Chemical Equilibrium Optimization Via Logarithmic Penalty Function Approach

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Abstract. Determining the chemical composition problem which is made up of a complex mixture specifically for chemical equilibrium has become one of the great importance, and it usually arises, especially in the performance of fuels and catalyst analysis and the fusion of the complicated organic compound. We implored a new logarithmic penalty function (LPF) to optimize (minimize) the objective function in the chemical equilibrium model. The objective function represents the expression of a mathematical model for the free energy of the chemical mixture under consideration. The result obtained happens to be more acceptable in terms of the optimal objective value and computational complexity.

1. Introduction
Chemical composition of a complex mixture under the conditions of chemical equilibrium is among the fundamental aspect of chemical process design that requires attention; this is as a result of the second law of thermodynamics. The mathematical expression of the free energy for the chemical mixture under consideration can be regarded as the objective function that needs to be minimized. The goal of the whole model is to minimize the value of free energy for the mixture, subject to possible reactions between mixture types. Many approaches to optimizing the chemical equilibrium model have been proposed.

McDonald and Floudas [1] implored global optimization for the phase, and chemical equilibrium, the global optimization (GOP) algorithm is used to guarantee convergence to an ε-global solution. McKinnon et al. [2] used the algorithmic approach based on Gibbs’ tangent-plane criterion to address the issue of minimizing free energy in the n-component, multi-phase equilibrium problem involving various thermodynamic models. Jia et al. [3] were able to optimized the struvite precipitation for ammonium recovery from anaerobic digester effluent, by applying a chemical equilibrium model. More researches for optimizing chemical equilibrium are still in progress (see, for instance [4], [5], [6]). The penalty function is one of the most recent approaches for optimizing a different kind of optimization problems. Zangwill [7] and Eremin [8] are the first to introduce a penalty function approach simultaneously in the 1960s; this approach attracts the attention of many researchers, especially in the field of optimization theory. Several other penalty functions were proposed in which each of the penalty methods has its peculiarities. Recently Hassan and Baharum [9], [10] proposed a logarithmic penalty function (LPF) approach which was capable in dealing with the irregularity of the problems.

Nevertheless, the approach was restricted to the problem with equality constraints only. Hassan and Baharum [11],[12] modified a Courant-Beltrami (MCB) penalty function for inequality to complement
the proposed LPF which lead to the general form of logarithmic penalty function approach [13] to handle the general structure of constrained optimization problem. As it has been mentioned earlier, optimizing a chemical equilibrium is of great interest, especially determining the chemical composition problem. In this paper, a new logarithmic penalty function has been used to minimize the objective function in the chemical equilibrium model. The chemical equilibrium model and formulation described by Bracken and McCormick [14] will be considered.

2. Description of the Chemical Equilibrium Model

The mixture of $m$ chemical elements will be considered for describing a chemical equilibrium model. Conventionally, the various types of $m$ different atoms may mix chemically to yield $n$ compound, where the monotonic atom is considered as a possible compound for our purpose. The variables can be defined as follows:

- $x_j$ is the number of moles for the compound $j$ present in the mixture at equilibrium,
- $x^*$ is the total number of moles in the mixture, where $x^* = \sum_{j=1}^{n} x_j$,
- $a_{ij}$ is the number of atoms of element $i$ in a molecule of compound $j$,
- $b_i$ is the number of atomic weights of element $i$ in the mixture.

The mass balance relationships that must hold for the $m$ elements are

$$\sum_{j=1}^{n} a_{ij} x_j = b_i, \quad i = 1, ..., m. \quad (1)$$

and

$$x_j \geq 0, j = 1, ..., n. \quad (2)$$

Determining the values of $x_j$ ($j = 1, ..., n$) that satisfy (1) and (2) is equivalent to the resolution of the mixture composition at equilibrium, as well as minimizing the mixture’s total free energy. The mathematical representation for the total free energy of the mixture is given by

$$\sum_{j=1}^{n} c_j + \ln\left(\frac{x_j}{x}\right), \quad (3)$$

where

$$c_j = \left(\frac{F^0}{RT}\right)_j + \ln P,$$

where $(F^0/RT)$ represent the modal standard (Gibbs) free energy function for the $j$th compound, and it can be found in the tables, also $P$ represent the total pressure in the atmosphere. Now, from the above equilibrium model, the nonlinear programming problem obtained can be expressed as follows:

The nonlinear objective function (3) is to be minimized by choosing $x_j$ ($j = 1, ..., n$), subject to linear constraints as in equation (1) and non-negativity restrictions as in equation (2).

3. Formulation

This type of equilibrium model expressed in the previous section has been solved initially by White, Johnson, and Dantzig [15]. The data used are specifically obtained from [15]. Bracken and McCormick [14] implored sequential unconstrained minimization technique to solve the nonlinear programming problem of the chemical equilibrium model. The result obtained is similar to result attained in [15]. Nevertheless, the value of the objective function is smaller (thus improved) than that obtain and presented in [15].

The problem to be addressed is determining the composition of the equilibrium resulting from subjecting the compound $\frac{1}{2}N_2H_4+\frac{1}{2}O_4$ to a temperature of 3500°K and a pressure of 750 psi. It has been shown in Table 1 that for each compound $j$ of 10 possible compounds (where the monotonic atoms are called compounds), the free energy function of Gibbs $(F^0/RT)_j$, the calculated value of $c_j$ for $P = 750$ psi, and number of molecules of H, N, and O atoms. It is known that the amount of atomic
weights of H, N, and O in the mixture is \( b_1 = 2, b_2 = 1 \), and \( b_3 = 1 \). The nonlinear objective function to be minimized in formulating the nonlinear programming model is as follows:

\[
x_1 \left[-6.089 + \ln \left( x_1 / \sum_{j=1}^{10} x_j \right) \right] + \cdots + x_{10} \left[-22.179 + \ln \left( x_{10} / \sum_{j=1}^{10} x_j \right) \right],
\]

and the linear constraints of the nonlinear programming are as follows:

\[
x_1 + 2x_2 + 2x_3 + x_6 + x_{10} = 2,
\]
\[
x_4 + 2x_5 + x_6 + x_7 = 1,
\]
\[
x_3 + x_7 + x_8 + 2x_9 + x_{10} = 1,
\]
\[
x_1 \geq 0, \ldots, x_{10} \geq 0
\]

### Table 1. Data on \( \frac{1}{2} N_2H_4 + \frac{1}{2} O_2 \) at 3500°K, 750 psi

| \( j \) | Compound | \( (F^0/RT)_j \) | \( c_j \) | \( a_{ij} \) |
|---|---|---|---|---|
| 1 | H | -10.021 | -6.089 | 1 | H | N | O |
| 2 | H\(_2\) | -21.096 | -17.164 | 2 | |
| 3 | H\(_2\)O | -37.986 | -34.054 | 2 | 1 |
| 4 | N | -9.846 | -5.914 | 1 | |
| 5 | N\(_2\) | -28.653 | -24.721 | 2 | |
| 6 | NH | -18.918 | -14.986 | 1 | 1 |
| 7 | NO | -28.032 | -24.100 | 1 | 1 |
| 8 | O | -14.640 | -10.708 | 1 | |
| 9 | O\(_2\) | -30.594 | -26.662 | 2 | |
| 10 | OH | -26.111 | -22.179 | 1 | |

### 4. Logarithmic Penalty Function

A penalty function approach has come into existence a few decades ago, and the method is of great interest to the practitioners and the theorist; it offers a simple and straightforward technique for handling constrained optimization problems that can easily be implemented without the use of sophisticated computer programming codes.

In a quest of overcoming its inherently slow convergence, and find it useful to bring into play virtually all aspects of optimization theory; including necessary conditions, Lagrange multipliers, and many other forms of optimization, Hassan and Baharum [9] proposed a new logarithmic penalty function (LPF), that has been tested to some simple theoretical problems from Hock-Schakowsky [16] collection of test problems, it was further harmonized it with modified Courant-Beltrami [11]. It was extended into a more general form as in [13] that can handle both equality and inequality constraints.

It is crucial to predict the behaviour of substances in equilibrium by using certain laws which are usually applied in industries seeking to lower the costs of producing specific chemicals. We implored the new LPF to minimize the objective function in the chemical equilibrium model and compare its optimal values with that of some of the previous approaches. The new logarithmic penalty function is of the following form:
\[ p_1(x) = \sum_{j=1}^{m} \ln \left[ \left( h_j(x) \right)^2 + 1^j \right] \] (4)

The new logarithmic penalty function (4) is specifically designed to handle equality constraints, the hybridization of equation (4) and a modified Courant-Beltrami penalty function (5) for inequality constraints below:

\[ p_2(x) = \sum_{q=1}^{s} \ln \left[ \left( g_q^+(x) \right)^2 + 1^q \right] \] (5)

leads to the general form of logarithmic penalty function introduced by Hassan and Baharum [13] as follows:

\[ p(x) = \sum_{q=1}^{s} \ln \left[ \left( g_q^+(x) \right)^2 + 1^q \right] + \sum_{j=1}^{m} \ln \left[ \left( h_j(x) \right)^2 + 1^j \right] \] (6)

Note that: \( g_q^+(x) = \max(0, g_q(x)) \).

Adding equation (6) to the objective function prescribes high cost for violation of the constraints for any infeasible point \( x \) and equation (6) will be zero for any feasible point. However, the penalized problem based on the LPF in equation (6) is

\[ Q(x) = f(x) + \sum_{q=1}^{s} \ln \left[ \left( g_q^+(x) \right)^2 + 1^q \right] + \sum_{j=1}^{m} \ln \left[ \left( h_j(x) \right)^2 + 1^j \right] \] (7)

where \( f(x) \) is the objective function of the original problem of nonlinear programming, \( h_j(x) \) are equality constraints and \( g_q(x) \) are inequality constraints.

Based on the formulation of chemical equilibrium model, it is a nonlinear programming problem with linear equality constraints. The reformulation of the equilibrium model can be done through the new LPF in equation (7). Therefore, the transformed unconstrained problem of chemical equilibrium model is as follows:

\[ Q(x) = x_1 \left[ -6.089 + \ln \left( x_1 / \sum_{j=1}^{10} x_j \right) \right] + \cdots + x_{10} \left[ -22.179 + \ln \left( x_{10} / \sum_{j=1}^{10} x_j \right) \right] + \ln \left[ (x_1 + 2x_2 + 2x_3 + x_6 + x_{10} - 1)^2 + 1 \right] + \ln \left[ (x_4 + 2x_5 + x_6 + x_7 - 1)^2 + 1 \right] + \ln \left[ (x_3 + x_7 + x_8 + 2x_9 + x_{10} - 1)^2 + 1 \right] \] (8)

Equation (8) is a transformed unconstrained problem via LPF, the problem can be solved by one the most successful approach of unconstrained minimization technique which is a quasi-newton algorithm.

5. Result and Discussion

The chemical equilibrium problem is among the mathematical form of a nonlinear programming problem. Many algorithms could be used to optimize its objective function, the setbacks that usually arises not only for this type of the problem but to several problems in decision theory, engineering, e.t.c. are irregularity and computational complexity. The sequential unconstrained minimization technique (SUMT) is among the most popular algorithms used to solve this type of nonlinear programming problem, in many cases, gradient-based algorithms are regarded as an essential approach to find a global minimum for the problem. However, differentiability of the transformed unconstrained problem is required to use those gradient-based algorithms. The new logarithmic penalty function (LPF) introduced by Hassan and Baharum [13] were able to handle irregularity and computational complexity.

Moreover, the new LPF guaranteed the applicability of those gradient-based algorithms due to its differentiability nature, that is what makes it possible to use any of the available unconstrained
minimization techniques. The penalized nonlinear programming problem of chemical equilibrium has been solved using quasi-newton algorithm via *fminunc* routine function, and we obtain the values of $x_j$ ($j = 1, \ldots, n$), the number of moles of the ten-compound present in the equilibrium mixture. The objective value is smaller (thus better) compared to the objective value obtained by Hock-Schittkowski [16] and also by Bracken and McCormick [14]. The values of $x_j$ of all the three different approaches are given in Table 2 while their corresponding objective values are given in Table 3.

**Table 2.** Result of the ten compounds from 3 methods

| $j$ | Compound | $x_j$(Bracken) | $x_j$ (Hock) | $x_j$ (LPF) |
|-----|----------|----------------|--------------|-------------|
| 1   | H        | 0.0407         | 0.01773548   | 0.1561      |
| 2   | H₂       | 0.1477         | 0.08200180   | 0.3465      |
| 3   | H₂O      | 0.7831         | 0.8825646    | 0.4683      |
| 4   | N        | 0.0014         | 0.7233256E-03| 0.0000      |
| 5   | N₂       | 0.4853         | 0.4907851    | 0.4320      |
| 6   | NH       | 0.0007         | 0.4335469E-03| 0.0343      |
| 7   | NO       | 0.0274         | 0.01727298   | 0.1643      |
| 8   | O        | 0.0180         | 0.007765639  | 0.0346      |
| 9   | O₂       | 0.0373         | 0.01984929   | 0.0937      |
| 10  | OH       | 0.0969         | 0.05269826   | 0.2281      |

**Table 3.** Objective values

| Objective value | (Bracken) | (Hock) | (LPF) |
|----------------|----------|--------|-------|
| -47.76         | -47.707579 | -48.4006 |

6. Summary

A new logarithmic penalty function (LPF) approach has been used to solve the chemical equilibrium model. The transformed nonlinear programming problem via LPF guarantees the applicability of the quasi-newton algorithm. A better objective value compared to the conventional constrained problem approach used by Hock-Schittkowski [16] and the sequential unconstraint minimization technique (SUMT) used by Bracken and McCormick [14] were presented in Table 2 and Table 3.

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