

# Tabu search for global optimization of continuous functions with application to phase equilibrium calculations

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## Abstract

Tabu (or taboo) search (TS) has been successfully applied to combinatorial optimization but it has not been used for global optimization of many continuous functions including phase equilibrium calculations via Gibbs free energy minimization. In this study, a version of TS, namely, enhanced continuous TS (ECTS), is first tried for benchmark test functions having multiple minima and then evaluated for phase equilibrium calculations. Examples for the latter involve several components, typical conditions and common thermodynamic models. Performance of ECTS is compared with a genetic algorithm (GA). The results show that both TS and GA have high reliability in locating the global minimum, and that TS converges faster than GA thus reducing the computational time and number of function evaluations.

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## 1. Introduction

Compared to genetic algorithms (GA) and simulated annealing (SA), taboo or tabu search (TS) has not received much attention from chemical engineers (Edgar, Himmelblau & Lasdon, 2001). It was originally developed by Glover (1989, 1990), and has been widely applied to combinatorial optimization (e.g. Wang, Quan & Xu, 1999; Díaz & Fernández, 2001; Youssef, Sait & Adiche, 2001; Józefowska, Waligóra & Węglarz, 2002). TS is a meta-heuristic method that guides and modifies other heuristics to produce solutions beyond those that are normally generated. The heuristics may be high level procedures or may embody nothing more than a description of available moves from one point to another, together with an associated evaluation rule (Glover & Laguna, 1997). The tabu or forbidden move concept is implemented in TS as a meta-heuristic method that guides and improves the search in the

solution space. The characteristics of TS, GA and SA, which are all meta-heuristic methods, are summarized in Table 1. For producing a new point, TS compares current alternatives with previous searches, and hence incorporates adaptive memory. It also takes advantage of responsive exploration or intelligent search (i.e. the supposition that a bad strategic choice can yield more information than a good random choice) (Glover & Laguna, 1997).

The TS algorithm is used mainly for diversification, i.e. searching the entire solution space including unvisited regions to generate solutions that differ in various ways from those seen before. A promising area having a lower value of objective function, will be identified for further inspection. Several promising areas are identified after a number of iterations. Then, in-depth searching, often referred as intensification, into the most promising area follows. For this, TS or a suitable local minimization method can be used. Up to now, only a few works deal with the application of TS to problems involving continuous functions (Hu, 1992; Cvijović & Klinowski, 1995; Siarry & Berthiau, 1997; Rajesh, Jayaraman & Kulkarni, 2000; Chelouah & Siarry, 2000).

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**Nomenclature**

$G/RT$	dimensionless Gibbs free energy
$h_{n/m}$	half-length of $m^{\text{th}}$ hyperrectangle
$\text{Iter}_{\text{Max}}$	maximum number of iterations
$n$	number of neighbors generated in hyperrectangles
$N$	number of decision variables
$nc$	total number of components
$np$	total number of phases
$n^k$	total number of moles in phase $k$
$n_i^k$	number of moles of component $i$ in phase $k$
$N_p$	size of promising list
$N_s$	number of initial sample points
$N_t$	size of tabu list
$\text{OF}_{\text{Opt}}$	analytical global minimum
$\text{OF}_{\text{Cal}}$	the best successful point found from the minimization
$P$	system pressure
$P_i^{\text{sat}}$	saturated vapor pressure of pure component $i$
$s, s'$	centroid of TS hyperrectangles
$\text{Sc}_{\text{Max}}$	maximum number of successive iterations without detection of a promising area
$T$	system temperature
$V$	total molar flowrate of vapor
$x_i$	mole fraction of component $i$ in liquid phase
$y_i$	mole fraction of component $i$ in vapor phase
$z_i$	mole fraction of component $i$ in the feed
<b>Greek letters</b>	
$\alpha$	shortest distance of a point from the lower bound
$\beta$	variable in equations (17) and (18)
$\varepsilon_p$	ball radius for points in the promising list
$\varepsilon_t$	ball radius for points in the tabu list
$\phi_i$	fugacity coefficient of component $i$
$\gamma_i$	activity coefficient of component $i$
<b>Subscripts</b>	
$*$	global minimum
$m$	index for hyperrectangle; used as a superscript also
<b>Superscripts</b>	
$k, j$	phase index
$L1$	liquid phase 1
$L2$	liquid phase 2
$V$	vapor phase
$\wedge$	partial property

Hu (1992) compared the performance of TS with random search (RS) and GA, on four mathematical functions of one and two variables. For one-dimensional problems, the number of function evaluations was

Table 1  
Characteristics of TS, GA and SA (Glover & Laguna, 1997)

	TS	GA	SA
Adaptive memory	Yes	No	No
Systematic neighborhood search	Yes	No	No
Random-sampling	Yes	Yes	Yes
Population-based approach	No	Yes	No

comparable for TS and GA. For two-dimensional problems, TS took at least three times less number of function evaluations than GA. In both cases, TS performed better than RS. In the study of Cvijović and Klinowski (1995), mathematical functions of two to six variables were tested. The reliability or success rate of TS was found to be at least 90%, with the final results within 2–3% of the global minimum. Starting from the final results of TS, a more accurate optimum was calculated using *findminimum*, a built-in local optimizer in MATHEMATICA. Cvijović and Klinowski (1995) concluded that TS avoids entrapment in local minima and finds near-optimal result, it can be applied to a wide range of problems, it is conceptually simpler than SA

and GA, it does not require any derivatives and it is easy to implement.

Siarry and Berthiau (1997) proposed and implemented an adaptation of TS, called continuous TS (CTS), and compared its computational performance with pure RS and SA. They found that the success rate of CTS for mathematical functions of two and three variables was 100%, but the success rate for functions of five and ten variables was less than 85%. In terms of the objective function evaluations, CTS was comparable to SA but took 30 times less than RS. When the number of variables increases, CTS required more function evaluations than SA, i.e. 20 times higher for Rosenbrock function of ten variables (Siarry & Berthiau, 1997). Note that CTS has only the diversification step. Thus, minimization can be done successfully by diversification only, provided more number of iterations is allowed. However, the final result may not be as accurate as the result obtained by including an intensification step.

Chelouah and Siarry (2000) proposed an enhanced continuous TS (ECTS) as an extension of CTS of Siarry and Berthiau (1997). In ECTS, intensification step and a “promising list” are added, and “concentric crowns” used in CTS are replaced by “hyperrectangles”. Chelouah and Siarry (2000) tested the ECTS on 20 benchmark problems of 2 to 100 variables, solving each problem 100 times. Their results show that the average number of function evaluations for CTS is higher than that for ECTS for the same stopping criterion. For functions of ten to 100 variables, the average number of objective function evaluations is tremendously high (more than  $10^6$ ) for CTS, but ECTS requires not more than 16 000 evaluations.

Rajesh et al. (2000) tested TS on several unconstrained and constrained functions involving two to seven variables, and solved each problem 25 times. TS found the minimum of these problems with 100% reliability and converged to within 1–2% of the global minimum. For unconstrained optimization problems of two variables, the performance of TS was compared with pure RS, multistart method, SA (based on stochastic differential equations) and SA, whereas, for constrained optimization problems of two to seven variables, it was compared with GA. For both unconstrained and constrained problems tested, TS required the lowest number of function evaluations.

The TS is thus attractive for global optimization of continuous functions. The main objective of this study is to test TS and compare with GA for benchmark multimodal functions and for phase equilibrium calculations, important in the design, development, operation and optimization of chemical processes. For this, ECTS of Chelouah and Siarry (2000) is selected and a program for it is developed and tested for benchmark functions having multiple minima and 2 to 20 variables. ECTS is then used for solving many phase equilibrium problems

involving either two or three phases at equilibrium (vapor–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE) and vapor–liquid–liquid equilibrium (VLLE)) and 2 to 11 components. The task in phase equilibrium calculations is to predict the correct number of phases at equilibrium and their compositions precisely. At equilibrium, Gibbs free energy of a system must be at the global minimum. Hence, to solve phase equilibrium problems, minimization of Gibbs free energy constrained for mass balances is a classic method. However, as Gibbs free energy function is nonlinear and complex, a reliable method for global minimization is highly desired.

White, Johnson and Dantzig (1958) was the first to propose Gibbs free energy minimization for phase equilibrium calculations. They used a method, called RAND for minimization of Gibbs free energy, in which the number of phases has to be assumed in advance. Gautam and Seider (1979) used the same method but, additionally, phases can be added or subtracted as necessary; an additional phase is postulated by splitting one of the phases into two. Castillo and Grossmann (1981) used a nonlinear programming method to determine the number and identity of phases at equilibrium. Soares, Medina, McDermott and Ashton (1982) proposed an optimization procedure based on Newton–Raphson algorithm, in which the Marquardt method is used to control magnitude of the correction vector and to remove problems caused by ill-conditioning of the Hessian matrix. Ohanomah and Thompson (1984) compared RAND, modified-RAND, geometric programming and perturbation theory of geometric programming for VLE applications. From the results, they observed that the modified-RAND is unreliable; a variation of the perturbation theory of geometric programming is the best among the minimization algorithms.

Lantagne, Marcos and Cayrol (1988) introduced a penalty function method to solve the constrained nonlinear optimization problem. Newton method and Broyden–Fletcher–Goldfarb–Shanno (BFGS) method were used to solve the unconstrained problem. They also applied a sequential quadratic programming (SQP) method to solve the constrained optimization problem and to compare with both the previous methods. Results show that Newton method converges faster than BFGS and SQP. Walraven and Van Rompay (1988) improved the phase split algorithm of Gautam and Seider (1979), mainly for LLE. Lucia, Padmanabhan and Venkataraman (2000) applied SQP for multiphase equilibrium flash calculations. The overall algorithmic framework consists of binary tangent plane analyses, bubble-point calculations and Gibbs free energy minimization. The binary tangent plane analyses and minimization of Gibbs free energy are solved using SQP method with BFGS approximation of the Hessian matrix of the

Lagrangian function. Recently, Teh and Rangaiah (2002) tested IMSL subroutines—DLCONF and DBCONF for Gibbs free energy minimization, and found them unreliable.

All the methods discussed above are implementations of local minimization of Gibbs free energy. The available global optimization methods can be classified into two broad categories: exact or deterministic methods and heuristic or stochastic methods. The former methods have the desirable property of guaranteed convergence to the global minimum under certain conditions. On the other hand, stochastic methods are attractive as they require little or no additional assumptions on the optimization problem and particularly suited for problems with ill- or unknown structure (Pardalos, Romeijn & Tuy, 2000). Thus, they are not restricted to any specific thermodynamic model, and can be used easily for developing new models (Lee, Chiew & Rangaiah, 2000).

McDonald and Floudas (1995a,b,c, 1997) have developed two global methods for phase equilibrium calculations: decomposition-based approach for using with NRTL model, and a branch and bound method for UNIFAC, ASOG and TK-Wilson models. In the first method, the problem is transformed into a bi-convex objective function, which is optimized over a set of bilinear constraints. Then, global optimization is used for convergence to global minimum regardless of the initial point. In the second method, Gibbs free energy expression for UNIFAC, ASOG and TK-Wilson models is transformed to suit the branch and bound method. The transformation allows the Gibbs free energy function to be expressed as the difference of two convex functions, where the concave portion is separable.

Among the stochastic methods, Pan and Firoozabadi (1998) and Lee, Rangaiah and Luus (1999) have, respectively, demonstrated that SA and the multipass Luus–Jaakola (LJ) are capable of locating the global minimum of Gibbs free energy for multi-phase equilibrium calculations. The SA method is reliable as it can escape from the local minima and converge to the global minimum; however, it is costly in computation (Pan & Firoozabadi, 1998). The LJ method is a direct search technique involving random sampling and systematic search region reduction. Application of GA and SA to phase equilibrium calculations and phase stability problems (Rangaiah, 2001), shows that both of them have good reliability for global minimization of free energy and tangent plane distance function, and that GA is more efficient than SA. Teh and Rangaiah (2002) tested GA on 11 VLE, six LLE and five VLLE examples, and compared its performance with both equation-solving and free energy minimization methods for phase equilibrium calculations. The results show that GA is the most reliable among the methods tested. Besides, it does not require a separate step to determine

phases at equilibrium as it can find the global minimum even when an extra phase is assumed.

Apart from the methods reviewed above, many other methods have been studied for phase equilibrium problems and for the related phase stability analysis. References to these methods can be found in Hua et al. (1998), Rangaiah (2001) and Teh and Rangaiah (2002). For the sake of brevity, only recent and relevant papers on these other methods are included here. Hua et al. (1998), Hua, Maier, Tessier, Brennecke and Stadtherr (1999) and Tessier, Brennecke and Stadtherr (2000) studied interval analysis for phase stability problems and successfully solved problems involving two to five components. The interval technique is independent of initialization and thermodynamic model, and it can find all the stationary points of the objective function. Zhu and Xu (1999) applied SA to phase stability of LLE systems described by NRTL and UNIQUAC models. Results on four examples show that it can solve these problems effectively. Later, Zhu, Wen and Xu (2000) introduced an enhanced SA to cope with systems having 3–5 components at high pressure and described by SRK and PR Equation of State. However, the enhanced SA was found to be slightly slower.

## 2. ECTS algorithm

For this study, ECTS algorithm of Chelouah and Siarry (2000) is selected because of its better performance for a range of problems including high dimensional problems. A flowchart of the algorithm is shown in Fig. 1. The main stages in ECTS are: (a) parameters setting; (b) diversification; (c) identifying the most promising area; and (d) intensification. The algorithm starts with selection of values for ECTS parameters such as size of tabu and promising lists, radius of tabu and promising balls. Then, a population of  $N_s$  points are randomly generated and the best of these points is selected as the current point,  $s$ . From this current point,  $n$ -neighbors are generated in  $n$ -concentric hyperrectangles, which is described in the next section.

To avoid from going back to those visited points, the generated  $n$ -neighbors are compared with those in the tabu and promising lists. The tabu list consists of “unpromising” points. The neighbors close (i.e. within a ball of radius specified by the user) to those in the tabu and promising lists, are rejected and the objective function at the remaining neighbors is evaluated. The best neighbor of  $s$ , even if it is worse than  $s$  itself, is selected as the new current point,  $s'$  and included into the promising list. This is to avoid entrapment in the local minima and to maintain the diversification of search. The tabu list is updated with the new “unpromising” neighbors; when it is full, the first solution entered will be replaced and so on. Promising list is also

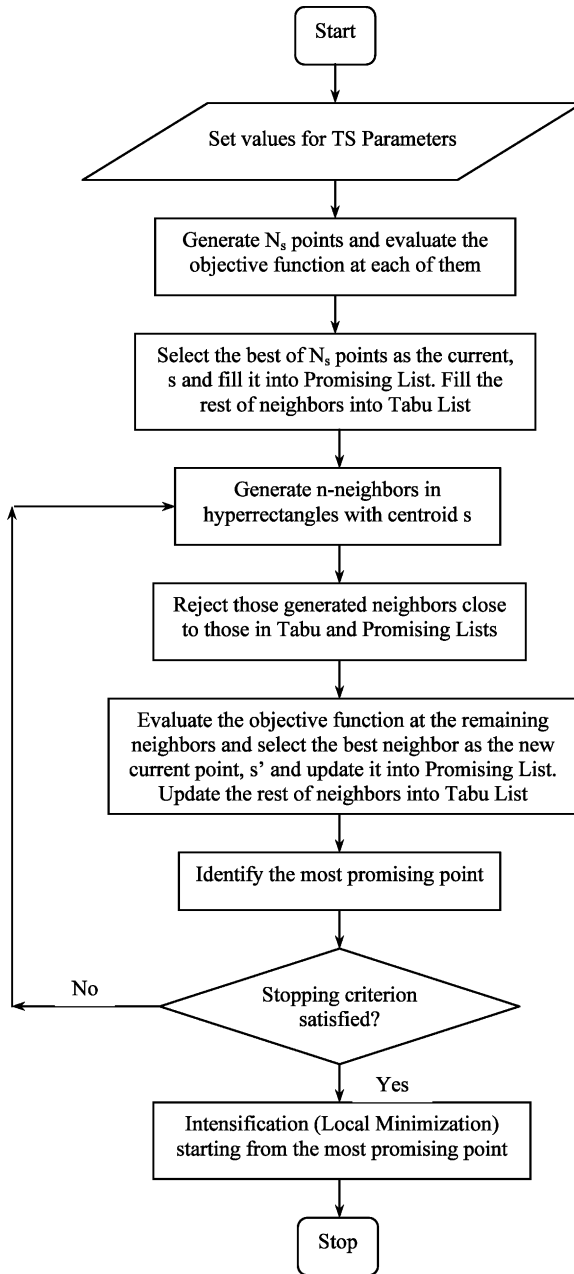


Fig. 1. Flowchart of ECTS algorithm including intensification.

updated in the same way. The procedure is repeated by generating  $n$ -neighbors of the new current point,  $s'$  until certain stopping criterion is reached. The number of iterations can be used as a stopping criterion.

Chelouah and Siarry (2000) employed the ECTS algorithm for intensification as well. However, in this study, local minimization methods, namely modified Simplex method of Nelder–Mead (NM) and quasi-Newton (QN) method in the IMSL subroutine, DBCONF, are used for intensification. Like TS, the former is a direct search method not requiring derivatives whereas the latter is an efficient gradient-based method. The most promising point identified by the

ECTS algorithm is utilized as the initial guess for these local minimization methods. The two algorithms consisting of ECTS followed by NM or QN are denoted as TS-NM and TS-QN.

### 3. Generation of neighbors in tabu search

In ECTS, Chelouah and Siarry (2000) replaced concentric balls with hyperrectangles because it is mathematically easier to generate and verify a point inside a specific hyperrectangle. The structure of hyperrectangles is illustrated in Fig. 2. To generate  $n$ -concentric balls, Siarry and Berthiau (1997) proposed three partitioning methods:

a) Geometrical partitioning

$$h_{n-m+1} = \frac{h_n}{2^{m-1}} \quad (m = 1, 2, \dots, n) \quad (1)$$

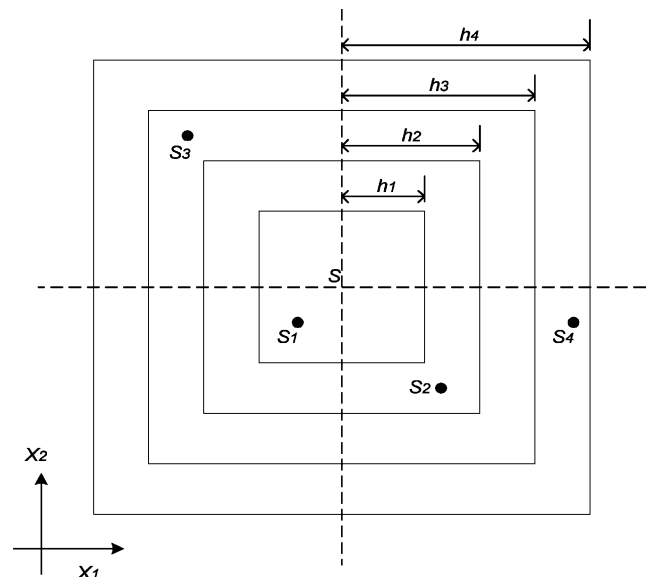
b) Linear partitioning

$$h_{n-m+1} = \frac{h_n(n-m+1)}{n} \quad (m = 1, 2, \dots, n) \quad (2)$$

c) Isovolum partitioning

$$h_m = \left( h_{m-1}^N - \frac{h_{m-1}^N}{n} \right)^{\frac{1}{N}} \quad (m = 1, 2, \dots, n) \quad (3)$$

where  $N$  is the number of decision variables. Siarry and Berthiau (1997) found that the geometrical and linear

Fig. 2. Four hyperrectangles, each with a randomly generated point, about the current point,  $s$ , in two dimensions.



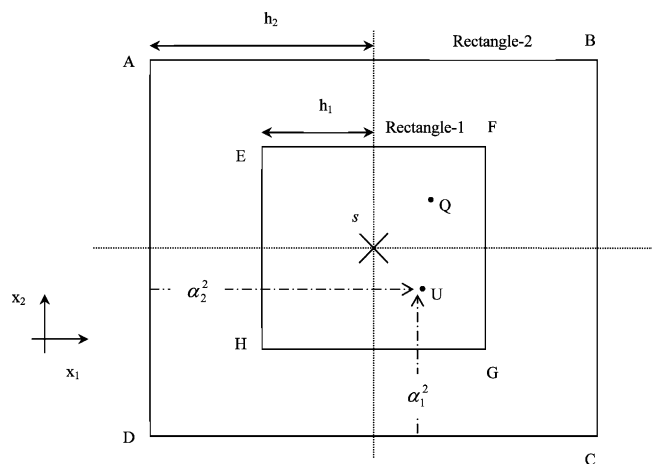


Fig. 3. Generation of a point in each of the first two hyperrectangles in two dimensions.

partitioning are better than the isovolume partitioning. The former is chosen for the present study. Implementation of the partitioning is simple but to ensure that only one neighbor or point is generated in the region enclosed by two adjacent hyperrectangles requires some precaution. For example, the first point, Q in the inner-most rectangle (EFGH in Fig. 3) can easily be generated; subsequently, the second point must be generated inside ABCD but excluding the area EFGH. No procedure is given in Chelouah and Siarry (2000) for doing this. Here, the following strategy is employed.

- 1) Calculate the half-length of  $n$ -hyperrectangles ( $h_1, h_2, \dots, h_n$ ) based on geometrical partitioning.
- 2) To generate a point in the inner-most rectangle, set  $m = 1$  and evaluate upper bounds ( $UB_k^m$  for  $k = 1, 2, \dots, N$ ) and lower bounds ( $LB_k^m$  for  $k = 1, 2, \dots, N$ ) for this rectangle. As shown in Fig. 3, the upper bound in  $x_1$ -direction is the horizontal displacement of boundary FG from the centroid,  $s$  to the right, and the lower bound is the displacement to the left shown as EH.
- 3) Generate a point,  $Q(x_1^m, x_2^m, \dots, x_N^m)$  randomly within the inner-most hyperrectangle using a rectangularly distributed random number,  $R$  in the interval  $[0, 1]$  and

$$x_k^m = LB_k^m + R(UB_k^m - LB_k^m) \quad (k = 1, 2, \dots, N) \quad (4)$$

- 4) Update  $m = m + 1$ . To generate a point in the next hyperrectangle, evaluate its upper and lower bounds ( $UB_k^m$  and  $LB_k^m$  for  $k = 1, 2, \dots, N$ ) for this  $m^{\text{th}}$  hyperrectangle and then generate a point,  $U(x_1^m, x_2^m, \dots, x_N^m)$  randomly using Equation (4).
- 5) Calculate the shortest distance of point U from the lower bound, i.e.  $\alpha_k^m$  shown in Fig. 3 for  $k = 1, 2, \dots, N$ .

- 6) If  $(h_m - h_{m-1} < \alpha_k^m < h_m + h_{m-1})$  for  $k = 1, 2, \dots, N$ , then this point is not in the region between the two adjacent hyperrectangles and so go to Step 4 to generate another point. Else, accept point U.
- 7) Repeat Steps 4–6 to generate a point in each of the remaining hyperrectangles.

#### 4. Mathematical functions

A FORTRAN program was developed for ECTS based on the flowchart in Fig. 1. For consistency, allowable range of each variable in the problem is normalized to  $[0, 1]$  using its bounds. The reliability and efficiency of TS-QN and TS-NM are tested and compared with GA-QN and GA-NM for several multi-modal functions, which were used by Chelouah and Siarry (2000). The maximum size of the selected functions is 20 since typical phase equilibrium problems have less than 20 decision variables. The selected functions are briefly described below and details of the global minimum are summarized in Table 2.

- 1) Goldstein and Price (GP<sub>2</sub>)

$$\begin{aligned} GP_2 = & [1 + (x_1 + x_2 + 1)^2 \\ & \times (19 - 14x_1 + 3x_1^2 - 14x_2 + 6x_1x_2 + 3x_2^2)] \\ & \times [30 + (2x_1 - 3x_2)^2 \\ & \times (18 - 32x_1 + 12x_1^2 + 48x_2 - 36x_1x_2 + 27x_2^2)] \end{aligned} \quad (5)$$

where the search domain is  $-2 \leq x_1, x_2 \leq 2$ .

- 2) Easom (ES<sub>2</sub>)

$$ES_2 = -\cos(x_1)\cos(x_2)\exp[-((x_1 - \pi)^2 + (x_2 - \pi)^2)] \quad (6)$$

where search domain is  $-100 \leq x_1, x_2 \leq 100$ .

- 3) Shubert (SH<sub>2</sub>)

$$\begin{aligned} SH_2 = & \left\{ \sum_{j=1}^5 j \cos[(j+1)x_1 + j] \right\} \\ & \times \left\{ \sum_{j=1}^5 j \cos[(j+1)x_2 + j] \right\} \end{aligned} \quad (7)$$

where search domain is  $-10 \leq x_1, x_2 \leq 10$ .

- 4) Hartmann (H<sub>3</sub>)

$$H_3 = -\sum_{j=1}^4 c_j \exp \left[ -\sum_{i=1}^3 a_{ji}(x_i - p_{ji})^2 \right] \quad (8)$$

where search domain is  $0 \leq x_1, x_2, x_3 \leq 1$  and constants are given in Table 3.

Table 2  
Global minimum of selected functions

Function	N	Global minimum	Remarks
GP <sub>2</sub>	2	3 at $x = \{0, -1\}$	Four local minima
ES <sub>2</sub>	2	−1 at $x = \{\pi, \pi\}$	Several local minima
SH <sub>2</sub>	2	−186.7309, at $x = \{0.0217, -0.9527\}$	18 global minima; 760 local minima
H <sub>3</sub>	3	−3.86278 at $x = \{0.114614, 0.555649, 0.852547\}$	Four local minima
R <sub>N</sub>	2, 5, 10, 20	0 at $x = \{1, \dots, 1\}$	Several local minima
Z <sub>N</sub>	2, 5, 10, 20	0 at $x = \{0, \dots, 0\}$	Several local minima

##### 5) Rosenbrock (R<sub>2</sub>, R<sub>5</sub>, R<sub>10</sub> and R<sub>20</sub>)

$$R_N = \sum_{j=1}^{N-1} [100(x_j^2 - x_{j+1})^2 + (x_j - 1)^2] \quad (9)$$

where search domain is  $-5 \leq x_j \leq 10$  for  $j = 1, \dots, N$ .

##### 6) Zakharov (Z<sub>2</sub>, Z<sub>5</sub>, Z<sub>10</sub> and Z<sub>20</sub>)

$$Z_N = \left( \sum_{j=1}^N x_j^2 \right) + \left( \sum_{j=1}^N 0.5jx_j \right)^2 + \left( \sum_{j=1}^N 0.5jx_j \right)^4 \quad (10)$$

where search domain is  $-5 \leq x_j \leq 10$  for  $j = 1, \dots, N$ .

The reliability and efficiency of the methods will be evaluated based on the following criteria of Chelouah and Siarry (2000): (a) success rate of finding the global minimum; (b) average number of objective function evaluations and (c) average deviation of the best objective function value in each run from the true minimum. The average number of objective function evaluations and average deviation are evaluated based on successful runs only. The average deviation is defined as the average of  $|OF_{Cal} - OF_{Opt}|$  where  $OF_{Cal}$  is the objective function value at the best point found in each successful run and  $OF_{Opt}$  is the known global minimum. The minimization is considered successful if

$$|OF_{Cal} - OF_{Opt}| < (10^{-4}OF_{Opt} + 10^{-6}) \quad (11)$$

is fulfilled. Note that the second term on the right hand side is to ensure that the criterion can be satisfied even when  $OF_{Opt}$  is zero or extremely small.

Table 3  
Constants in the Hartmann function

j	a <sub>j1</sub>	a <sub>j2</sub>	a <sub>j3</sub>	c <sub>j</sub>	p <sub>j1</sub>	p <sub>j2</sub>	p <sub>j3</sub>
1	3.0	10.0	30.0	1.0	0.3689	0.1170	0.2673
2	0.1	10.0	35.0	1.2	0.4699	0.4387	0.7470
3	3.0	10.0	30.0	3.0	0.1091	0.8732	0.5547
4	0.1	10.0	35.0	3.2	0.0381	0.5743	0.8828

## 5. Phase equilibrium problems

TS was applied and its performance is compared with GA for the phase equilibrium examples in Table 5. The objective function for these problems is the dimensionless Gibbs free energy,  $G/RT$  given by one of the following equations.

- 1) For VLE or VLLE with vapor and liquid phases described by different thermodynamic models:

$$\frac{G}{RT} = \sum_{\substack{k \in np \\ \text{(Liquid phases only)}}} \sum_{i=1}^{nc} n_i^k [\ln(x_i^k \gamma_i^k P_i^{\text{sat}})] + \sum_{i=1}^{nc} n_i^V [\ln(y_i \hat{\phi}_i^V P)] \quad (12)$$

where the superscript k and V refer to liquid phase and vapor phase, respectively. The first summation in the first term is for all liquid phases only. The first term in Equation (12) is valid only for activity coefficient models.

- 2) For VLE with both phases described by the same thermodynamic model:

$$\frac{G}{RT} = \sum_{\substack{k \in np \\ \text{(Liquid phases only)}}} \sum_{i=1}^{nc} n_i^k [\ln(x_i^k \hat{\phi}_i^k)] + \sum_{i=1}^{nc} n_i^V [\ln(y_i \hat{\phi}_i^V)] \quad (13)$$

- 3) If only liquid phases exist (such as LLE), Equation (12) can be simplified by ignoring  $P_i^{\text{sat}}$  (which remains unchanged in a particular example) and by eliminating the second term for vapor phase, to

$$\frac{G}{RT} = \sum_{k=1}^{np} \sum_{i=1}^{nc} n_i^k [\ln(x_i^k \gamma_i^k)] \quad (14)$$

In the above equations, the decision variables are number of moles of component i in phase k,  $n_i^k$  (including vapor phase). Other quantities are: np is the number of phases expected at equilibrium, nc is the number components in the system,  $x_i^k = n_i^k/n^k$  (where  $n^k$  is the total number of moles in phase k),  $\gamma_i^k$  is the activity

coefficient of component  $i$  in phase  $k$ ,  $P_i^{\text{sat}}$  is the saturated vapor pressure of component  $i$ ,  $y_i = n_i^V/n^V$ ,  $\phi_i^k$  is the partial fugacity coefficient of component  $i$  in phase  $k$  and  $P$  is the system pressure. More details on the above equations can be found in Rangaiah (2001).

Bounds on the variables are:

$$0 \leq n_i^k \leq z_i F \quad i = 1, 2, \dots, nc \quad (15)$$

where  $z_i$  and  $F$  are, respectively, the mole fraction of component  $i$  and total moles in the feed. Constraints in the phase equilibrium problems are the component balances given by

$$\sum_{k=1}^{np} n_i^k = z_i F \quad i = 1, 2, \dots, nc \quad (16)$$

The Gibbs free energy minimization problem can be simplified by introducing new variables  $\beta_i^k$  (for  $i = 1, 2, \dots, nc$ ;  $k = 1, 2, \dots, np-1$ ) instead of mole numbers  $n_i^k$  (for  $i = 1, 2, \dots, nc$ ;  $k = 1, 2, \dots, np$ ) as the decision variables. The new variables,  $\beta_i^k$ , each of which is bounded by 0 and 1, are related to  $n_i^k$  by:

$$n_i^1 = \beta_i^1 z_i F \quad i = 1, 2, \dots, nc \quad (17)$$

$$n_i^k = \beta_i^k \left( z_i F - \sum_{j=1}^{k-1} n_i^j \right) \quad (18)$$

$$i = 1, 2, \dots, nc; \quad k = 2, \dots, np-1$$

$$n_i^{np} = \left( z_i F - \sum_{j=1}^{np-1} n_i^j \right) \quad i = 1, 2, \dots, nc \quad (19)$$

Thus the equality constraints in equation (16), which are satisfied due to equations (17)–(19), need not be considered during minimization, and the number of decision variables is reduced to  $nc(np-1)$ . The bounds on decision variables are set as:

$$1 \times 10^{-5} \leq \beta_i^k \leq 1.0 \quad i = 1, 2, \dots, nc \quad (20)$$

The lower bound of  $1 \times 10^{-15}$  instead of 0 is employed to avoid numerical difficulties in evaluating Gibbs free energy when moles of a component in a phase are zero. The simplified problem can now be solved using an unconstrained optimization method.

## 6. Results and discussion

### 6.1. Parameters tuning

Initially, TS-QN and functions: GP<sub>2</sub>, ES<sub>2</sub>, SH<sub>2</sub>, R<sub>5</sub>, R<sub>10</sub> and R<sub>20</sub> are used for tuning the following ECTS parameters: size of tabu and promising lists ( $N_t$  and  $N_p$ ), tabu and promising ball radii ( $\varepsilon_t$  and  $\varepsilon_p$ ), initial population size ( $N_s$ ), half-length of the most external hyperrectangle ( $h_n$ ), maximum number of iterations

(Iter<sub>Max</sub>) and maximum number of successive iterations without detection of a promising area (Sc<sub>Max</sub>). Tuning these parameters by simultaneously varying all of them is exhaustive but very difficult and may not be worthwhile as there is no best combination that can work perfectly for all problems. Hence, a practical approach is taken for tuning the parameters. First, nominal values of parameters are selected based on the work of Chelouah and Siarry (2000). Some parameters are grouped into sets based on their characteristics (i.e.  $N_t$  and  $N_p$  are considered as one set, and  $\varepsilon_t$  and  $\varepsilon_p$  as another set). The tuning was performed by varying one parameter (or set) while the rest are fixed. Based on the results, the following values of ECTS parameters are selected to achieve high reliability without requiring excessive number of function evaluations (Teh, 2002):  $N_t = 10$ ;  $N_p = 10$ ;  $\varepsilon_t = 0.01$ ;  $\varepsilon_p = 0.01$ ;  $N_s = 20$  N;  $h_n = 0.50$ ; Iter<sub>Max</sub> = 50 N; Sc<sub>Max</sub> = 6 N; and stopping criterion for TS-diversification is Sc<sub>Max</sub> or Iter<sub>Max</sub>.

For phase equilibrium calculations, Examples 11a (two variables), 17 (six variables) and 18 (six variables) in Table 5, which are found to be difficult in Teh and Rangaiah (2002), are selected for tuning TS parameters for phase equilibrium calculations. Initial trials have shown that the parameter, Sc<sub>Max</sub> may cause premature convergence of TS in some examples. Hence, this parameter was not included in the TS program for phase equilibrium calculations. As before, tests were conducted on the three selected examples by varying one parameter (or set) in TS (Teh, 2002). Suitable values of parameters were the same as those obtained for mathematical functions except  $\varepsilon_t = \varepsilon_p = 0.02$  and Iter<sub>Max</sub> = 100 N (instead of 0.01 and 50 N, respectively). This may be because of few but nearly comparable minima in phase equilibrium problems.

The GA program used in the present study is the same as that used by Lee (2000). The tuning of GA parameters for phase equilibrium calculations was done by Lee (2000) by considering the phase equilibrium of *n*-butyl acetate and water (Example 11a in Table 5b). After choosing a particular GA variant (with floating-point coding, stochastic universal sampling selection, modified arithmetic crossover and non-uniform mutation) and 100 generations, he varied population size (100, 200, 300), crossover probability (0.5–0.9) and mutation probability (0.001–0.5). From the results obtained, Lee (2000) identified the following optimal parameter values for high reliability and efficiency: number of generations = 100, population size = 200, crossover probability = 0.8 and mutation probability = 0.1. In the present work, GA parameters were tuned for mathematical functions by considering GP<sub>2</sub>, ES<sub>2</sub>, SH<sub>2</sub>, R<sub>5</sub>, R<sub>10</sub> and R<sub>20</sub>, and varying one parameter with the rest fixed at nominal values. The optimal parameters of Lee (2000) were found to be appropriate for the mathematical functions as well.



### 6.2. Performance of TS on mathematical functions

All the selected mathematical functions are solved 100 times (each time with a different random number seed thus changing the search for global optimum) by both TS-QN, TS-NM, GA-QN and GA-NM. The results obtained are summarized in Table 4 along with those of Chelouah and Siarry (2000) by ECTS in which TS was implemented for both diversification and intensification. The results in Table 4 show that the reliability of TS-QN and TS-NM is comparable to that of GA-QN and GA-NM, respectively, except in some examples for which TS is slightly less reliable. Among these four methods, the two with QN have the same or higher success rate, require lower number of function evaluations, and give more accurate solution than the other two with NM. These are due to differences in the strategies of QN (a gradient search method) and NM (a direct search method). Although reliability of TS-QN and GA-QN is high and good, they do not achieve the reliability of ECTS reported by Chelouah and Siarry (2000). Number of function evaluations for TS-QN is less than that for ECTS for some problems whereas it is the other way for the remaining problems. As shown by the extremely small average deviations for all functions tested, results obtained by TS-QN and GA-QN are more accurate than those by ECTS, perhaps due to the use of TS for intensification in ECTS. TS-QN is more efficient than GA-QN with the former requiring significantly less number of function evaluations.

### 6.3. Performance of TS for phase equilibrium calculations

To study the reliability of TS and GA, each selected phase equilibrium problem in Table 5 was solved 25 times, each time with a different random number seed. Often, number of phases at equilibrium is unknown although this can be found by bubble- and dew-point calculations in the case of VLE. Hence, each of the examples in Table 5 are solved (a) assuming correct number of phases (Tables 6 and 8) and (b) assuming an extra liquid phase wherever possible, i.e. VLE Examples 4–10 and LLE Examples 13–15 (Table 7) and VLLE Examples 19 and 20 (Table 9). The optimal solutions obtained are summarized in the Appendix (Tables A1 and A2) and they were the same as those reported in Teh and Rangaiah (2002). The local solutions found are given in Table A3. The average number of function evaluations and average computation time for solving an example by TS-QN, TS-NM, GA-QN and GA-NM in all 25 runs, are summarized in Tables 6–9. In Tables 6–9, success rate of a method is 100% unless otherwise stated; computation time is for executing the respective program on a Pentium II/300 MHz computer excluding compilation time.

Table 4

Comparison of results obtained by TS-QN, TS-NM, GA-QN, GA-NM, and ECTS for mathematical functions

	Success Rate (%)				Average Function Evaluations				Average Deviation						
	TS-QN	TS-NM	GA-QN	GA-NM	ECTS	TS-QN	TS-NM	GA-QN	GA-NM	ECTS	TS-QN	TS-NM	GA-QN	GA-NM	ECTS
GP <sub>2</sub>	99	99	100	100	100	301	355	20013	20130	231	7.61e-10	7.99e-07	1.19e-11	2.54e-09	0.0020
ES <sub>2</sub>	85	85	100	100	100	433	463	20007	20141	1284	1.07e-06	1.80e-06	1.07e-06	1.07e-06	0.01
SH <sub>2</sub>	92	92	100	100	100	355	680	20007	21072	370	8.73e-06	1.49e-05	8.83e-06	2.35e-05	0.001
R <sub>2</sub>	100	100	100	100	100	475	550	20038	20100	480	2.19e-08	6.92e-07	1.85e-11	7.40e-09	0.02
Z <sub>2</sub>	100	100	100	100	100	343	404	20003	20120	195	1.76e-08	7.12e-07	4.24e-11	5.25e-10	2e-7
H <sub>3</sub>	100	100	100	100	100	386	456	20009	20141	548	2.50e-06	1.89e-06	2.57e-06	2.57e-06	0.09
R <sub>5</sub>	79	77	100	100	100	2081	2493	20197	20711	2142	3.09e-10	1.02e-06	4.01e-12	9.00e-09	0.08
Z <sub>5</sub>	100	100	100	100	100	1294	1471	20077	20303	2254	3.91e-09	8.26e-07	2.10e-10	8.90e-09	4e-6
R <sub>10</sub>	78	48	94	85	85	8541	13890	21977	27499	15720	3.13e-10	4.20e-05	4.53e-12	5.80e-08	0.02
Z <sub>10</sub>	100	100	100	100	100	8473	8900	20246	21575	4630	4.77e-10	2.30e-06	8.49e-11	9.78e-08	2e-7
R <sub>20</sub>	75	0	89	0	n.a.	22074	–	25378	–	n.a.	6.83e-10	–	7.06e-12	–	n.a.
Z <sub>20</sub>	100	100	100	0	n.a.	19157	21039	21170	–	n.a.	3.45e-10	2.43e-05	9.88e-11	–	n.a.

Note: Results of ECTS are taken from Chelouah and Siarry (2000). But, results for R<sub>20</sub> and Z<sub>20</sub> are not available in this reference.

Table 5  
Selected examples for VLE/LLE/VLLE

Number	Mixture	Feed	Pressure and temperature	Model	Reference
<i>(a) Selected examples for VLE</i>					
1	Methane (1), propane (2)	$F = 1.0 \text{ mol}$ , $z_i = \{0.68, 0.32\}$	100 bar, 277.6 K	SRK	Hua et al. (1998)
2	Carbon dioxide (1), methane (2)	$F = 1.0 \text{ mol}$ , $z_i = \{0.20, 0.80\}$	60.8 bar, 220 K	PR	Hua et al. (1998)
3	Hydrogen sulfide (1), methane (2)	$F = 1.0 \text{ mol}$ , $z_i = \{0.0187, 0.9813\}$	40.53 bar, 190 K	SRK	Hua et al. (1998)
4	Nitrogen (1), methane (2), ethane (3)	$F = 1.0 \text{ mol}$ , $z_i = \{0.15, 0.30, 0.55\}$	76 bar, 270 K	PR	Hua et al. (1998)
5	Methane (1), carbon dioxide (2), hydrogen sulfide (3)	$F = 1.0 \text{ mol}$ , $z_i = \{0.4989, 0.0988, 0.4023\}$	48.6 bar, 227.55 K	PR	Sun and Seider (1995)
6a	Benzene (1), acetonitrile (2), water (3)	$F = 1.0036 \text{ mol}$ , $z_i = \{0.34359, 0.30923, 0.34718\}$	0.1 atm, 300 K	Ideal (V) NRTL (L)	Castillo and Grossmann (1981)
6b	Benzene (1), acetonitrile (2), water (3)	$F = 1.0036 \text{ mol}$ , $z_i = \{0.34359, 0.30923, 0.34718\}$	0.1 atm, 300 K	Ideal (V) UNIFAC (L)	–
7	Nitrogen (1), argon (2), oxygen (3)	$F = 9.38529 \text{ mol}$ , $z_i = \{0.78112, 0.00930, 0.20958\}$	607.95 kPa, 100.79 K	PR	PRO/II (1993)
8	Methane (1), ethane (2), propane (3), <i>i</i> -butane (4), <i>n</i> -butane (5), <i>i</i> -pentane (6), <i>n</i> -pentane (7), <i>n</i> -hexane (8), <i>n</i> -pentadecane (9)	$F = 0.96890 \text{ mol}$ , $z_i = \{0.61400, 0.10259, 0.04985, 0.00898, 0.02116, 0.00722, 0.01187, 0.01435, 0.16998\}$	19.84 atm, 314 K	SRK	Castillo and Grossmann (1981)
9	Mixture of ten hydrocarbons (see Teh and Rangaiah, 2002 for details)	$F = 35.108 \text{ mol}$	3998.95 kPa, 287.48 K	PR	Hyprotech (1998)
10	Mixture of 11 chemicals (see Teh and Rangaiah, 2002 for details)	$F = 10.0 \text{ mol}$	101.325 kPa, 303.15 K	Ideal (V) NRTL (L)	Hyprotech (1998)
<i>(b) Selected examples for LLE</i>					
11a	<i>n</i> -Butyl-acetate (1), water (2)	$F = 1.0 \text{ mol}$ , $z_i = \{0.50, 0.50\}$	1.0 atm, 298 K	NRTL	Heidemann and Mandhane (1973)
11b	<i>n</i> -Butyl-acetate (1), water (2)	$F = 1.0 \text{ mol}$ , $z_i = \{0.50, 0.50\}$	1.0 atm, 298 K	UNIFAC	McDonald and Floudas (1997)
12	Toluene (1), water (2)	$F = 1.0 \text{ mol}$ , $z_i = \{0.50, 0.50\}$	1.0 atm, 298 K	NRTL	Castillo and Grossmann (1981)
13	Furfural (1), 2,2,4-trimethyl pentane (2), cyclohexane (3)	$F = 1.0 \text{ mol}$ , $z_i = \{0.10, 0.10, 0.80\}$	1.0 atm, 298 K	UNIQUAC	Prausnitz, Anderson, Grens, Eckert, Hsieh & O'Connell, (1980)
14	Benzene (1), acetonitrile (2), water (3)	$F = 1.0036 \text{ mols}$ , $z_i = \{0.34359, 0.30923, 0.34718\}$	1.0 atm, 333 K	NRTL	Castillo and Grossmann (1981)
15	Toluene (1), water (2), aniline (3)	$F = 0.9987 \text{ mol}$ , $z_i = \{0.29989, 0.20006, 0.50005\}$	1.0 atm, 298 K	NRTL	Castillo and Grossmann (1981)
<i>(c) Selected examples for VLLE</i>					
16	Benzene (1), acetonitrile (2), water (3)	$F = 1.0036 \text{ mol}$ , $z_i = \{0.34359, 0.30923, 0.34718\}$	0.769 atm, 333 K	Ideal (V) NRTL (L)	Castillo and Grossmann (1981)
17	Methanol (1), methyl acetate (2), water (3)	$F = 1.0 \text{ mol}$ , $z_i = \{0.15, 0.45, 0.40\}$	0.965 atm, 325 K	Ideal (V) UNIFAC (L)	McDonald and Floudas (1997)
18	Ethanol (1), benzene (2), water (3)	$F = 1.0 \text{ mol}$ , $z_i = \{0.20, 0.35, 0.45\}$	1.0 atm, 338 K	Ideal (V) UNIFAC (L)	Prokopakis and Seider (1983)
19	Ethylene glycol (1), dodecanol (2), nitromethane (3), water (4)	$F = 1.0 \text{ mol}$ , $z_i = \{0.30, 0.10, 0.50, 0.10\}$	0.43 atm, 350 K	Ideal (V) UNIFAC (L)	McDonald and Floudas (1997)
20	2,2,4-Trimethyl pentane (1), furfural (2), cyclohexane (3), benzene (4)	$F = 1.0 \text{ mol}$ , $z_i = \{0.10, 0.30, 0.40, 0.20\}$	10.0 kPa, 288 K	Virial (V), UNIQUAC (L)	Wu and Bishnoi (1986)

Table 6

Average number of function evaluations and average computation time for VLE and LLE examples (assuming correct number of phases)

Number	Number of function evaluations (computation time in seconds)			
	TS-QN	TS-NM	GA-QN	GA-NM
1	1412 (0.13)	2710 (0.25)	20 017 (1.39)	20 677 (1.52)
2	1349 (0.14)	1498 (0.15)	20 018 (1.59)	20 204 (1.62)
3	1187 (0.13)	1349 (0.17)	20 024 (1.51) <sup>a</sup>	20 176 (1.56) <sup>a</sup>
4	1777 (0.21)	3407 (0.38)	20 238 (2.09)	21 308 (2.24)
5	1511 (0.18)	5499 (0.56)	20 027 (2.06)	23 213 (2.43)
6a	1616 (0.14)	2155 (0.17)	20 089 (1.14)	21 064 (1.38)
6b	1648 (0.17)	1782 (0.14)	20 088 (1.41)	20 189 (1.57)
7	1894 (0.29)	2474 (0.34)	20 054 (2.68)	20 609 (2.71)
8	10 040 (3.84)	11 765 (3.74)	20 515 (4.85)	22 856 (5.99)
9	Trivial	Trivial	Trivial	Trivial
10	12 631 (3.46)	18 632 (3.77)	21 579 (3.95)	22 455 (4.01)
11a	1425 (0.09)	1528 (0.07)	20 018 (1.04)	20 160 (1.05)
11b	1369 (0.13)	1441 (0.11)	20 024 (1.36)	20 138 (1.44)
12	1367 (0.07)	1468 (0.11)	20 026 (1.02)	20 154 (1.05)
13	1571 (0.13)	1451 (0.33) <sup>b</sup>	20 028 (1.50) <sup>c</sup>	20 885 (1.69) <sup>c</sup>
14	1557 (0.12)	2771 (0.19)	20 033 (1.30)	20 917 (1.50)
15	1719 (0.12)	1877 (0.12)	20 069 (1.20)	20 241 (1.77)

Note that numbers 1–10 are VLE examples while numbers 11–15 are LLE examples.

<sup>a</sup> Success rate = 80%.<sup>b</sup> Success rate = 4%.<sup>c</sup> Success rate = 76%.

Table 7

Average number of function evaluations and average computation time for VLE and LLE examples (assuming an extra liquid phase)

Number	Number of function evaluations (computation time in seconds)			
	TS-QN	TS-NM	GA-QN	GA-NM
4	5937 (1.14)	8878 (1.36)	20 472 (2.58)	22 963 (2.86)
5	5477 (1.09)	11 169 (1.71)	20 104 (2.59)	25 549 (3.41)
6a	5570 (0.73)	7104 (0.81)	20 433 (1.52)	21 237 (1.62)
6b	5920 (0.93)	6094 (0.92)	20 441 (2.01)	20 469 (2.04)
7	6311 (1.48)	8737 (1.83)	20 212 (3.31)	22 484 (3.94)
8	18 181 (6.44)	18 315 (6.62)	22 210 (7.84)	22 389 (7.92)
9	Trivial	Trivial	Trivial	Trivial
10	18 823 (4.93)	18 424 (4.67)	25 085 (6.24)	22 310 (6.08)
13	5297 (0.78)	5091 (0.70) <sup>a</sup>	20 167 (2.00)	21 648 (2.21)
14	5506 (0.73)	7256 (0.85)	20 164 (1.66)	20 631 (1.80)
15	5526 (0.73)	6019 (0.76)	20 147 (1.54)	20 496 (1.60)

Note that numbers 4–10 are VLE examples while numbers 13–15 are LLE examples.

<sup>a</sup> Success rate = 0%.

### 6.3.1. Two-phase equilibrium (VLE and LLE) calculations

For two-phase equilibrium calculations with correct number of phases or an extra liquid phase, results in Tables 6 and 7 show that TS-QN is more efficient and reliable than TS-NM. For Example 13, success rate of

TS-NM is very low i.e. 4 and 0% with correct number of phases and an extra phase respectively. Since the diversification is by the same algorithm in both TS-QN and TS-NM, this low success rate is due to the use of NM instead of QN. Success rate of NM did not improve even with a lower tolerance of  $10^{-13}$  and  $10^{-14}$ , instead of the default tolerance of  $10^{-12}$ . Fig. 4 shows a plot of G/RT versus average absolute deviation,

$$AAD = \frac{1}{nc \times np} \sum_{k=1}^{np} \sum_{i=1}^{nc} |n_i^k - n_i^{k(*)}| \quad (21)$$

for all final solutions obtained by TS-NM, which are really near-global solutions with less than 1% discrepancy in G/RT from the global minimum. Discrepancy in G/RT is relatively more for the case of correct number of phases whereas AAD is relatively large for the case of an extra phase. In any case, near-global solutions are not acceptable in phase equilibrium calculations since very accurate results are required.

Reliability of GA-QN and GA-NM for VLE and LLE calculations is comparable, with the former slightly more efficient than the latter. When Example 13 was solved assuming correct number of phases, both GA-QN and GA-NM had a success rate of only 76%. Interestingly, they both found the global minimum with 100% success rate when an extra liquid phase was included in the calculations. This may be due to the effect of additional variables on the shape of the objective function. Reliability of both TS-QN and GA-QN is similar except that the former has 100% success rate compared with 80% success rate of the latter for Example 3. For Example 9, both these methods converged to trivial solutions in all 25 runs irrespective of number of phases assumed. The difficulty in solving this example by Gibbs free energy minimization was already discussed in Teh and Rangaiah (2002).

Results in Tables 6 and 7 show that for VLE and LLE, number of function evaluations and the computational time can be reduced by using TS, instead of GA. It is probably because GA involves thorough search on the entire solution space. In contrast, TS is capable of avoiding the previously visited solutions and hence more efficient in searching. Reduction in the number of function evaluations by using TS instead of GA, depends on the problem size and number of phases assumed. The reduction for small problems (Examples 1–7, 11–15) is by a factor of about 4–17 (when the correct number of phases is assumed) to nearly 2–4 (when an extra phase is assumed). However, the reduction is smaller (20–50%) in Examples 8 and 10 involving nine to 22 decision variables. Computational efficiency of GA may be improved by reducing the number generations and/or population size; but this may lower its reliability.

Table 8

Average number of function evaluations and average computation time for VLLE examples (assuming correct number of phases)

Number	Number of function evaluations (computation time in seconds)			
	TS-QN	TS-NM	GA-QN	GA-NM
16	5615 (0.74)	6410 (0.72)	20 212 (1.50)	20 976 (1.64)
17	5627 (0.95)	6244 (0.92) <sup>a</sup>	20 254 (2.17) <sup>b</sup>	20 714 (2.29) <sup>b</sup>
18	5479 (0.88) <sup>c</sup>	6192 (0.91) <sup>c</sup>	20 262 (2.00)	20 719 (2.28)
19	9213 (2.43)	10 787 (2.47)	20 302 (3.33)	21 025 (4.71)
20	9314 (5.26)	11 858 (5.91) <sup>d</sup>	20 398 (9.14)	22 581 (10.76) <sup>d</sup>

<sup>a</sup> Success rate = 92%.

<sup>b</sup> Success rate = 84%.

<sup>c</sup> Success rate = 80%.

<sup>d</sup> Success rate = 0%.

Table 9

Average number of function evaluations and average computation time for VLLE examples (assuming an extra liquid phase)

Number	Number of function evaluations (computation time in seconds)			
	TS-QN	TS-NM	GA-QN	GA-NM
19	13 330 (4.64)	15 123 (5.01)	20 675 (5.13)	22 007 (5.18)
20	13 549 (8.06)	18 590 (9.92) <sup>a</sup>	20 746 (10.92)	24 070 (12.95) <sup>a</sup>

<sup>a</sup> Success rate = 0%

### 6.3.2. Three-phase equilibrium (VLLE) calculations

Performance of all methods for VLLE examples is summarized in Tables 8 and 9 for the case of correct number of phases and an extra liquid phase, respectively. Both TS and GA when followed by QN, have 100% success rate in four out of the five examples tried. TS-QN converged to the local minimum (VLE solution) in five out of 25 trials on Example 18 while GA-QN converged to the local minimum (VLE solution) in four out of 25 trials on Example 17. Hence, the reliability of TS and GA for diversification (i.e. exploration) seems to be comparable for VLLE calculations. For VLLE too, TS-QN requires less number of function evaluations and computational time compared to GA-QN. The reduction is by a factor of about 4 (for Examples 16–18 with three components) to 2 (for Examples 19 and 20 with four components) when the correct number of phases is assumed. The reduction in computational effort is less when an extra liquid phase is included.

Similar to two-phase equilibrium calculations, NM for intensification is less successful for VLLE too. In particular, both TS-NM and GA-NM failed completely to find the global minimum for Example 20 irrespective of the number of phases assumed. Final results by TS-NM, although differed from one run to another run, were close to the global minimum. The converged solutions of TS-NM in 25 trials are shown in Fig. 5 as

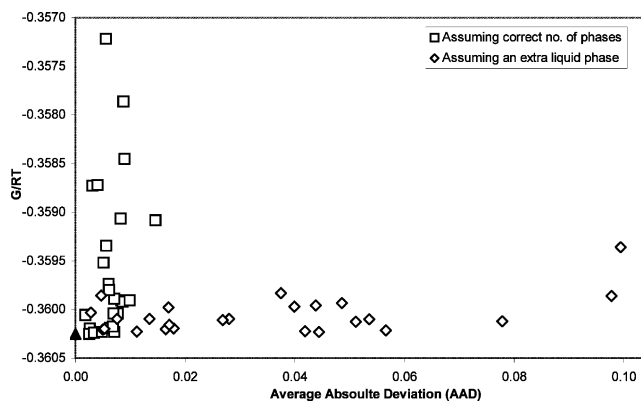


Fig. 4. Converged solutions obtained by TS-NM in 25 runs for Example 13 assuming correct number of phases and an extra liquid phase. The global minimum ( $\blacktriangle$ ) is  $-0.360253$  at  $AAD = 0$ .

a plot of  $G/RT$  versus  $AAD$  (Equation (21)); discrepancy in  $G/RT$  and  $AAD$  are comparable irrespective of the number of phases assumed.

### 6.3.3. Comparison of TS and GA with deterministic methods

Computational times for solving phase equilibrium problems by TS-QN and GA-QN are compared with two reported methods: GLOPEQ for free energy minimization (McDonald & Floudas, 1997) and enhanced interval analysis for phase stability (Hua et al., 1998) in Table 10. CPU times in different works are not easy to compare because of different computer systems used. According to the performance database at <http://www.netlib.org>, MFlops (million floating point operations per second) for the LINPACK benchmark program for a matrix of order 100 are 24 and 76–75, respectively, for HP9000/730 (employed by McDonald & Floudas, 1997) and Sun Ultra 1 mod. 170. The latter is the closest in the database to Sun Ultra 1/170 workstation stated by Hua et al. (1998). On the other hand, Pentium II/300 employed in the present study was found to have 16 MFlops for the LINPACK benchmark program for a matrix of order 100. Hence, the computer system used in this study is marginally slower than HP9000/730 and very slow compared to Sun Ultra 1 mod. 170. The results in Table 10 show that TS-QN is more efficient than enhanced interval analysis (Hua et al., 1998) for Examples 1–4 and GLOPEQ (McDonald & Floudas, 1997) for Examples 11a, 11b, 17 and 19. The phase equilibrium results obtained in the present study, are exactly the same as those obtained by McDonald and Floudas (1997) for Examples 11a, 11b, 17 and 19; but they are slightly different from those in Hua et al. (1998) (less than 5% difference in mole fractions for Examples 1 and 4, and less than 10% for Examples 2 and 3), probably due to differences in the property data and

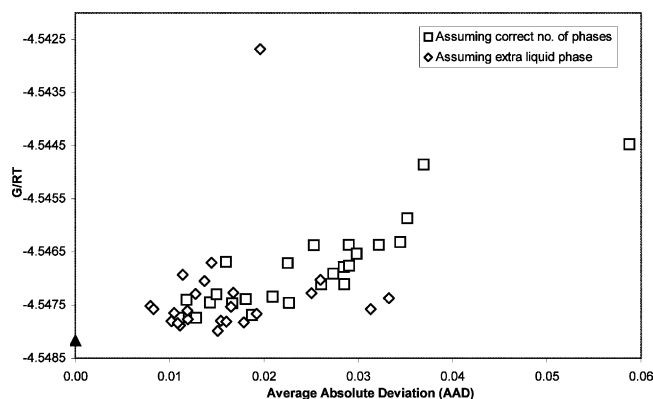


Fig. 5. Converged solutions obtained by TS-NM in 25 runs for Example 20 assuming correct number of phases and an extra liquid phase. The global minimum ( $\blacktriangle$ ) is  $-4.548170$  at  $AAD = 0$ .

mixing rule used; see Teh and Rangaiah (2002) for the effect of mixing rule in one case.

## 7. Conclusions

Application of TS for continuous optimization and phase equilibrium calculations is studied. The TS program developed is first tested on benchmark test functions and the results show that efficiency of TS-QN is comparable to that of ECTS of Chelouah and Siarry (2000); but the former is more accurate and somewhat less reliable than the latter. Parameters of TS are then tuned on three difficult examples for phase equilibrium calculations, and optimal settings are found to be the same as those for test functions except for two parameters. TS-QN, TS-NM, GA-QN and GA-NM are thoroughly tested on many VLE, LLE and VLLE

examples. Performance of TS-QN and GA-QN is better than that of TS-NM and GA-NM, respectively. The former two have comparable reliability and found the global minimum with 100% success rate except in a few examples. The results of this study show that TS-QN requires less number of objective function evaluations compared to GA-QN for mathematical functions and Gibbs free energy minimization. This finding is consistent with the results of Rajesh et al. (2000). The method used for intensification after exploration by TS or GA, plays a vital role in determining the accuracy of the results; NM is appealing as it does not require derivatives but QN is better suited for intensification. More importantly, although TS is found to be more efficient than GA, they both require further improvement to achieve 100% success rate for all examples.

## Appendix A

Table A1: Global minimum of selected VLE and LLE problems

Example number	G/RT	Moles of components in the liquid phase <sup>a</sup>
1	-1.295567	{0.525346, 0.272667}
2	-0.951211	{0.012603, 0.015619}
3	-0.453972	{0.001244, 0.017343}
4	-1.490243	{0.020937, 0.052081, 0.133576}
5	-1.859754	{0.079822, 0.064395, 0.366407}
6a	-3.412342	{3.237498e-06, 4.897779e-04, 1.585800e-02}
6b	-3.412249	{2.005020e-06, 2.874412e-04, 1.240055e-02}
7	-6.539358	{0.127964, 0.002849, 0.082418}
8	-3.134058	{0.021855, 0.014338, 0.016138, 0.004529, 0.012216, 0.005382, 0.009299, 0.012810, 0.164692}
9	-161.541565	{6.535514, 5.076586, 3.700231, 3.771703, 3.446610, 3.126375, 2.694768, 3.169396, 1.814900, 1.359007}
10	-31.640032	{0.267014, 9.452710, 4.023876e-10, 2.661724e-04, 3.321607e-05, 9.038115e-05, 9.031422e-05, 6.568039e-05, 2.147536e-04, 5.418779e-05, 9.720539}
11a	-0.020198	{0.499286, 0.344121}
11b	-0.034068	{0.499838, 0.045141}
12	-0.001272	{0.499950, 0.001279}
13	-0.360253	{0.055551, 0.099619, 0.793892}
14	-1.407816	{0.344014, 0.286511, 0.037850}
15	-0.352498	{0.299488, 0.065509, 0.498730}

<sup>a</sup>These values correspond to the sequence of components in the examples given in Table 5. Moles of components in the second phase (vapor in the case of VLE and liquid in the case of LLE) can be calculated via Equation (16).

Table 10

Comparison of TS-QN and GA-QN with the recent results in the literature

Example number and details	Computation time (s)		
	TS-QN <sup>a</sup>	GA-QN <sup>a</sup>	Literature
1 (VLE, SRK)	0.13	1.39	0.643 <sup>b</sup>
2 (VLE, PR)	0.14	1.59	0.484 <sup>b</sup>
3 (VLE, SRK)	0.13	1.51	0.290 <sup>b</sup>
4 (VLE, PR)	0.21	2.09	4.977 <sup>b</sup>
11a (LLE, NRTL)	0.09	1.04	0.23 <sup>c</sup>
11b (LLE, UNIFAC)	0.13	1.36	0.37 <sup>c</sup>
17 (VLLE, UNIFAC)	0.95	2.17	8.8 <sup>c</sup>
19 (VLLE, UNIFAC)	2.43	3.33	1493.3 <sup>c</sup>

<sup>a</sup> Present results on a Pentium II/300 computer system.

<sup>b</sup> Results for Examples 1–4 are from Hua et al. (1998), who solved them for phase stability on a Sun Ultra 1/170 workstation.

<sup>c</sup> Results for Examples 11a, 11b, 17 and 19 are from McDonald and Floudas (1997) on a HP9000/730 computer system.



Table A2: Global minimum of selected VLLE problems

Example number	G/RT	Moles of components in liquid phase 1 <sup>a</sup>	Moles of components in liquid phase 2 <sup>a</sup>
16	—	{0.239455, 0.227012,	{0.000731, 0.021692,
	1.408518	0.033652}	0.262353}
17	—	{0.082674, 0.050384,	{0.017757, 0.078012,
	1.334461	0.339536}	0.011185}
18	—	{0.152985, 0.003727,	{0.001195, 0.209603,
	1.235896	0.405565}	0.000806}
19	—	{0.081775, 0.098039,	{0.214899, 0.001873,
	3.265524	0.247696, 0.016923}	0.018687, 0.034697}
20	—	{0.084000, 0.082709,	{0.010584, 0.216783,
	4.548170	0.289625, 0.121985}	0.055744, 0.066425}

<sup>a</sup>These values correspond to the sequence of components in the examples given in Table 5. Moles of components in the vapor phase can be calculated via Equation (16).

Table A3: Known local minimum for Examples 11a and 17–20

Example number	G/RT	Moles of components in the liquid phase <sup>a</sup>
11a	—	{0.497866, 0.034530}
	0.019606	
	—	{0.00173, 0.37544}
	0.01730 <sup>b</sup>	
17	—	{0.087810, 0.054895, 0.339586}
	1.334404	
18	—	{0.099460, 0.002220, 0.337223}
	1.233294	
19	—	{0.296907, 0.099932, 0.308237,
	3.242667	0.056310}
20	—	{0.090996, 0.299208, 0.318677,
	4.539724	0.185069}

<sup>a</sup>These values correspond to the sequence of components in the examples given in Table 5. Moles of components in the second phase (liquid for Example 11a and vapor for Examples 17–20) can be calculated via Equation (16).

<sup>b</sup>Local maximum (e.g. see McDonald & Floudas, 1997).

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