isotherm for methane (10, 11) are shown in Table 2. When the nonlinear regression program and the INLP program are started at the same initial point, the final results are comparable, but the INLP takes half as many iterations, with equivalent computation time at each iteration. Other results for the INLP program show that although the objective function is fairly sensitive to variations in γ, the program does not force γ toward an optimal value. This is due primarily to the relatively small contribution of the term involving γ in the objective function compared to the term involving C_0. The slack variables are sufficient to correct for errors in γ without forcing it to vary.

The major importance of the INLP method is in the inherent ease with which additional thermodynamic properties may be considered. All that is necessary when adding a new type of property data to the problem is the addition of a constraint equation for that property. The relative "tightness" of the constraint may then reflect the experimental accuracy of the property data. It is this factor, the ease with which a large variety of multiproperty data may be incorporated, that makes the INLP method very attractive for use in equation of state development.

NOMENCLATURE

b_i	constants of inequality
d_i	differences, defined in Eq. 8, 9
$g_i(\underline{x})$	general functions of $\underline{x}$
k	number of variables
m	number of constraints plus one
v_i	value of $g_i(\underline{x})$ at $\underline{x}^\circ$
w_{ij}	value of $\frac{\partial g_i}{\partial x_j}$ at $\underline{x}^\circ$
$\underline{x}$	parameter set
$\underline{y}^*$	optimal set of changes in parameters

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