EVALUATION OF DIFFERENTIAL EVOLUTION AND TABU SEARCH FOR BENCHMARK AND PHASE STABILITY PROBLEMS

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ABSTRACT

Phase stability (PS) problems play a crucial role in the simulation, design and optimization of separation process such as distillation and extraction. The problem involves the global minimization of tangent plane distance function (TPDF) known as tangent plane criterion. In this work, two promising global optimization techniques: differential evolution (DE) and tabu search (TS) have been evaluated for the first time and compared for benchmark and PS problems. A local optimization technique is used at the end of both TS and DE to improve the accuracy of the final solution. Benchmark problems involve 2 to 20 variables with a few to hundreds of local minima whereas PS problems consist of multiple components and modeled with popular thermodynamic models. The results show that DE is more reliable but computationally less efficient compared to TS for benchmark and PS problems tested.

Keywords: Phase stability problems; Tangent plane distance function; Benchmark problems; Differential evolution; Taboo search

INTRODUCTION

Phase stability (PS) problems play a significant role in the design and analysis of chemical processing operations. The problem involves determining whether a given phase with certain composition, pressure and temperature is stable or will split into multiple phases. Phase stability is often tested using the well known tangent plane criterion (Baker et al., 1982). The criterion formulates the tangent plane distance function (TPDF), defined as the vertical distance between the molar Gibbs free energy surface and the tangent plane at the given composition, as the objective function. The problem can be solved using two approaches namely: solving a system of non-linear equations for stationary points (Michelsen, 1982) and the direct minimization of TPDF function. The former approach is conventional approach where the solution obtained may be trivial or local, and is mainly dependent on the initial guess. The latter approach employs the global minimization techniques because of the high nonlinearity associated with the objective function. The presence of comparable minima (i.e., function value at a local minimum is nearly equal to that at the global minimum) in TPDF poses a computationally challenging problem to many of the global optimization methods. The complexicity in the TPDF is mainly due to the thermodynamic models that are used to describe the non ideality in the Gibbs free energy function.

A review of several works using tangent plane criterion for PS problems can be found in Rangaiah (2001). Recently, Tessier et al. (2000) implemented interval Newton technique for PS analysis. The examples are modeled by non-random two liquid (NRTL) and universal

quasi-chemical (UNIQUAC) thermodynamic models. They also proposed two enhancements for interval Newton method. The results indicate that the computational efficiency of the enhanced methods is better compared to the original one. Nichita et al. (2002) used a global optimization method namely, tunneling method for PS analysis. The problem has been formulated both in conventional approach (i.e., composition space) and in reduced variable approach. In the latter case, the number of variables does not depend on the number of components in the mixture. The results show that, the method is reliable in solving the PS problems. Balogh et al. (2003) used a modified TPDF such that the zeros of the objective function become its minima, since it is advantageous to search for minima with known zero minimum value. They employed a method namely, stochastic sampling and clustering to locate the minima of the modified TPDF. The results show that the method is able to solve small to moderate size problems in an efficient and reliable way.

However, most of the methods employed for PS problems are local in nature and relatively few stochastic global optimization techniques have been explored for these problems. Stochastic optimization techniques are as powerful as deterministic techniques and are computationally efficient than the latter. Differential evolution (DE) (Storn and Price, 1997) and tabu search (TS) (Chelouah and Siarry, 2000) are some of the most promising methods reported in the literature. Even though they have been tested for many applications in chemical engineering and other fields (Mayer et al., 2005; Lin and Miller, 2004a; Lin and Miller, 2004b; and Bingul, 2004), they have not been applied to PS problems. Also, DE and TS have not been comprehensively compared for benchmark problems. Hence, in this work, both DE and TS are first evaluated and compared for benchmark problems with 2 to 20 variables but involving a few to hundreds of local minima. The methods are then tested for PS problems involving multiple components and popular thermodynamic models. The evaluation includes both reliability and computational efficiency using practical stopping criteria.

DIFFERENTIAL EVOLUTION

DE (Storn and Price, 1997) is a population based direct search method. The algorithm implemented in this study (Figure 1) starts with specifying the optimal tuning parameters namely, amplification factor (A), crossover constant (CR), type of strategy, population size (NP) and maximum number of generations (Gen_{max}). The algorithm generates the initial population randomly using the uniform distribution to cover the entire solution space. The individuals are checked for the boundary violation to see if any individual is generated in the infeasible region. The infeasible points are replaced by generating new individuals. The objective function values of all the individuals are calculated and the best point is determined. The algorithm then performs three main steps: mutation, crossover and selection. Mutation and crossover operations are performed to diversify the search thus escaping from the local minima. The mutant vector is generated for each randomly chosen target vector $X_{i, G}$ by

$$V_{i, G+1} = X_{r1, G} + A\,(X_{r2, G} - X_{r3, G}); \qquad i = 1, 2, 3, \ldots, NP. \tag{1}$$

where r_1, r_2 and r_3 belongs to the set {1, 2, 3, …, NP} and $X_{r1, G}$, $X_{r2, G}$ and $X_{r3, G}$ represents the three random individuals chosen in the current generation, G, to produce the mutant vector for the next generation, $V_{i, G+1}$. The random numbers r_1, r_2 and r_3 should be different from the running index, i, and hence NP should be • 4 to allow mutation. A is a real value between 0 and 2 which controls the amplification of the differential variation between the two random vectors.

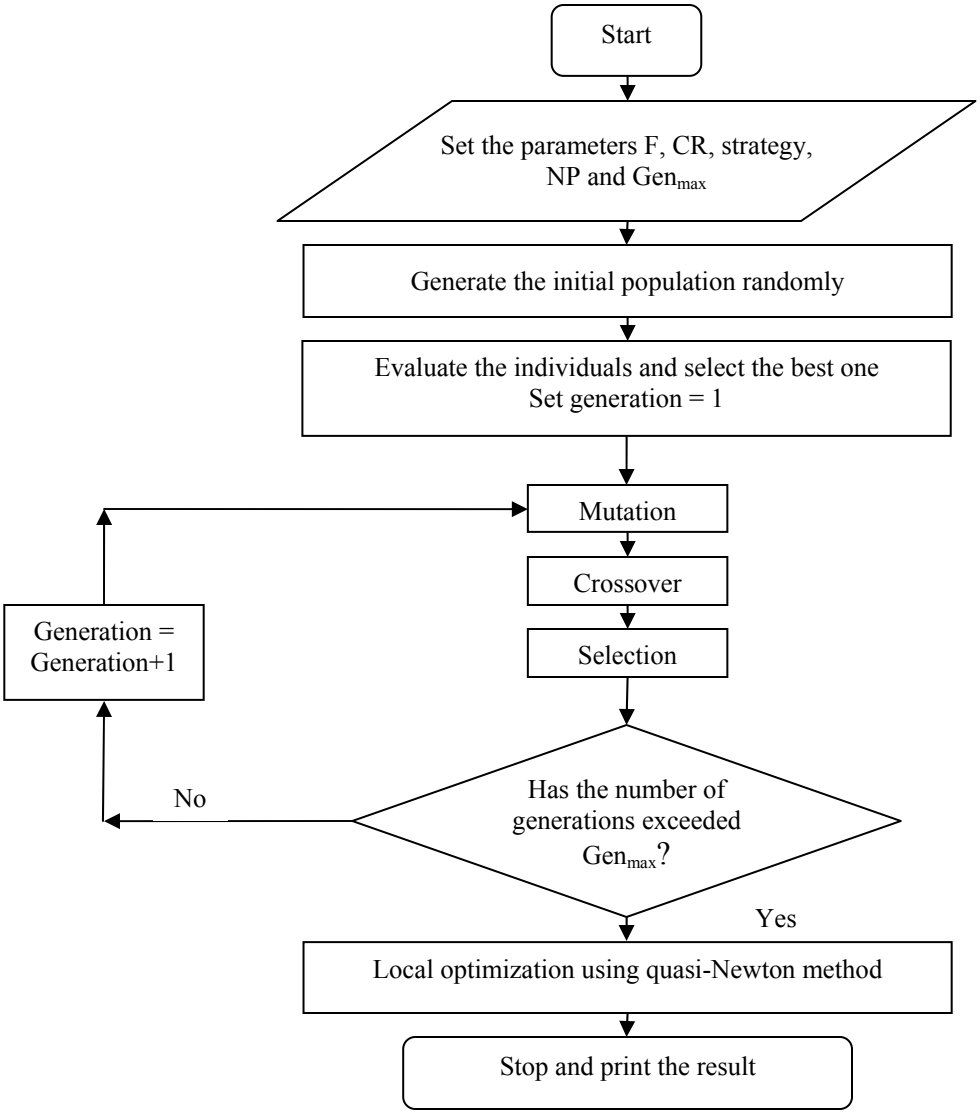


Figure 1: Flow chart of DE-QN algorithm

In the crossover step, the trial vector, $U_{i,\ G+1}$ is produced by copying some elements of the mutant vector, $V_{i,\ G+1}$ to the target vector $X_{i,\ G}$ with probability equal to CR. As illustrated in Figure 2, a random number (ran) is generated for each element of the target vector. If ran • CR, the element of mutant vector is copied else the target vector element is copied. After mutation and cross over operations, the trial vector competes with the target vector for selection into the next generation. A greedy criterion based on objective function value is used to screen the trial vector. If the trial vector has a better value compared to the target vector, it replaces the target vector allowing the best solution into further generations. The process of mutation, crossover and selection is repeated until a termination criterion such as maximum number of generations is satisfied. The algorithm then terminates providing the best point that has been explored over all the generations. The best point is further refined using a fast

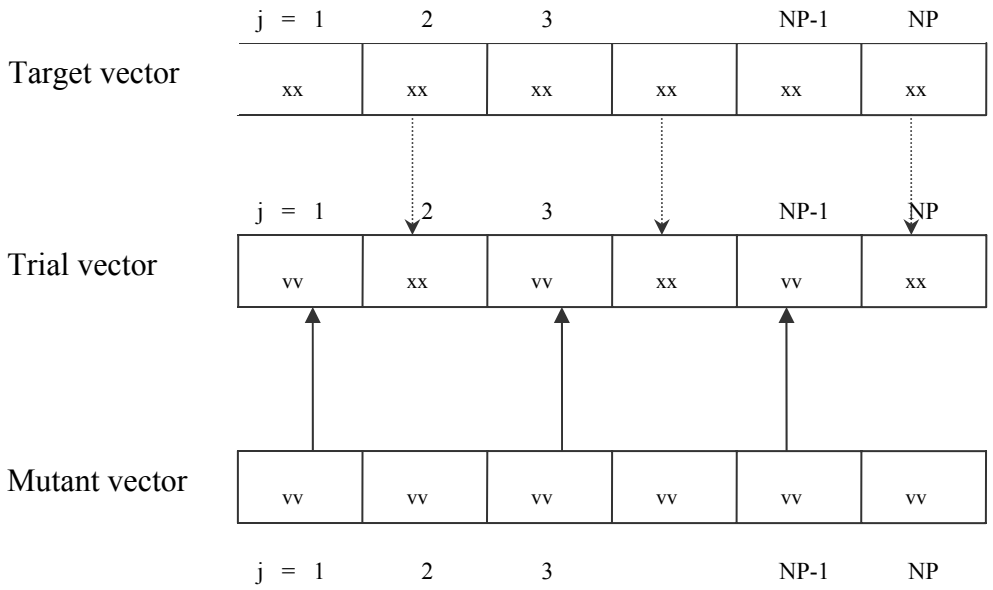


Figure 2: Schematic diagram of crossover operation; for continuous lines ran • CR and for dotted lines ran > CR.

convergent quasi-Newton method to achieve the best minimum which is declared to be the global minimum.

TABU SEARCH

TS, first developed by Glover (1989, 1990), has been widely used for combinatorial optimization (Youssef et al., 2001) but its use is very limited in continuous optimization (Hu, 1992; Chelouah and Sirarry, 2000; Teh and Rangaiah, 2003; Lin and Miller, 2004a and Lin and Miller, 2004b). TS is a meta heuristic that guides the heuristics to escape from the local minima. The main concepts of TS include diversification and identifying the most promising region. The diversification step performs exhaustive search in the entire solution space by generating solutions that are not seen before. To implement this, TS maintains tabu list (consisting of unpromising points) and promising list to avoid repeated visits to the same place in the search region which in turn improves the computational efficiency. After a specified maximum number of iterations, in-depth search known as intensification is performed from the most promising point.

The algorithm can be explained using the flowchart in Figure 3. It starts with the selection of values for the parameters: tabu list size (N_t), promising list size (N_p), tabu and promising radii ($_t$ and $_p$), length of the hyper rectangle (h_n), population size (NP), number of neighbors (N_{neigh}) and maximum number of iterations ($Iter_{max}$). The algorithm then randomly generates a population of specified size and evaluates the objective function value at each individual. The best point is filled into the promising list and the remaining will be sent to the tabu list. The best point found is selected as the current centroid (s) of the hyper rectangle, which is used to generate neighbors to explore for better points in the neighborhood. The generation of neighbors can be executed in many ways, i.e., either by using hyper circles or hyper rectangles etc. In this study, hyper rectangles have been used to generate the

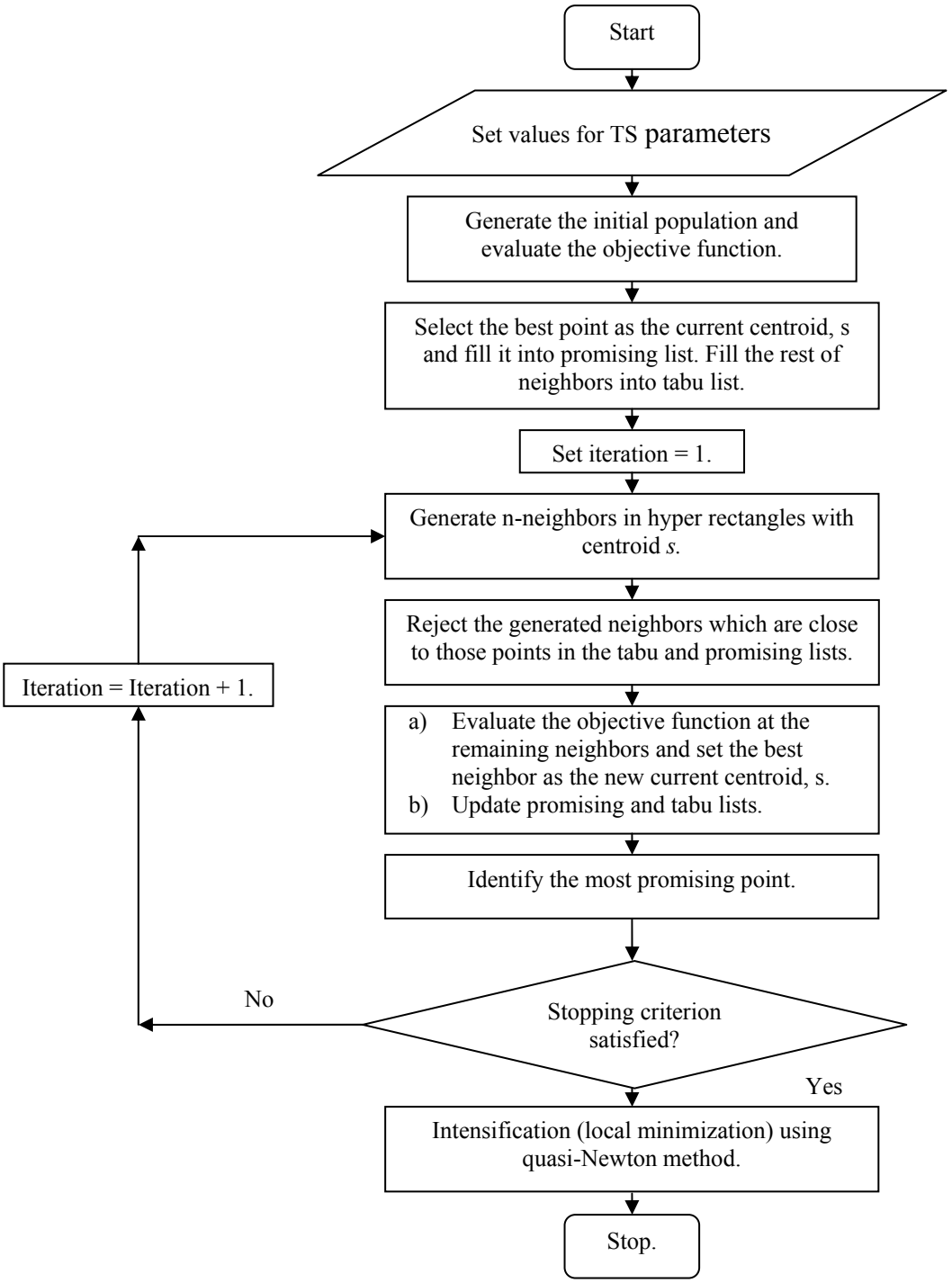


Figure 3: Flow chart of TS-QN algorithm.

neighbors. A detailed explanation about the generation of neighbors using hyper rectangles is available in Teh and Rangaiah (2003). The neighbors are then compared with the points in tabu and promising lists, and only those that are different from the latter are evaluated. The rejection of the neighbors which are nearer to the points in tabu and promising list improves the computational efficiency of TS avoiding repeated visits to the same place during the

search. The algorithm selects the best point found in the current iteration as the centroid of the hyper rectangle to generate neighbors for the next iteration. The best point in the current iteration is accepted even if it is worse than that of the previous iterations to avoid entrapment in the local minima. The process of generating neighbors is repeated and the tabu and promising lists are updated in each iteration. After a specified number of iterations, most promising area is identified and is further investigated by intensification step. Generally, a local optimization technique is used in this step; a fast convergent quasi-Newton technique is used in this study. The algorithm then terminates by declaring the final solution as the global minimum.

IMPLEMENTATION OF DE AND TS

A Matlab code for DE is taken from the website http://www.icsi.berkeley.edu/~storn/code.html and a boundary violation check is implemented in the code. For the local minimization step, an in-built subroutine from the Matlab optimization tool box namely, FMINCON is used. The objective function for DE code is written in FORTAN and simple gateway functions are used to call it from the Matlab. This is adopted as all our programs for PS are in FORTRAN. For TS, the FORTRAN code developed by Teh and Rangaiah (2003) is used; it uses the IMSL subroutine namely, DBCONF for the local minimization step. Both FMINCON and DBCONF employ the fast convergent quasi-Newton method with BFGS update for the Hessian matrix.

BENCHMARK PROBLEMS

Several benchmark problems having 2 to 20 variables and a few to several hundreds of local minima are used to evaluate both DE followed by quasi-Newton method (DE-QN) and TS followed by quasi-Newton method (TS-QN). A brief description of the functions and the global minima are given in Table 1.

Table 1: Details of the benchmark problems

Function	Number of variables (N)	Global minimum	Remarks
Goldstein and Price function (GP_2)	2	3 at x = {0, -1}	Four local minima
Easom function (ES_2)	2	-1 at x = $\{\pi, \pi\}$	Several local minima
Shubert function (SH_2)	2	-186.7309 at x = {-0.8427, -0.1889}	18 global minima; 760 local minima
Hartmann function (H_3)	3	-3.86278 at x = {0.114614, 0.555649, 0.852547}	Four local minima
Rosenbrock function (ROS_N)	2,5,10 and 20	0 at x = {1, …, 1}	Several local minima
Zakharov function (ZAK_N)	2,5,10 and 20	0 at x = {0, …, 0}	Several local minima

Two types of stopping criteria are used in this study. They are namely, maximum number of iterations/generations ($Iter_{max}$ in TS-QN and Gen_{max} in DE-QN) (referred as stopping criterion 1 (SC1)) and maximum number of iterations/generations or maximum number of

successive iterations/generations (Sc_{max}) without improvement in the best function value (referred as stopping criterion 2 (SC2)). Some of the published studies (Cai and Shao, 2002) employed convergence to the global minimum as a stopping criterion. On the contrary, we used the stopping criteria SC1 and SC2, because in reality, global minimum of application problems is unknown *a priori*. The performance of the two methods is evaluated based on the reliability (i.e., number of trials in which global minimum is successfully located out of 100 trials) and the computational efficiency (i.e., number of function evaluations (NFE) required to reach the global minimum). The gradient is calculated numerically and the NFE includes the function calls for evaluating both the objective function and the gradient in the quasi-Newton method.

Parameter Tuning

Test functions GP_2, ES_2, SH_2, ROS_5, ROS_{10} and ROS_{20} have been selected to tune the parameters of TS-QN and DE-QN. The parameter values are optimized to find the global minimum with good reliability and computational efficiency. The nominal parameter values chosen for TS-QN are N_t and N_p =10; $_t$ and $_p$ = 0.01; h_n = 0.5; NP = 20N, where N is the dimension of the problem; N_{neigh} = 2N (subject to a minimum of 10 and a maximum of 30); Sc_{max} = 5N and $Iter_{max}$ = 50N; and for DE-QN are A = 0.4; CR = 0.1; NP = 50; Sc_{max} = 5N and Gen_{max} = 50. The nominal values for TS-QN and DE-QN are chosen based on the optimum

Table 2: Optimal parameter values for TS-QN and DE-QN

Parameters	Benchmark problems	Phase stability problems
TS-QN		
N_t and N_p	10	10
$_t$ and $_p$	0.01	0.02
NP	20N	20N
N_{neigh}	2N	2N
h_n	0.5	0.5
$Iter_{max}$	50N	min {50N, 100}
Sc_{max}	6N	2N
DE-QN		
A	0.5	0.3
CR	0.5	0.9
NP	50	min {50N, 100}
Gen_{max}	60N	50
Sc_{max}	10N	6N

Note 1: N – Dimension of the problem; N_t and N_p – Size of tabu and promising lists; $_t$ and $_p$ – Tabu and promising radii; NP – Population size; N_{neigh} – Number of neighbors; h_n – Length of the hyper rectangle; $Iter_{max}$ – Maximum number of iterations; Sc_{max} – Maximum number of successive iterations without improvement in the best function value; A – Amplification factor; CR – Crossover constant; Gen_{max} – Maximum number of generations.

Note 2: N_{neigh} is restricted to a minimum of 10 and a maximum of 30 for benchmark, and is restricted to 20 to 30 for PS problems to have good reliability and computational efficiency.

values available in Chelouah and Siarry (2000), and preliminary numerical experience with some of the benchmark problems respectively. The tuning is performed by varying one parameter at a time while the rest are fixed at their nominal/recent optimum values. The optimal parameters obtained for TS-QN and DE-QN are given in Table 2. The optimal parameters found for TS-QN are the same as its nominal parameters. This may be because the nominal parameters are chosen based on the optimal settings given in Chelouah and Siarry (2000).

Results and Discussion

The results for solving the benchmark problems by TS-QN and DE-QN are given in the Table 3. Each benchmark problem is solved 100 times, each time by generating a random initial estimate. The results are compared in terms of success rate (SR) and NFE, which is the average of all100 trials.

It is evident from Table 3 that the reliability of DE-QN is better compared to TS-QN using both SC1 and SC2. This is perhaps due to the different escaping mechanisms associated with these two methods. DE performs mutation and crossover over a set of individuals (i.e., population), whereas TS accepts the best point in each iteration as the new centroid of the hyper-rectangle for generating neighbors even though it is worse than the previous best points in order to escape from the local minima. The reliability of TS-QN is less for ES function because the function is flat everywhere in the feasible region except near the center (global minimum region). As the function is flat, all the neighbors generated in TS-QN will have the same value trapping the search in that region, where as DE-QN explored the

Table 3: Success rate (SR) and Number of Function Evaluations (NFE) using DE-QN and TS-QN for benchmark problems

Function	TS-QN				DE-QN			
	SC1		SC2		SC1		SC2	
	SR	NFE	SR	NFE	SR	NFE	SR	NFE
GP_2	100	918	99	301	100	6071	100	4711
ES_2	90	1040	85	433	100	6058	75	3935
SH_2	100	1033	92	355	99	6090	100	2260
ROS_2	99	2021	100	475	100	6067	100	2985
ZAK_2	100	1009	100	343	100	6058	100	2470
H_3	100	987	100	386	100	9070	100	5029
ROS_5	76	5275	79	2081	100	15074	100	9368
ZAK_5	100	2629	100	1294	100	15067	100	7668
ROS_{10}	74	17051	78	8541	100	30085	100	22422
ZAK_{10}	100	8491	100	8473	100	30081	100	16839
ROS_{20}	82	44869	75	22074	95	60112	95	60112
ZAK_{20}	100	19157	100	19157	100	60104	100	38064

global minimum region by generating different new individuals by the process of mutation and crossover. The reliability of both TS-QN and DE-QN for Shubert function is high even though it has 760 local minima. This may be because locating one of the several global minima (around 18) in this example is sufficient to achieve the best function value. The reliability of TS-QN is less for Rosenbrock functions because of narrow global minimum region in these functions.

Even though reliability of DE-QN is more than TS-QN, its computational efficiency is less compared to TS-QN (Table 3). NFE for DE-QN is 1.3 (ROS_{20}) to 6.6 times (GP_2) more than that for TS-QN using SC1 and is 2 to 15 times more than that of TS-QN using SC2 for the corresponding functions. This could be because of avoiding repeated visits to the same place in TS by keeping track (i.e., by maintaining tabu and promising lists) of the previous search points which in turn improves the computational efficiency. NFE for both TS-QN and DE-QN increases with the number of variables due the increase in the size of the solution space which makes both the algorithms to generate more points.

DE-QN and TS-QN have also been evaluated using SC2. The computational efficiency and reliability (Table 3) are better and comparable using SC2 compared to that of SC1 for both DE-QN and TS-QN. NFE of DE-QN using SC1 is 1.3 (GP_2 function) to 2.4 times (ZAK_2 function) more compared to SC2, and is 2 (ROS_{10} function) to 4.2 times (ROS_2 function) more compared to SC2 for TS-QN. This is because the algorithms will terminate if the best function value does not change successively even after specified maximum number of iterations/generations causing low reliability and good computational efficiency with SC2.

PHASE STABILITY PROBLEMS

For a given temperature (T), pressure (P) and composition $\mathbf{x}= (x_1, x_2, x_3, \ldots, x_{nc})$, the molar Gibbs free energy, g of the system is given as the summation of the product of mole fraction and partial molar Gibbs free energy, $\overline{G_i}$ for all components (Rangaiah, 2001):

$$g = \sum_{i=1}^{nc} x_i \overline{G}_i \tag{2}$$

The tangent plane, t at a specified composition $\mathbf{x}^* = (x_1^*, x_2^*, x_3^*, \ldots, x_{nc}^*)$ is given as:

$$t = \sum_{i=1}^{nc} x_i \overline{G}_i^* \tag{3}$$

where superscript * represents evaluation at composition x* and thus the TPDF can be expressed as:

$$H = g - t = \sum_{i=1}^{nc} x_i (\overline{G}_i - \overline{G}_i^*) \tag{4}$$

Depending on the expressions of $\overline{G}_i$ and $\overline{G}_i^*$, different forms of H exist. If the non-ideality of the phase is described by fugacity approach, then the dimensionless H can be expressed as:

$$H = \sum_{i=1}^{nc} x_i \left[\ln(\phi_i x_i) - \ln(\phi_i^* x_i^*)\right] \tag{5}$$

where ϕ_i represents the fugacity coefficient of the component i in the given phase. If the excess Gibbs free energy approach is used to represent the non-ideality, then the dimensionless F can be expressed as:

$$H = \sum_{i=1}^{nc} x_i \left[\ln(x_i) - \ln(x_i^* \gamma_{iL}^*) \right] \quad (6)$$

where γ_{iL} represents the activity coefficient of component i in the liquid phase L. Depending upon the approach, the objective function is either equation 5 or 6, and the constraints are:

$$\sum_{i=1}^{nc} x_i = 1 \quad (7)$$

and $0 \bullet x_i \bullet 1$ (8)

The decision variables are x_i for i = 1, 2, …, nc. The constrained problem can be reformulated into an unconstrained problem by introducing the variables, $_i$ (for i = 1, 2, …, nc-1) (Teh and Rangaiah, 2002) instead of mole fractions x_i (for i = 1, 2,…, nc). To avoid the computational difficulties, the lower bounds are taken as 10^{-15} instead of 0. The examples considered include multi-components (2 to 9), different feed conditions and different thermodynamic models. Several compositions are considered for each example. The number of components, feed composition, temperature and pressure of all these examples can be found in Rangaiah (2001) except for example 5 (Table 4). The last local, global minima and the composition at the last local minimum for all these cases are given in Table 5. The composition at the global minima can be found in Rangaiah (2001) and Table 5.

Table 4: Details of the example 5[#] of phase stability problem – toluene (1), water (2) and aniline (3) at 298 K and 1.0 atm

Composition	Component	x_i^*		Global solution	
		Liquid 1	Liquid 2	Objective function value	X
1	1	0.29989	-	-0.29454012	0.000067
	2	0.20006	-		0.996865
	3	0.50005	-		0.003068
2	1	0.34673	0.00009	0.0	0.346740
	2	0.07584	0.99495		0.075840
	3	0.57742	0.00496		0.577420

Note: The above example is a liquid-liquid equilibrium problem and * represents the feed composition.
[#] Castillo and Grossmann (1981).

Table 5: Global and last local minima for PS problems

Composition	Function value	
	Global minimum	**Last local minimum**
Example 1 (1)		
1	-0.03246624	0 at {0.5; 0.5}
2	-0.21418620	No local minima
3	-0.07427426	-6.06283×10^{-3} at {0.39221; 0.60778}
4	-0.00671171	0 at {0.65; 0.35}
5	-0.00070557	0 at {0.93514; 0.06486}
6	0	1.11127×10^{-3} at {0.93476; 6.5230×10^{-2}}
Example 2 (2)		
1	-0.11395074	0 at {0.4; 0.3; 0.3}
2	-0.05876117	-4.11636×10^{-6} at {0.61986; 0.00562; 0.37452}
3	-0.22827470	-2.71678×10^{-3} at {0.20145; 0.43018; 0.368351}
4	-0.02700214	-3.09637×10^{-6} at {0.03001; 0.00211; 0.96788}
5	0.0	1.323587×10^{-6} at {0.69280; 0.00399; 0.30321}
Example 3 (3)		
1	-0.00395983	1.08905×10^{-2} at {0.11520; 0.88479}
2	-0.08252179	-5.68944×10^{-2} at {0.11813; 0.88186}
3	-0.00246629	0 at {0.112; 0.888}
Example 4 (4)		
1	-1.48621570	-1.48554 at {0.94672; 4.35930e-2; 7.85484×10^{-3} ; 1×10^{-15}; 1.2478×10^{-3} ; 1.96839×10^{-4}; 2.63986×10^{-4}; 1.20802×10^{-4}}
Example 5		
1	-0.29454012	0 at {0.29989; 0.20006; 0.50005}
2	0	No local minima

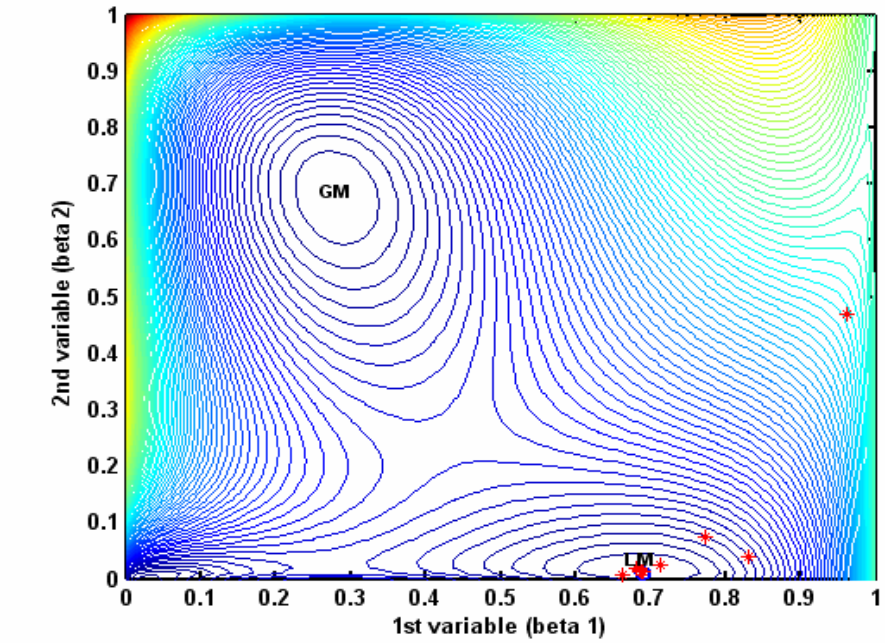
Note: The number in the bracket refers to the example number in Rangaiah (2001).

Parameter Tuning

Compositions 2, 4 and 5 of Example 2, which are found to be difficult in the preliminary trials, are chosen to tune the parameters of TS-QN and DE-QN. For PS examples, a random way of generating neighbors from the centroid in TS-QN is also studied along with the systematic way (using hyper rectangles) of generating neighbors. This is because, for some examples, generation of neighbors using hyper rectangles did not give good reliability, perhaps due to the distribution of local and global minima in these examples. As shown in Figure 4a, the problem (2nd example, 5th composition) has the local minimum at = (0.692780, 0.012996) and the global minimum at = (0.278990, 0.682251) with function values 1.323587×10^{-6} and 0 respectively. Initially the TS-QN using hyper rectangles to generate neighbors found a best point (circle in Figure 4a) in the local minimum region and set it as a new centroid of hyper rectangles to generate neighbors. As the local minimum is close to the boundary, the distribution of neighbors is not spread to the global minimum region (Figure 4a) (i.e., one side of the hyper rectangle becomes the lower boundary of the variables forcing many points near the boundary). To circumvent this difficulty, a random way of generating neighbors is implemented as shown in Figure 4b to explore better points in the global minimum region for

these problems. A mixed (generating half of the total number of neighbors using hyper rectangles and the rest randomly) way of generating neighbors is also studied.

(a)



(b)

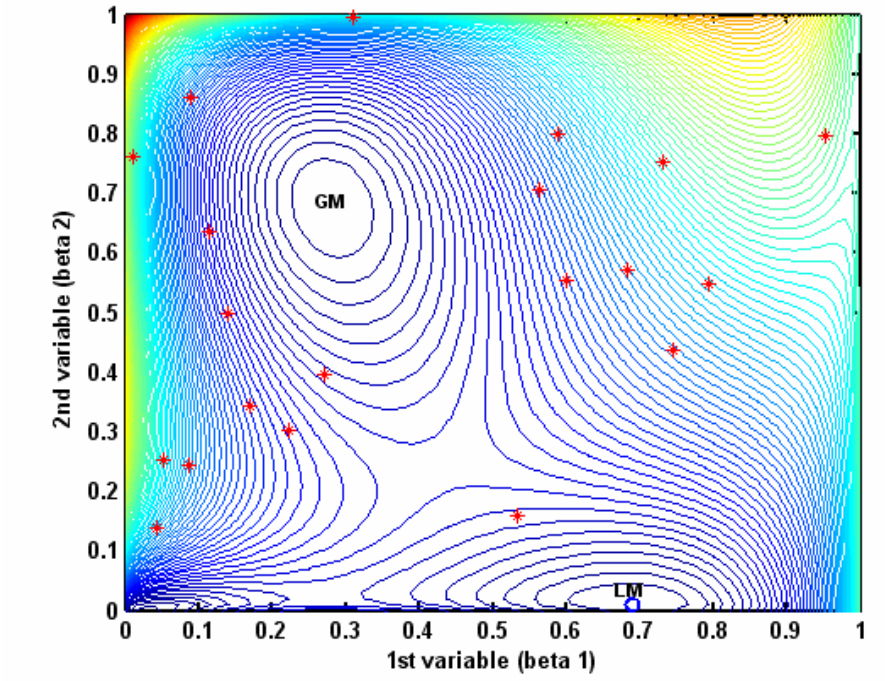


Figure 4: Generation of neighbors for example 2 (composition 5) (a) using hyper- rectangles (b) randomly using TS-QN. * represents the neighbor and circle (o) at = {0.69280, 0.01299} represents the best point.

The optimal parameter values obtained for TS-QN and DE-QN are given in Table 2. The parameters ($_t$ and $_p$, Sc_{max} and $Iter_{max}$ for TS-QN A, CR, Sc_{max} and Gen_{max} for DE-QN) are different compared to benchmark problems because the number of variables (i.e., components) in these examples is less compared to the benchmark examples.

Results and Discussion

All the PS examples are solved 100 times each from a different randomly chosen point in the feasible region. Initially the examples are solved with SC1 to study the performance of TS-QN with different ways of generating neighbors and the results (averaged over the 100 trials) of TS-QN and DE-QN are given in Table 6. The results for TS-QN are given for three types of generating neighbors: TS-S-QN (systematic using hyper rectangles), TS-R-QN (randomly) and TS-M-QN (mixed).

Table6: SR and NFE of DE-QN, TS-S-QN, TS-M-QN and TS-R-QN for phase stability problems using SC1

Composition	NFE of TS-S-QN	NFE of TS-M-QN	NFE of TS-R-QN	NFE of DE-QN
Example 1				
1	567 (99%)	360	684	2568
2	563	330	645	2562
3	465	361	681	2566
4	571	332	642	2569
5	583	324	640	2557
6	581	325	639	2567
Example 2				
1	1196	1890	1989	5112
2	1273 (64%)	1768	2023	5115
3	1272	1956	2035	5116
4	1240 (91%)	1810	1987	5111
5	1277 (84%)	1878 (85%)	1984 (76%)	5114
Example 3				
1	569	645	757	2584
2	577	523	759	2582
3	558	646	758	2582
Example 4				
1	2100	2203	2767	5143
Example 5				
1	1306	1095	2048	5120
2	1280	1026	1981	5108

Note: SR is 100% for all the examples except for some of them for which SR is given in brackets.

The results in Table 6 show that both DE-QN and TS-QN have high reliability in locating the global minimum. The reliability of DE-QN is comparable to TS-M-QN and TS-R-QN, and is better than TS-S-QN. This shows that the systematic way of generating neighbors has less reliability for these problems. The SR of TS-M-QN, TS-R-QN and DE-QN are 100%

for all the examples except for 2nd example with 5th composition for which TS-QN with all types of generating neighbors is low compared to DE-QN. This is because of the presence of comparable minima (function value at local and global minima are 1.32358×10^{-6} and 0 respectively) in this example. As the function value at the local minimum is close to the global minimum, the better region (Figure 5) becomes narrower and narrower causing failure of TS-QN to locate the global minimum region, where as DE-QN is able to explore the global minimum region with its escaping mechanism (mutation and crossover).

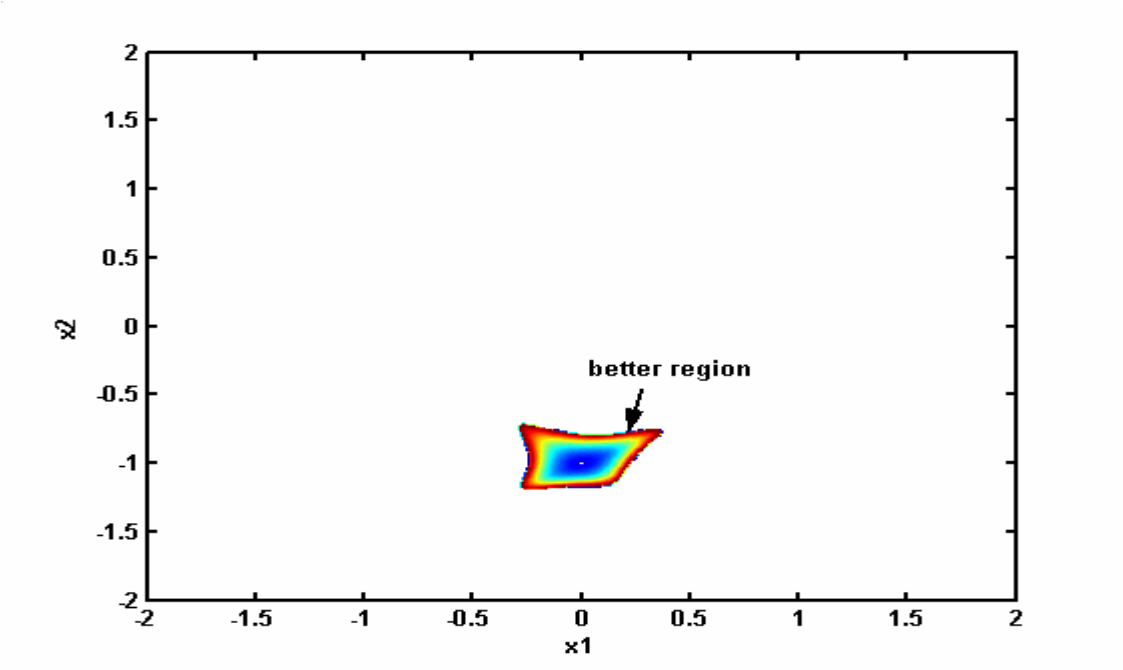


Figure 5: Better region (i.e. the global minimum region) with respect to the last local minimum for Goldstein and Price (GP) function

The computational efficiency of TS-M-QN is better compared to TS-S-QN and TS-R-QN. This may be because some neighbors in the mixed type of generation may be close enough such that they are near to the points in the tabu list which in turn avoids repeated evaluations. Even though DE-QN is more reliable than TS-QN, the latter is computationally more efficient than the former. The NFE of DE-QN is around 2.3 times (4th example) to 7.1 times (1st example, 1st composition) more than TS-M-QN. This is due to avoiding repeated visits to the same place by keeping track of the previous points during the search.

The examples are also solved with the SC2 for TS-M-QN (shown to be the best among all types) and DE-QN, and the results (Table 7) show that there is no improvement in the computational efficiency of TS-QN using SC2 compared to that of SC1. This is because the maximum number of iterations is reached before the specified Sc_{max} number of iterations. This also shows that the parameter $Iter_{max}$ is fine tuned. The results show that the computational efficiency of DE-QN using SC2 is better than that of SC1, and is due to the termination of the algorithm once the specified Sc_{max} number of iterations is reached irrespective of maximum number of iterations. NFE of DE-QN with SC1 is 1.1 (2nd example, 2nd

composition) to 4 times (1st example, 6th composition) more compared to that of SC2. For Example 4, the NFE of DE-QN is same with both SC1 and SC2. This is because here the optimum Sc_{max} value (i.e., $6N \cong 48$) is high because of more number of variables and the number of iterations reaches its maximum number (i.e., $Iter_{max} = 50$ for these problems) earlier than Sc_{max} terminating the algorithm. For Example 5, the NFE of DE-QN for composition 1 is higher than that of composition 2 even though optimum Sc_{max} value is the same for both of them. This may be because of the different gradients of the corresponding objective functions.

Table 7: Comparison of SR and NFE of DE-QN and TS-M-QN for phase stability problems using SC1 and SC2

Composition	TS-M-QN		DE-QN	
	SC1	SC2	SC1	SC2
Example 1				
1	360	360	2568	755
2	330	330	2562	779
3	361	361	2566	869
4	332	332	2569	727
5	324	324	2557	647
6	325	325	2567	643
Example 2				
1	1890	1890	5112	3808(99%)
2	1768	1768	5115	4624(96%)
3	1956	1956	5116	4824
4	1810	1810	5111	4024
5	1878 (85%)	1878 (85%)	5114	3642(99%)
Example 3				
1	645	645	2584	716
2	523	523	2582	764
3	646	646	2582	698
Example 4				
1	2203	2203	5143	5143
Example 5				
1	982	982	5120	5018
2	910	910	5108	3566

Note: SR is 100% for all the examples except for some of them for which SR is given in brackets.

CONCLUSIONS

Two most promising methods, namely, DE and TS have been implemented along with a local minimization method (QN) at the end to refine the solution, and evaluated for benchmark and PS problems. Initially both DE-QN and TS-QN are tested on benchmark problems comprising of 2 to 20 variables and a few to hundreds of local minima. The methods are then tested for PS problems involving multi components. The generation of neighbors in TS is implemented in different ways i.e., using hyper rectangles, mixed and random way of generation, to study the performance of TS-QN. The results show that the methods successfully located the global minima with DE-QN being more reliable compared to TS-QN and the latter being computationally more efficient than the former for both benchmark and PS problems. The above all results show that the process of mutation and crossover in DE-QN is more reliable than the escaping mechanism of TS-QN. They also show that TS-QN is computationally more efficient than DE-QN, perhaps due to avoiding revisits to the same place during the search.

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OMENCLATURE

A	Amplification factor
CR	Crossover constant
F	Total moles of feed
$\overline{G}$	Partial molar Gibbs free energy
H	Dimensionless tangent plane distance function
h	Length of the hyper rectangle
nc	Number of components
NP	Population size
P	System pressure
s	Centroid of the hyper rectangle
T	System temperature
t	Tangent plane
U	Trial vector
V	Mutated vector
X	Target vector
x	Mole fraction of the given phase

Greek letters

γ_i	Activity coefficient of component i
ϕ_i	Fugacity coefficient of component i
β_i	i^{th} component of the decision variable
	Radius

Subscripts

G	Generation
t	Tabu point
P	Promising point
neigh	Neighbor point
max	Maximum number