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Phase Equilibrium Modeling in Non-Reactive Systems Using Harmony Search

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1. Introduction

In recent years, a significant work has been performed in the area of software development for solving global optimization problems in science and engineering applications (Floudas et al., 1999). In particular, global optimization has and continues to play a major role in the design, operation, scheduling and managing of chemical industrial processes and, according to several authors; it will remain as a major challenge for future research efforts (Floudas et al., 1999; Biegler & Grossmann, 2004; Grossmann & Biegler, 2004; Rangaiah, 2010). In the context of chemical engineering, several algorithmic and computational contributions of global optimization have been used for process optimization. As expected, finding the global optimum is more challenging than finding a local optimum and, in some applications such as the phase equilibrium modeling, the location of this global optimum is crucial because it corresponds to the correct and desirable solution (Floudas et al., 1999; Teh & Rangaiah, 2002; Wakeham & Stateva, 2004; Rangaiah, 2010).

Specifically, the modeling of phase equilibrium in multicomponent systems is essential in the design, operation, optimization and control of separation schemes. The phase behavior of multicomponent systems has a significant impact in several issues of process design including the determination of the equipment and energy costs of separation and purification strategies (Wakeham & Stateva, 2004). Note that phase equilibrium calculations (PEC) are usually executed thousands of times in process simulators and, as a consequence, these calculations must be performed, reliably and efficiently, to avoid design uncertainties and erroneous conclusions about process performance. However, literature indicates that the development of reliable methods for PEC has long been a challenge and is still a research topic of continual interest in the chemical engineering community (Teh & Rangaiah, 2002; Wakeham & Stateva, 2004).

Basically, PEC involve two main problems: a) phase stability analysis is used to determine if a tested system under specified operating conditions is stable or not, and b) phase split calculations are performed to establish the number and identity (i.e., composition and type) of phases existing at the equilibrium (Wakeham & Stateva, 2004). These thermodynamic calculations can be formulated as global optimization problems where the tangent plane

distance function (*TPDF*) is used as optimization criterion for stability analysis and the Gibbs free energy function (*G*) is minimized for phase split computations. Formally, both optimization problems can be stated as follows: minimize $f(u)$ subject to $u \in \Omega$ where u is a continuous variable vector with domain $\Omega \in \Re^n$, and $f(u):\Omega \Rightarrow \Re$ is a real-valued function. The major challenge of solving global optimization problems for phase equilibrium modeling is that both $f(u) = TPDF$ and *G* are generally non-convex, highly non-linear with many decision variables, and often have unfavourable attributes such as discontinuity and non-differentiability. In fact, these objective functions may have several local optimums including trivial and nonphysical solutions especially for multicomponent and multiphase systems. Therefore, traditional optimization methods are not suitable for solving phase equilibrium problems under these conditions (Teh & Rangaiah, 2002; Wakeham & Stateva, 2004).

In view of the above, there has been a significant and increasing interest in the development of deterministic and stochastic global optimization strategies for reliably performing PEC (Wakeham & Stateva, 2004). For example, global optimization studies using deterministic strategies have been focused on the application of homotopy continuation methods (Sun & Seider, 1995; Jalali et al., 2008), branch and bound global optimization (McDonald & Floudas, 1996; Harding & Floudas, 2000), and interval mathematics (Hua et al., 1998; Xu et al., 2005). Although deterministic methods have proven to be promising, several of them are model dependent, may require problem reformulations or significant computational time especially for multicomponent systems (Nichita et al., 2002a; 2002b). On the other hand, stochastic optimization techniques have often been found to be as reliable and effective as deterministic methods but may offer advantages for PEC. These methods are robust numerical tools that present a reasonable computational effort in the optimization of multivariable functions (generally less time than deterministic approaches); they are applicable to ill-structure or unknown structure problems, require only calculations of the objective function and can be used with all thermodynamic models (Henderson et al., 2001). The study of stochastic optimization methods for PEC has become an active research area in the field of chemical engineering because various problems that are very challenging to solve by conventional techniques can be solved by meta-heuristics. To date, a number of stochastic global optimization methods have been studied and tested for PEC in non-reactive mixtures. These methods include: the Random Search method (Lee et al., 1999), Simulated Annealing (Zhu & Xu, 1999; Zhu et al., 2000; Henderson et al., 2001; Rangaiah, 2001; Bonilla-Petriciolet et al., 2006), Genetic Algorithms (Rangaiah, 2001; Teh & Rangaiah, 2003), Tabu Search (Teh & Rangaiah, 2003; Srinivas & Rangaiah, 2007a), Tunnelling method (Nichita et al., 2002a; 2002b; Srinivas & Rangaiah, 2006), Clustering method with stochastic sampling (Balogh et al., 2003), Differential Evolution (Srinivas & Rangaiah, 2007a; 2007b), and Particle Swarm Optimization (Rahman et al., 2009; Bonilla-Petriciolet & Segovia-Hernández, 2010). These meta-heuristics usually show a robust performance in PEC but, in some difficult problems, they may fail to locate the global optimum. Thus, alternative optimization strategies should be studied to identify a better approach for solving phase equilibrium problems.

In particular, Harmony Search (HS) is a novel meta-heuristic algorithm, which has been conceptualized using the musical process of searching for a perfect state of harmony (Geem et al., 2001). This optimization method is based on the analogy with music improvisation process where music players improvise the pitches of their instruments to obtain a better harmony. In the optimization context, each musician is replaced with a decision variable,

and the possible notes in the musical instruments correspond to the possible values for the decision variables. So, the harmony in music is analogous to the vector of decision variables, and the musician's improvisations are analogous to local and global search schemes in optimization techniques (Lee & Geem, 2005). This novel optimization method is simpler, both in formulation and computer implementation, than other stochastic optimization methods such as Genetic Algorithms or Particle Swarm Optimization (Lee & Geem, 2005). Until now, HS has been successfully applied to solve various engineering and optimization problems such as water network design, vehicle routing, soil stability analysis, heat exchanger design, and transportation energy modeling (Lee & Geem, 2005; Geem, 2009). In the field of chemical engineering, there are few studies concerning the application of this stochastic method and, to the best of our knowledge, the performance of HS for PEC in non-reactive systems has not yet been reported.

This chapter introduces the application of HS-based algorithms to solve phase stability and equilibrium problems in multicomponent non-reactive systems. Particularly, the performance and capabilities of HS in the modeling of phase equilibrium is studied and discussed. The remainder of this chapter is organized as follows. In Section 2, we briefly introduce HS and the common approaches for its modification or adaptation. The formulation of global optimization problems for phase equilibrium modeling (i.e., phase stability and phase split calculations) is presented in Section 3. Results of PEC using HS-based algorithms are reported in Section 4. Finally, in Section 5, we provide some remarks and conclusions about the application of HS for PEC in non-reactive systems.

2. Harmony Search optimization method

Harmony Search is a music-inspired meta-heuristic algorithm, which has been introduced by Geem et al. (2001). This stochastic optimization method is based on the underlying principles of the musician improvisation of the harmony. Specifically, when musicians improvise they may perform the following steps: playing an existing score from memory, performing variations on an existing piece, or creating an entirely new composition. In the optimization context, HS combines heuristic rules and randomness to imitate this music improvisation process. A comprehensive explanation of HS is provided by Geem et al. (2001) and a flow chart describing its principal stages is given in Figure 1.

In summary, HS involves the following parameters: the harmony memory size (HMS), the harmony memory considering rate (HMCR), the pitch adjusting rate (PAR), the bandwidth or step size for variable perturbation during pitch adjustment (bw), and the number of improvisations (NI). The harmony memory is a memory location where a set of solution vectors for decision variables is stored. The parameters HMCR and PAR are used to improve the solution vector and to increase the diversity of the search process (Geem et al., 2001; Lee & Geem, 2005). In HS, a new harmony (i.e., a new solution vector) is generated using these parameters and the following procedures: a) memory consideration, b) pitch adjustment, and c) random selection. To illustrate the concepts of HS, consider the following unconstrained global optimization problem: minimize $f(u)$ such that $lb_i \leq u_i \leq ub_i$ where u is a solution vector of n_{opt} continuous decision variables with lower (lb_i) and upper (ub_i) bounds for each decision variable (i.e., u_i). To solve this optimization problem, HS performs the following steps (Geem et al., 2001; Omran & Mahdavi, 2008):

1. *Initialize a harmony memory*. First, the parameters of HS (e.g., HMS, HMCR, PAR, bw) are defined and the harmony memory is initialized. This harmony memory preserves the

history of optimization sequence and is useful to identify promising areas for global optimization because good harmonies can be considered as elements of new solution vectors. Usually, the initial values of harmony memory are generated from a uniform distribution in the bounds of decision variables: $u_i = lb_i + rand \, (ub_i - lb_i)$ where $rand \in (0, 1)$ is a random number.

2. *Improvise a new harmony*. As stated, a new harmony vector (v_i) is obtained using the following stages: memory consideration, pitch adjustment and random selection. These stages can be summarized using the following pseudo-code (Omran & Mahdavi, 2008):

> **for** $i = 1$ to n_{opt} **do**
>   **if** $rand \in (0, 1) \leq$ HMCR **then** perform *memory consideration*
>   **begin**
> $v_i = u_{ij}$ where $j \in (1,\ldots,$HMS$)$
>   **if** $rand \in (0, 1) \leq$ PAR **then** perform *pitch adjustment*
>   **begin**
> $v_i = v_i + (0.5 - rand) \cdot bw_i$ where bw_i is the bandwidth (i.e., step size)
>   **end if**
>   **else** perform *random selection*
> $v_i = lb_i + rand \, (ub_i - lb_i)$
>   **end if**
>   **end for**

These stochastic operators are used to perform both diversification and intensification stages in HS. The diversification is controlled by the pitch adjustment and random selection operators, while memory consideration is generally associated to the intensification. In particular, HMCR is used to determine the degree of contribution of harmony memory (i.e., promising solutions) during random search. On the other hand, PAR and *bw* are used to control the additional random perturbation of decision variables when memory consideration is applied. In addition, the random selection is useful to explore different regions of objective function and also contributes to increase the diversity of solution vectors. Note that the proper combination of these operators is important to favor the performance of HS in global optimization. The generation of a new harmony (i.e., new solution vector) is called improvisation.

3. *Update harmony memory*. In this stage, a new harmony (v) replaces the worst harmony in harmony memory only if its value of objective function is lower than that of the worst harmony. The decision vectors stored in harmony memory are useful to exploit the history and experience of the search process, being an intensification mechanism of HS method.

4. *Check the stopping condition*. This iterative procedure is repeated until satisfying a proper convergence criterion. Similar to other stochastic methods, the choice of stopping condition can significantly affect the performance of HS. In the literature, the stopping criterions commonly used in HS are based on the number of function evaluations (NFE) or improvisations (NI). The best solution found by HS, which is stored in harmony memory, is expected to be a near global optimum solution.

It is convenient to remark that a boundary violation check must be implemented, principally during pitch adjustment, to verify the feasibility of v; if v is infeasible, a new harmony is randomly generated inside lower and upper bounds of decision variables. A local optimization technique can be used at the end of global search for efficiently improving the

accuracy of the best solution obtained by HS. Note that stochastic optimization methods may require a significant computational effort to improve the accuracy of global solution because they explore the search space of decision variables by creating random movements instead of determining a logical optimization trajectory. Thus, this additional intensification step is required for rapid convergence in the final stage of HS.

```
┌──────────────────────┐
│  Define parameters of │
│   Harmony Search      │
└──────────────────────┘
           │
┌──────────────────────┐
│ Initialize harmony memory │
└──────────────────────┘
           │
┌──────────────────────┐
│ Improvise a new harmony │
└──────────────────────┘
           │
      ╱────────────╲
     ╱ Add new harmony ╲  Yes   ┌──────────────────────┐
    ╲ to harmony memory? ╱─────▶│ Update harmony memory │
      ╲────────────╱            └──────────────────────┘
           │ No
      ╱────────────╲
 No  ╱ Termination criteria ╲
────╲    satisfied?      ╱
      ╲────────────╱
           │ Yes
┌──────────────────────┐
│  Local optimization   │
└──────────────────────┘
```
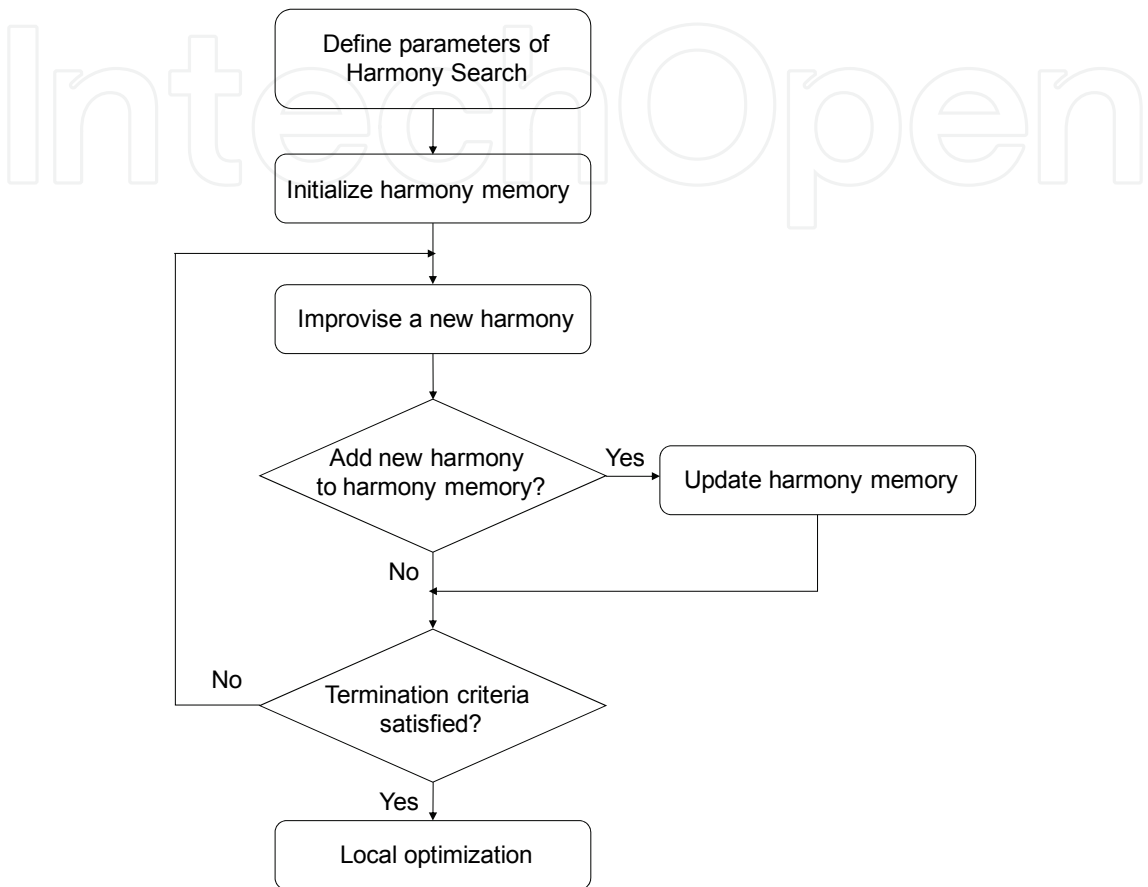
Fig. 1. Flowchart of Harmony Search (HS) stochastic optimization method

As indicated, the parameters HMS, HMCR, PAR and *bw* are important to determine the performance (i.e., reliability and efficiency) of HS in global optimization. For example, some authors have suggested that small values of HMS may lead to the HS to be trapped in local solutions (Mahdavi et al., 2007). However, increasing HMS generally provides better solution vectors but at the expense of more function evaluations. Therefore, the fine tuning of these parameters is very crucial for solving global optimization problems (Mahdavi et al., 2007; Omran & Mahdavi, 2008). Traditionally, fixed values for HS parameters, which can not be changed during new improvisations, are used in global optimization (Geem et al., 2001; Geem, 2009). So, this standard version of HS algorithm is referred as HSC in this chapter.

In the literature, some modifications have been proposed to improve the convergence performance of the original HS. According to Geem (2009), the variations proposed for HS may involve: a) mechanisms for the proper initialization of HS parameters, b) mechanisms for the dynamic adaptation of HS parameters during optimization sequence, and c) the application of new or modified HS operators, which includes hybrid methods using other meta-heuristics such as Simulated Annealing or Differential Evolution. Below, two typical variants of HS are briefly discussed, which has been used in the present study.

Particularly, the dynamic adaptation of HS parameters is the most common approach to overcome the drawbacks of original HS. Results reported by Mahdavi et al. (2007) indicated that small PAR values with large *bw* values may affect the performance of HS and increase the calculations needed to find the global optimum. Although, small *bw* values in final iterations (i.e., improvisations) increase the fine-tuning of solution vectors but, in early iterations, *bw* should take a bigger value to diversify the solution vectors. Furthermore, large PAR values with small *bw* values may cause the improvement of best solutions in final improvisations. Based on this fact, Mahdavi et al. (2007) introduced the Improved Harmony Search (IHS), which uses dynamic values of both parameters PAR and *bw*. Specifically, PAR dynamically changes with improvisation number as follow

$$PAR_{k+1} = PAR_{\min} + \frac{(PAR_{\max} - PAR_{\min})}{NI} * k \tag{1}$$

where PAR_{min} and PAR_{max} are the minimum and maximum pitch adjusting rates, and k is an improvisation counter. On the other hand, the bandwidth for each improvisation is given by

$$bw_{k+1} = bw_{\max} \exp\big((k/NI)\ln(bw_{\min}/bw_{\max})\big) \tag{2}$$

being bw_{min} and bw_{max} the minimum and maximum values for bandwidth, respectively. Note that PAR_{min}, PAR_{max}, bw_{min} and bw_{max} are defined by the user and are problem dependent. Mahdavi et al. (2007) showed that this variant of HS has proven to be competitive with respect to other HS algorithms for solving benchmark and some engineering optimization problems. Therefore, we have considered IHS for solving global optimization problems in phase equilibrium modeling.

Recently, Omran & Mahdavi (2008) proposed an alternative version of HS called Global-Best Harmony Search (GHS), which is inspired by the concept of swarm intelligence used in Particle Swarm Optimization. This method modifies the pitch-adjustment step of HS to encourage that a new harmony can mimic the best harmony stored in the harmony memory. Results reported for several benchmark optimization problems showed that GHS may offer a better performance than those reported for HSC and IHS (Omran & Mahdavi, 2008). In general, GHS has the same structure as IHS with the exception of pitch adjustment step used in the improvisation of a new harmony. Specifically, the pseudo-code to improvise a new harmony in GHS is defined as follows (Omran & Mahdavi, 2008):

```
for i = 1 to n_opt do
    if rand ∈ (0, 1) ≤ HMCR then perform memory consideration
      begin
      v_i = u_ij where j ∈ (1,…,HMS)
      if rand ∈ (0, 1) ≤ PAR then perform pitch adjustment
        begin
        v_i = u_i,best where best is the index of the best harmony in the harmony memory
      end if
    else perform random selection
      v_i = lb_i + rand (ub_i – lb_i)
    end if
end for
```

With respect to the parameters of GHS, Omran & Mahdavi (2008) have suggested that using a constant value of PAR improves its performance and this scheme is even better than GHS using a dynamical value of PAR. So, this approach has been adopted in the present study for GHS.

Although these modern optimization methods have been successfully applied in different science and engineering fields, their capabilities have not yet been studied in the modeling of phase equilibrium. Therefore, these HS-based optimization methods have been used in this study for performing PEC in non-reactive systems. All methods have been implemented in Fortran subroutines that can be applied for solving global optimization problems with continuous variables. These codes are available to interested readers upon request to the corresponding author. Finally, with respect to the stopping condition, the following criteria can be applied for global optimization using HS: 1) a maximum number of successive improvisations (SNI_{max}) without improvement in the best function value, or 2) a maximum number of improvisations (NI). Both criteria have been applied in this study and implemented for all HS algorithms.

3. Formulation of global optimization problems for phase stability and equilibrium calculations in non-reactive systems

3.1 Phase stability

Phase stability analysis is a fundamental stage in PEC and allows identification of the thermodynamic state that corresponds to the global minimum of Gibbs free energy (Michelsen, 1982; Wakeham & Stateva, 2004). A mixture at a fixed temperature T, pressure P and overall composition z is stable if and only if the Gibbs free energy surface is at no point below the tangent plane to the surface at the given mixture composition (Michelsen, 1982). This statement is a necessary and sufficient condition for global phase stability. As mentioned in the introduction, this stability analysis can be performed using the Tangent Plane Distance Function (*TPDF*). This function is geometrically defined as the distance between the Gibbs free energy surface at a trial composition y and the tangent plane constructed to this surface at composition z. Properly, phase stability of a non-reactive systems with c components and a global composition $z(z_1,…,z_c)$ in mole fraction units, at constant P and T, is analyzed by the global minimization of *TPDF* (Michelsen, 1982)

$$TPDF = \sum_{i=1}^{c} y_i \left(\mu_i\big|_y - \mu_i\big|_z \right) \tag{3}$$

where $\mu_i\big|_y$ and $\mu_i\big|_z$ are the chemical potentials of component i calculated at compositions y and z, respectively. To perform a stability analysis, *TPDF* must be globally minimized with respect to composition of a trial phase y, which is subject to an equality constraint. This constrained global optimization problem can be written as

$$\min_{y} \ TPDF(y)$$

$$\text{subject to } \sum_{i=1}^{c} y_i = 1 \tag{4}$$

$$0 \leq y_i \leq 1 \quad i = 1,…,c$$

where the decision variables in phase stability problems are the mole fractions y_i. If the global minimum of $TPDF(y) < 0$, the mixture under analysis is considered unstable; otherwise it is a globally stable system. The global minimization of $TPDF$ is difficult and requires robust numerical methods since this function is multivariable, non-convex and highly non-linear. To date, several deterministic and stochastic global optimization methods have been reported for performing phase stability calculations (e.g., Sun & Seider, 1995; McDonald & Floudas, 1996; Hua et al., 1998; Harding & Floudas, 2000; Henderson et al., 2001; Rangaiah, 2001; Teh & Rangaiah, 2002; Nichita et al., 2002a; Balogh et al., 2003; Xu et al., 2005; Bonilla-Petriciolet et al., 2006; Srinivas & Rangaiah, 2007a; 2007b; Bonilla-Petriciolet & Segovia-Hernández, 2010).

To simplify this global optimization problem, the constrained problem given by Equation (4) can be transformed into an unconstrained problem by using new decision variables β_i instead of y_i as decision vector (Rangaiah, 2001; Srinivas & Rangaiah, 2007a; 2007b). These new decision variables $\beta_i \in (0, 1)$ are related to composition variables y_i as follows

$$n_{iy} = \beta_i z_i n_F \quad i = 1,...,c \tag{5}$$

$$y_i = n_{iy} \bigg/ \sum_{j=1}^{c} n_{jy} \quad i = 1,...,c \tag{6}$$

where $n_F = \sum_{i=1}^{c} n_{iF}$ is the total amount of conventional moles in the feed composition used for stability analysis, and n_{iy} is the conventional mole number of component i in the trial phase y, respectively. Note that the feed mole fractions z_i are obtained from $z_i = n_{iF}/n_F$. Then, we state the unconstrained global optimization problem for phase stability analysis

$$\min_{\beta} \; TPDF(\beta)$$
$$0 \leq \beta_i \leq 1 \quad i = 1,...,c \tag{7}$$

For phase stability calculations, the number of decision variables is c for non-reactive systems of c components. In summary, this unconstrained formulation has been used for all phase stability calculations performed in this study using HS optimization methods.

3.2 Phase equilibrium calculations

After identifying an unstable system in phase stability analysis, the subsequent stage corresponds to a phase split calculation. In this thermodynamic problem, the main objectives are to correctly establish the number and types of phases existing at equilibrium as well as the composition and quantity of each phase such that the Gibbs free energy of the system is a minimum (Wakeham & Stateva, 2004). At constant T and P, a c multicomponent and π multiphase non-reactive system achieves equilibrium when its molar Gibbs free energy of mixing (g) is at the global minimum. Properly, the objective function for Gibbs free energy minimization using activity or fugacity coefficients is given by

$$g = \sum_{j=1}^{\pi} \sum_{i=1}^{c} n_{ij} \ln(x_{ij}\gamma_{ij}) = \sum_{j=1}^{\pi} \sum_{i=1}^{c} n_{ij} \ln\left(\frac{x_{ij}\hat{\varphi}_{ij}}{\varphi_i}\right) \tag{8}$$

where n_{ij} is the mole number of component i in phase j, γ_{ij} is the activity coefficient of component i in phase j, $\hat{\phi}_{ij}$ is the fugacity coefficient of component i in phase j, and φ_i is the fugacity coefficient of pure component i, respectively. Here, the Gibbs free energy of mixing (g) is used to avoid the calculation of pure component free energies, which do not influence equilibrium and stability results.

In a non-reactive system, g must be globally minimized with respect to the set of n_{ij} subject to the mass balance constraints. Thus, the constrained global optimization problem for Gibbs free energy minimization is

$$\min_{n} \ g(n)$$

$$\text{subject to } \sum_{j=1}^{\pi} n_{ij} = z_i n_F \quad i = 1,...,c \tag{9}$$

$$0 \le n_{ij} \le z_i n_F \quad i = 1,...,c \quad j = 1,...,\pi$$

where z_i is the mole fraction of component i in the feed used for phase-split calculations. This objective function is generally multivariable and non-convex due to the non-linear nature of thermodynamic models. Both stochastic and deterministic methods are available for Gibbs free energy minimization (Teh & Rangaiah, 2002; Wakeham & Stateva, 2004). In particular, the methods: Simulated Annealing (Rangaiah, 2001; Henderson et al., 2001), Genetic Algorithms (Rangaiah, 2001; Teh & Rangaiah, 2003), Tabu Search (Teh & Rangaiah, 2003), Tunnelling method (Nichita et al., 2002b; Srinivas & Rangaiah, 2006), Differential Evolution (Srinivas & Rangaiah, 2007a; 2007b), and Particle Swarm Optimization (Rahman et al., 2009; Bonilla-Petriciolet & Segovia-Hernández, 2010) have been applied for Gibbs free energy minimization in non-reactive systems.

To perform an unconstrained minimization of g, we can use again alternative variables instead of n_{ij} as optimization targets. The use of these variables eliminates the restrictions imposed by material balances, reduces problem dimensionality, and the optimization problem is transformed to an unconstrained one (Rangaiah, 2001). For multi-phase non-reactive systems, real variables $\beta_{ij} \in (0, 1)$ are defined and employed as decision vector by using the following expressions

$$n_{i1} = \beta_{i1} z_i n_F \quad i = 1,...,c \tag{10}$$

$$n_{ij} = \beta_{ij} \left(z_i n_F - \sum_{m=1}^{\pi-1} n_{im} \right) \quad i = 1,...,c \quad j = 2,...,\pi-1 \tag{11}$$

$$n_{i\pi} = z_i n_F - \sum_{j=1}^{\pi-1} n_{ij} \quad i = 1,...,c \tag{12}$$

Using Equations (10)-(12), all trial compositions will satisfy the material balances allowing the easy application of optimization strategies. Thus, the unconstrained global minimization problem is defined as

$$\min_{\beta} \; g(\beta)$$
$$0 \le \beta_{ij} \le 1 \quad i = 1,...,c \quad j = 1,...,\pi - 1 \tag{13}$$

For Gibbs free energy minimization, the number of phases existing at the equilibrium is assumed to be known *a priori* and the number of decision variables is $c\pi - c$ for non-reactive systems of c components with π phases. So, the problem formulation given by Equation (13) has been adopted in the present study for phase-split calculations in non-reactive systems.

4. Results of phase equilibrium calculations using HS-based optimization methods

4.1 Description of phase equilibrium problems
In our study, various phase equilibrium problems from the literature have been used to assess the performance of HS-based optimization algorithms. These problems include multicomponent systems with vapor-liquid and liquid-liquid equilibrium. Feed composition, operating conditions, thermodynamic models, and global optimum of these problems are reported in Tables 1 and 2. It is convenient to note that these problems have

No.	System	Temperature and pressure	Model
1	*n*-butyl acetate + water	298 K and 101.325 KPa	NRTL
2	toluene + water + aniline	298 K and 101.325 KPa	NRTL
3	$N_2 + C_1 + C_2$	270 K and 7600 KPa	SRK EoS
4	$H_2S + C_1$	190 K and 4053 KPa	SRK EoS
5	$H_2O + CO_2 + $ 2-propanol + ethanol	350 K and 2250 KPa	SRK EoS
6	$C_2 + C_3 + C_4 + C_5 + C_6$	390 K and 5583 KPa	SRK EoS
7	$C_1 + C_2 + C_3 + C_4 + C_5 + C_6 + C_{7-16} + C_{17+}$	353 K and 38500 KPa	SRK EoS
8	$C_1 + C_2 + C_3 + iC_4 + C_4 + iC_5 + C_5 + C_6 + iC_{15}$	314 K and 2010.288 KPa	SRK EoS
9	$C_1 + C_2 + C_3 + C_4 + C_5 + C_6 + C_7 + C_8 + C_9 + C_{10}$	435.35 K and 19150 KPa	SRK EoS

Table 1. Examples selected for phase stability and equilibrium calculations in non-reactive systems using Harmony Search-based optimization methods.

No.	Feed composition, z	Global optimum	
		TPDF	g
1	Z (0.5, 0.5)	-0.0324662	-0.0201983
2	Z (0.29989, 0.20006, 0.50005)	-0.2945401	-0.3529567
3	Z (0.3, 0.1, 0.6)	-0.0157670	-0.5477911
4	Z (0.0187, 0.9813)	-0.0039320	-0.0198922
5	Z (0.99758, 0.00003, 0.00013, 0.00226)	-0.0126500	-0.0048272
6	Z (0.401, 0.293, 0.199, 0.0707, 0.0363)	-0.0000021	-1.1836525
7	Z (0.7212, 0.09205, 0.04455, 0.03123, 0.01273, 0.01361, 0.07215, 0.01248)	-0.0026876	-0.8387826
8	Z (0.614, 0.10259, 0.04985, 0.008989, 0.02116, 0.00722, 0.01187, 0.01435, 0.16998)	-1.4862053	-0.7697724
9	Z (0.6436, 0.0752, 0.0474, 0.0412, 0.0297, 0.0138, 0.0303, 0.0371, 0.0415, 0.0402)	-0.0000205	-1.1211758

Table 2. Global minimum of selected phase stability and equilibrium problems.

considered for testing the performance of other stochastic optimization methods such as Simulated Annealing, Genetic Algorithms, Tabu Search, Differential Evolution and Particle Swarm Optimization (e.g., Rangaiah, 2001; Teh & Rangaiah, 2003; Bonilla-Petriciolet et al., 2006; Srinivas & Rangaiah, 2007a; 2007b; Bonilla-Petriciolet & Segovia-Hernández, 2010). The objective functions (i.e., *TPDF* and *g*) have at least one local minimum, which corresponds to a trivial solution, for all tested conditions. Therefore, these optimization problems have different degrees of difficulty and features, so that the performance of HS methods can be tested systematically.

4.2 Parameter tuning of HSC, IHS and GHS

The key parameters of HSC, IHS and GHS have been tuned by finding the global minimum of some phase stability and equilibrium problems. Following previous studies (e.g., Bonilla-Petriciolet et al., 2006; Bonilla-Petriciolet & Segovia-Hernandez, 2010), the parameters of HS-based methods were tuned using examples No. 4 and 5, which were found to be challenging in preliminary trials. Specifically, parameter tuning was performed by varying one parameter at a time while the rest are fixed at nominal values, which were established using values reported in the literature and results of preliminary calculations (not reported in this chapter). For parameter tuning, all HS methods were run 100 times, with random initial values for decision variables (i.e., β_i and β_{ij}) and random number seed, on each of the selected problems using different conditions for HS parameters. The suggested values for parameters of HSC, IHS and GHS are reported in Table 3. For all calculations performed in this study, we set HMS = $10n_{opt}$ (i.e., harmony memory) in HSC, GHS and IHS. Overall, our preliminary calculations indicate that values given in Table 3 are a reasonable compromise between numerical effort and reliability of HS-based optimization methods for performing PEC.

Method	Parameter	Suggested value
HSC	HMCR	0.5
	PAR	0.75
	bw	$ub_i - lb_i$
GHS	HMCR	0.5
	PAR	0.75
	bw	$ub_i - lb_i$
IHS	HMCR	0.5
	PAR_{min}	0.5
	PAR_{max}	0.95
	bw_{min}	0.001
	bw_{max}	$ub_i - lb_i$

Table 3. Suggested values of parameters in HSC, IHS and GHS for solving global optimization problems in phase equilibrium modeling.

4.3 Performance of HSC, IHS and GHS in phase stability and equilibrium calculations

In this section, we compare the performance of HSC, IHS and GHS for both phase stability and equilibrium calculations in non-reactive systems. These methods are evaluated based on both reliability and computational efficiency in locating the global minimum of these thermodynamic problems. Each test problem is solved 100 times using HS methods, each

time with a different random number seed such that the initial values of decision variables and random operators are different in each trial.

With illustrative purposes, Tables 4 and 5 summarize the mean value of the objective function (i.e., *TPDF* and *g*) calculated by HS methods over 100 runs performed on some selected examples at different levels of computational efficiency, which are obtained by changing the stopping conditions NI and SNI_{max}. As stated, the stopping conditions NI and

| | | | NI/HMS | | | | | |
$f(u)$	No.	Method	25	50	100	500	1000	1500
TPDF	1	HSC	-0.032121	-0.032450	**-0.032466**	-0.032466	-0.032466	-0.032466
		GHS	-0.031792	-0.032297	-0.032455	-0.032466	-0.032466	-0.032466
		IHS	**-0.032460**	**-0.032466**	**-0.032466**	-0.032466	-0.032466	-0.032466
	2	HSC	-0.119234	-0.175243	-0.230080	-0.290298	-0.293195	-0.293929
		GHS	**-0.235608**	**-0.271328**	-0.286175	-0.293712	-0.294317	-0.294416
		IHS	-0.130544	-0.242552	**-0.293399**	**-0.294533**	**-0.294537**	**-0.294538**
	8	HSC	-1.393909	-1.419570	-1.435958	-1.459419	-1.465537	-1.468035
		GHS	**-1.463179**	**-1.473019**	**-1.477031**	**-1.483464**	**-1.484407**	**-1.484719**
		IHS	-1.441306	-1.459395	-1.469119	-1.481068	-1.483426	-1.484304
g	1	HSC	-0.019942	-0.020110	-0.020140	-0.020193	-0.020196	-0.020197
		GHS	-0.019815	-0.019975	-0.020081	-0.020191	-0.020196	-0.020197
		IHS	**-0.020052**	**-0.020189**	**-0.020197**	**-0.020198**	**-0.020198**	**-0.020198**
	2	HSC	-0.332641	-0.335935	-0.339952	-0.351137	-0.352288	-0.352559
		GHS	**-0.338794**	**-0.345940**	**-0.350732**	-0.352721	-0.352873	-0.352910
		IHS	-0.332065	-0.336039	-0.349790	**-0.352946**	**-0.352952**	**-0.352953**
	8	HSC	-0.734627	-0.743442	-0.749865	-0.761014	-0.764000	-0.764984
		GHS	**-0.762602**	**-0.765662**	**-0.767486**	**-0.768955**	**-0.769369**	-0.769361
		IHS	-0.748691	-0.758576	-0.764873	-0.768615	-0.769123	-0.769332

Table 4. Mean values of *TPDF* and *g* calculated by HS-based methods at different levels of computational efficiency, using NI alone as stopping condition, for phase stability and equilibrium calculations of non-reactive systems.

| | | $SNI_{max}/(n_{opt} \cdot HMS)$ | | | | | |
| | | *TPDF* | | | *G* | | |
No.	Method	5	10	15	5	10	15
1	HSC	**- 0.031404**	**-0.032419**	**- 0.032463**	**-0.019697**	**-0.020010**	**-0.020128**
	GHS	- 0.030894	-0.032082	- 0.032339	-0.019623	-0.019879	-0.019949
	IHS	- 0.031358	-0.032364	- 0.032406	-0.019657	-0.019937	-0.020060
2	HSC	- 0.119623	-0.191368	- 0.224470	-0.332387	-0.335297	-0.339812
	GHS	**- 0.266324**	**-0.279203**	**- 0.287641**	**-0.346430**	**-0.350512**	**-0.351517**
	IHS	- 0.118653	-0.195152	- 0.217033	-0.333279	-0.336683	-0.338551
8	HSC	- 1.435201	-1.447226	- 1.452705	-0.748590	-0.754997	-0.758230
	GHS	**- 1.480936**	**-1.482794**	**- 1.484031**	**-0.768323**	**-0.768881**	**-0.769098**
	IHS	- 1.419238	-1.438575	- 1.453591	-0.745669	-0.749071	-0.754977

Table 5. Mean values of *TPDF* and *g* calculated by HS-based methods at different levels of computational efficiency, using SNI_{max} alone as stopping condition, for phase stability and equilibrium calculations of non-reactive systems.

SNI$_{max}$ also contribute to the trade-off between efficiency and reliability of HS. Therefore, the performance of all HS methods is illustrated by changing these stopping conditions. This approach is adopted in the present study because generally no correlation can be established *a priori* between an optimization problem and the required numerical effort for finding the global optimum. So, the proper stopping condition has to be determined by a sensitivity analysis.

Our results indicate that the performance of HS, GHS and IHS varies with the type of stopping condition and, as a consequence, the numerical effort. In general, these results show that increasing the value of both stopping conditions (i.e., NI or SNI$_{max}$) improves the performance of all HS methods for PEC. But, results indicate that the reliability of HSC, GHS and IHS is generally better using stopping condition NI compared to SNI$_{max}$. Particularly, GHS and IHS can find solution vectors very close to the global minimum solution and their performance is usually better than that of HSC using either NI or SNI$_{max}$ as convergence criterion. For example, Figures 2 and 3 provide the convergence histories of the norm of $\hat{f}^{cal} - f^{*}$ for all HS methods in the global minimization of *TPDF* and *g* of examples No. 2 and 8. This norm is based on the average (over 100 runs) of the best objective function $\hat{f}^{cal}$ recorded in the harmony memory at different improvisations (i.e., NFE). Note that the mean value of best harmony (i.e., solution vector) obtained by GHS and IHS is usually lower than that achieved by HSC in both phase stability and equilibrium calculations. Moreover, it appears that the convergence curves of GHS and IHS are faster than that of HSC. These results are in agreement with the observations reported by Mahdavi et al. (2007) and Omran & Mahdavi (2008). Specifically, these authors have indicated that the modifications of traditional HS may allow performing global optimization, efficiently and reliably.

Following our previous study (Bonilla-Petriciolet & Segovia-Hernández, 2010) and, in order to facilitate understanding and to make the performance difference between HSC, GHS and IHS more explicit, we have employed the performance profile reported by Dolan & More (2002). Performance profiles (PP) are an alternative tool for evaluating and comparing the performance of several solvers on a set of test problems. The results of PP allow us to identify the expected performance differences among several solvers and to compare the quality of their solutions by eliminating the bias of failures obtained in a small number or problems. A brief overview of PP is provided in this chapter, and a detailed description of this mathematical approach is given by Dolan & More (2002).

Suppose that a set of N_{prob} problems and a set of S solvers are considered for applying performance profiles. In our study, this problem set corresponds to the collection of phase stability and equilibrium problems reported in Table 1, while the solver set is given by HSC, IHS and GHS. For these conditions, we establish a performance metric $t_{ij} \geq 0$ for every solver $i \in S$ and problem $j \in N_{prob}$. For example, this performance metric should give information on solver reliability, efficiency or another performance measure useful to characterize the capabilities of the solver under evaluation. For each problem $j \in N_{prob}$, we calculate

$$t_j^{*} = \min \left\{ \left. t_{ij} \right| \ solver \ i \in S \right\} \tag{14}$$

where t_j^{*} is the best possible performance for problem j among all the solvers tested. For a particular solver i, the set of performance ratios σ_{ij} is determined by
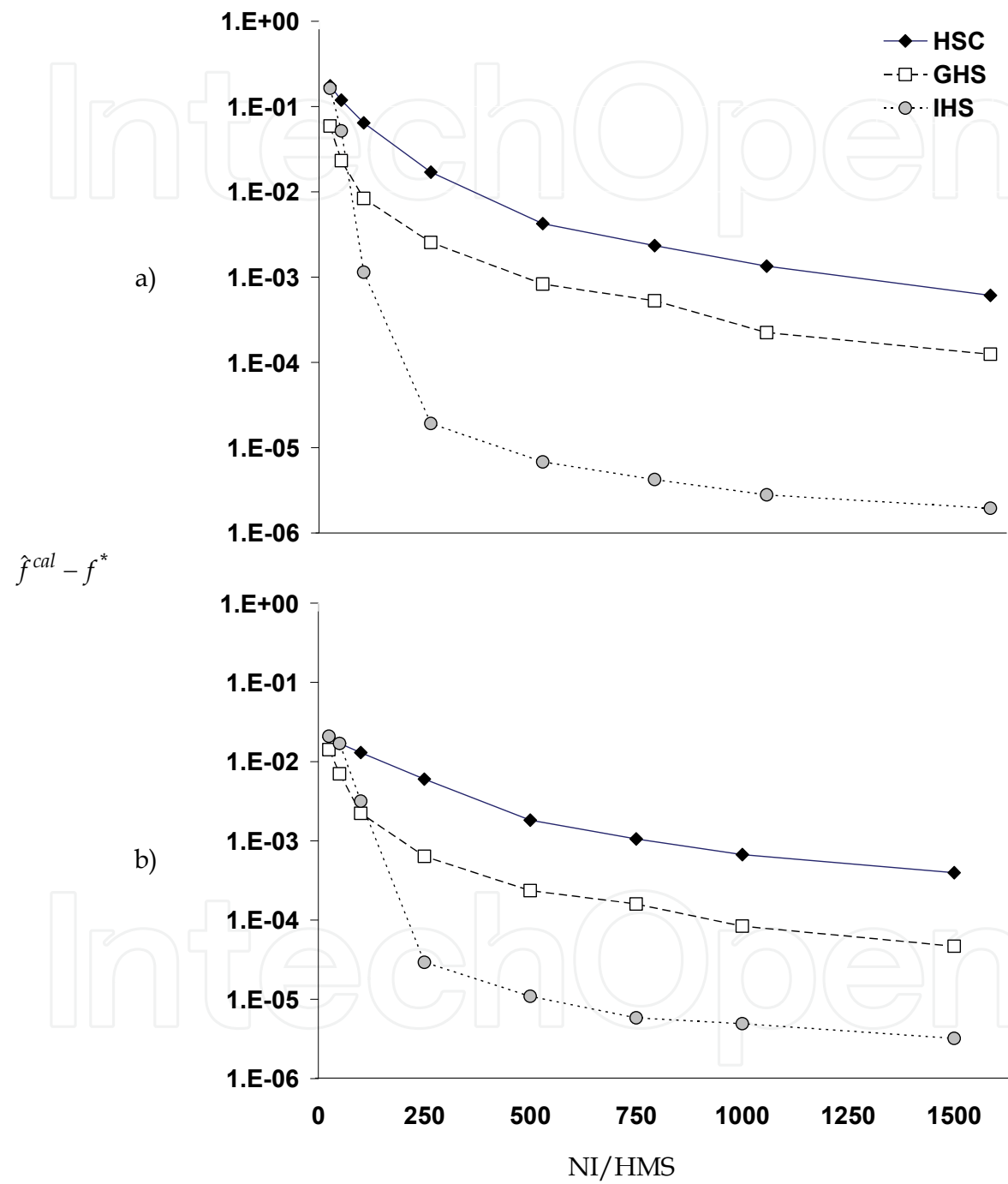
Fig. 2. Convergence profiles for solving phase equilibrium example No. 2 by HSC, GHS and IHS. Objective function: a) *TPDF* and b) *g*
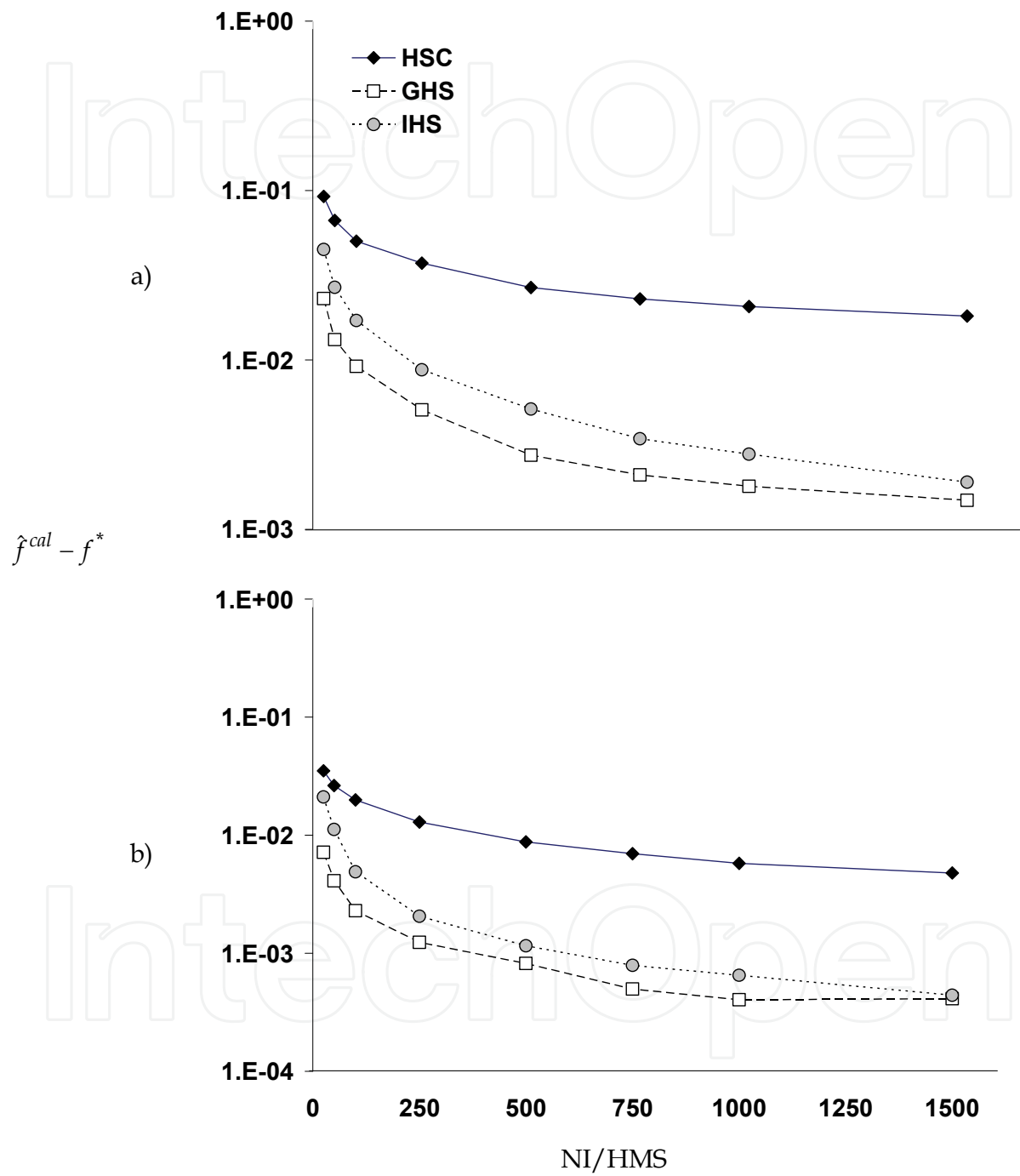
Fig. 3. Convergence profiles for solving phase equilibrium example No. 8 by HSC, GHS and IHS. Objective function: a) *TPDF* and b) *g*

$$\sigma_{ij} = t_{ij} / t_j^* \qquad j \in N_{prob} \tag{15}$$

where the performance ratio σ_{ij} of method i for problem j is defined as the ratio of the method's performance to the best performance value over all solvers for the same problem (Dolan & More, 2002). The value of this performance ratio is equal to unity for the solver i that performs best on a specific problem j. For every solver $i \in S$, let $\rho_i(\xi)$ be the fraction of problems for which $\sigma_{ij} \le \xi$ where $\xi \ge 1$. Then, we have

$$\rho_i(\xi) = \frac{1}{N_{prob}} size\left\{ j \in N_{prob} : \sigma_{ij} \le \xi \right\} \tag{16}$$

where the "size" is the number of problems such that the performance ratio σ_{ij} is less than or equal to ξ for solver i. The parameter $\rho_i(\xi)$ indicates the fraction of problems for which solver i is within a factor of ξ of the best solver (according to the performance metric used for solver comparison). In summary, the performance profile of a solver represents the cumulative distribution function of its performance ratios and is a plot of $\rho_i(\xi)$ *versus* ξ. It is convenient to note that $\rho_i(1)$ is the probability (i.e., fraction of problems tested) for which solver i was the best solver overall. Therefore, to identify the best solver using PP, it is only necessary to compare the values of $\rho_i(1)$ for all solvers and to select the highest one.

Base on the fact that, our study compares how well the HS methods can estimate the global optimum relative to another in phase equilibrium problems, we have used the following performance metric for a systematic assessment of HSC, GHS and HIS:

$$t_{ij} = \hat{f}_{ij}^{cal} - f_j^* \tag{17}$$

where f_j^* is the known global optimum of the objective function for problem j, which are reported in Table 2, and $\hat{f}_{ij}^{cal}$ is the mean value of the objective function calculated by the stochastic method i over 100 runs performed with random initial values for decision variables of problem j. This performance metric is useful to identify the algorithm that provides the most accurate value of the global minimum in phase stability and equilibrium problems. In fact, our group has successfully used this performance metric and performance profiles for comparison of several stochastic optimization methods in the context of phase equilibrium modeling (e.g., Bonilla-Petriciolet & Segovia-Hernández, 2010).

Figure 4 shows the results of $\rho_i(1)$ *versus* NI for HSC, IHS and GHS in phase stability and equilibrium calculations using Equation (17) as performance metric. Our results confirm that both GHS and IHS offer the best performance and show the highest probability for finding the best solutions in the collection of phase equilibrium problems used in this study. Figure 4 shows that the probability $\rho_i(1)$ of GHS is better than that obtained for IHS and HSC especially in early NI. However, this probability decreases as NI increased while IHS outperformed HSC and GHS in solving phase equilibrium problems if a larger NI is permitted. Note that HSC showed the worst performance for solving the global optimization problems analyzed in this chapter. Overall, PP indicate that the best solutions found by HSC are worse than the best solution found by both GHS and IHS in the global optimization of *TPDF* and *g*. In summary, GHS and IHS are the best from the standpoint of algorithm reliability and appear to be suitable for solving phase stability and equilibrium problems in non-reactive systems.
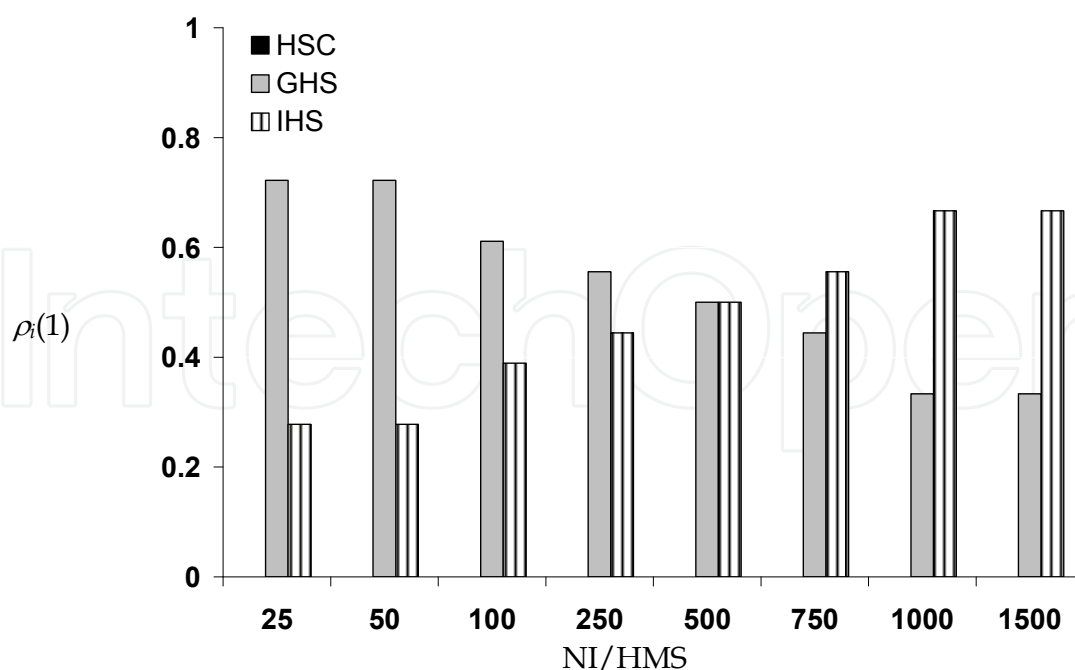
Fig. 4. Results of performance profiles for the comparison of HSC, GHS and IHS in phase stability and equilibrium calculations of non-reactive systems. Performance metric: $t_{ij} = \hat{f}_{ij}^{cal} - f_j^*$. Stopping condition is the maximum number of improvisations and HMS = $10n_{opt}$. The missing bars indicate that the probability $\rho_i(1)$ for solver i is 0.0.

Finally, we have compared the reliability of GHS and IHS in combination of a quasi-Newton method for solving these thermodynamic calculations accurately and efficiently. Specifically, the best harmony stored in harmony memory of both GHS and IHS is used as initial guess for a local optimization technique. This local optimization method corresponds to the subroutine DBCONF from IMSL library, where the default values of DBCONF parameters in IMSL library have been used in these calculations. Under these conditions, GHS and IHS are evaluated based on the reliability in locating the global minimum, which is measured in terms global success rate (GSR). This performance metric is defined as the number of times the algorithm located the global minimum to the specified accuracy out of all trials performed in the collection of phase equilibrium problems. Properly, in these calculations a trial is considered successful if the global optimum is obtained with an absolute error of 10^{-5} or lower in the objective function value, i.e. $\left| f^* - f^{cal} \right| \le 10^{-5}$ where f^* is the known global optimum and f^{cal} is the solution provided by GHS or IHS method. In some examples, an absolute error of 10^{-7} in the objective function was used to avoid counting local minima as the global optimum.

In general, the GSR ranged from 70.8 to 73.8 % for GHS and from 70.1 to 70.7 % for IHS throughout the tested range of NI. Results of individual problems indicate that both GHS and HIS, each followed by the local optimization method, show high reliability for examples No. 1 - 4 and 8 in phase stability analysis, and examples No. 1 - 4 and 7 - 9 in Gibbs free energy minimization. Both methods failed several times to find the global optimum in phase stability examples No. 5-7 and 9, while phase equilibrium examples No. 5 and 6 are difficult global optimization problems for both HS-based methods.

5. Conclusion

This chapter introduces the application of Harmony Search-based methods for solving global optimization in phase equilibrium modeling of non-reactive systems. Specifically, we have compared the performance of classical HS and some of its variants for performing phase stability and equilibrium calculations. Our results indicate that HS-based optimization algorithms are capable of handling the difficult characteristics of global optimization problems in PEC. In particular, the Global-Best Harmony Search offers the best performance from the standpoint of algorithm reliability, whereas the classical Harmony Search method is the worst for performing the global optimization of objective functions involved in phase equilibrium modeling. In summary, our results indicate that GHS is a suitable and alternative global optimization strategy for phase equilibrium calculations in non-reactive systems. Further research will be focused on the application of this stochastic method in other thermodynamic calculations.

6. References

Balogh, J.; Csendes, T. & Stateva, R.P. (2003). Application of a stochastic method to the solution of the phase stability problem: cubic equations of state. *Fluid Phase Equilibria*, Vol. 212, No. 1-2, 257-267.

Biegler, L.T. & Grossmann, I.E. (2004). Retrospective on optimization. *Computers and Chemical Engineering*, Vol. 28, No. 8, 1169-1192.

Bonilla-Petriciolet, A. & Segovia-Hernández, J.G. (2010). A comparative study of particle swarm optimization and its variants for phase stability and equilibrium calculations in multicomponent reactive and non-reactive systems. *Fluid Phase Equilibria*, Vol. 289, No. 2, 110-121.

Bonilla-Petriciolet, A.; Vázquez-Román, R.; Iglesias-Silva, G.A. & Hall, K.R. (2006). Performance of stochastic optimization methods in the calculation of phase stability analyzes for nonreactive and reactive mixtures. *Industrial Engineering Chemistry Research*, Vol. 45, No. 13, 4764-4772.

Dolan, E.D. & More, J.J. (2002). Benchmarking optimization software with performance profiles. *Mathematical Programming Series A*, Vol. 91, No. 2, 201-213.

Floudas, C.A.; Pardalos, P.M.; Adjiman, C.S.; Esposito, W.R.; Gumus, Z.H.; Harding, S.T.; Klepeis, J.L.; Meyer, C.A. & Schweiger, C.A. (1999). *Handbook of test problems in local and global optimization*, Kluwer Academic Publishers, ISBN: 0-7923-5801-5, Netherlands.

Geem, Z.W. (2009). *Music-inspired harmony search algorithm theory and applications*, Springer, ISBN: 978-3-642-00184-0, United Sates.

Geem, Z.W.; Kim, J.H. & Loganathan, G.V. (2001). A new heuristic optimization algorithm: harmony search. *Simulation*, Vol. 76, No. 2, 60-68.

Grossmann, I.E. & Biegler, L.T. (2004). Part II. Future perspective on optimization. *Computers and Chemical Engineering*, Vol. 28, No. 8, 1193-1218.

Harding, S.T. & Floudas, C.A. (2000). Phase stability with cubic equations of state: Global optimization approach. *AIChE Journal*, Vol. 46, No. 7, 1422-1440.

Henderson, N.; de Oliveira, J.R.; Amaral Souto, H.P. & Pitanga, R. (2001). Modeling and analysis of the isothermal flash problem and its calculation with the simulated

annealing algorithm. *Industrial Engineering Chemistry Research*, Vol. 40, No. 25, 6028-6038.

Hua, J.Z.; Brennecke, J.F. & Stadtherr, M.A. (1998). Reliable computation of phase stability using interval analysis: cubic equation of state models. *Computers and Chemical Engineering*, Vol. 22, No. 9, 1207-1214.

Jalali, F.; Seader, J.D. & Khaleghi, S. (2008). Global solution approaches in equilibrium and stability analysis using homotopy continuation in the complex domain. *Computers and Chemical Engineering*, Vol. 32, No. 10, 2333-2345.

Lee, K.S. & Geem, Z.W. (2005). A new meta-heuristic algorithm for continuous engineering optimization: harmony search theory and practice. *Computer Methods in Applied Mechanics and Engineering*, Vol. 194, No. 36-38, 3902-3933.

Lee, Y.P.; Rangaiah, G.P. & Luus, R. (1999). Phase and chemical equilibrium calculations by direct search optimization. *Computers and Chemical Engineering*, Vol. 23, No. 9, 1183-1191.

Mahdavi, M.; Fesanghary, M. & Damangir, E. (2007). An improved harmony search algorithm for solving optimization problems. *Applied Mathematics and Computation*, Vol. 188, No. 2, 1567-1579.

McDonald, C.M. & Floudas, C.A. (1996). GLOPEQ: A new computational tool for the phase and chemical equilibrium problem. *Computers and Chemical Engineering*, Vol. 21, No. 1, 1-23.

Michelsen, M.L. (1982). The isothermal flash problem. Part I. Stability. *Fluid Phase Equilibria*, Vol. 9, No. 1, 1-19.

Nichita, D.V.; Gomez, S. & Luna, E. (2002a). Phase stability analysis with cubic equations of state by using a global optimization method. *Fluid Phase Equilibria*, Vol. 194-197, No. 1, 411-437.

Nichita, D.V.; Gomez, S. & Luna, E. (2002b). Multiphase equilibria calculation by direct minimization of Gibbs free energy with a global optimization method. *Computers and Chemical Engineering*, Vol. 26, No. 12, 1703-1724.

Omran, M.G.H. & Mahdavi, M. (2008). Global-best harmony search. *Applied Mathematics and Computation*, Vol. 198, No. 2, 643-656.

Rahman, I.; Das, A.Kr.; Mankar, R.B. & Kulkarni, B.D. (2009). Evaluation of repulsive particle swarm method for phase equilibrium and phase stability problems. *Fluid Phase Equilibria*, Vol. 282, No. 2, 65-67.

Srinivas, M. & Rangaiah, G.P. (2006). Implementation and evaluation of random tunnelling algorithm for chemical engineering applications. *Computers Chemical Engineering*, Vol. 30, No. 9, 1400-1415.

Srinivas, M. & Rangaiah, G.P. (2007a). A study of differential evolution and tabu search for benchmark, phase equilibrium and phase stability problems. *Computers Chemical Engineering*, Vol. 31, No. 7, 760-772.

Srinivas, M. & Rangaiah, G.P. (2007b). Differential evolution with tabu list for global optimization and its application to phase equilibrium and parameter estimation problems. *Industrial Engineering Chemistry Research*, Vol. 46, No. 10, 3410-3421.

Sun, A.C. & Seider, W.D. (1995). Homotopy-continuation method for stability analysis in the global minimization of the Gibbs free energy. *Fluid Phase Equilibria*, Vol. 103, No. 2, 213-249.

Teh, Y.S. & Rangaiah, G.P. (2002). A study of equation-solving and Gibbs free energy minimization methods for phase equilibrium calculations. *Chemical Engineering Research and Design*, Vol. 80, No. 7, 745-759.

Teh, Y.S. & Rangaiah, G.P. (2003). Tabu search for global optimization of continuous functions with application to phase equilibrium calculations. *Computers Chemical Engineering*, Vol. 27, No. 11, 1665-1679.

Rangaiah, G.P. (2001). Evaluation of genetic algorithms and simulated annealing for phase equilibrium and stability problems. *Fluid Phase Equilibria*, Vol. 187-188, No. 1, 83-109.

Rangaiah, G.P. (2010). *Stochastic Global Optimization: Techniques and Applications in Chemical Engineering*, World Scientific Publishing Co., ISBN: 978-981-4299-20-6, Singapore.

Wakeham, W.A. & Stateva, R.P. (2004). Numerical solution of the isothermal, isobaric phase equilibrium problem. *Reviews in Chemical Engineering*, Vol. 20, No. 1-2, 1-56.

Xu, G.; Haynes, W.D. & Stadtherr, M.A. (2005). Reliable phase stability analysis for asymmetric models. *Fluid Phase Equilibria*, Vol. 235, No. 2, 152-165.

Zhu, Y. & Xu, Z. (1999). A reliable prediction of the global phase stability for liquid-liquid equilibrium through the simulated annealing algorithm: application to NRTL and UNIQUAC equations. *Fluid Phase Equilibria*, Vol. 154, No. 1, 55-69.

Zhu, Y.; Wen, H. & Xu, Z. (2000). Global stability analysis and phase equilibrium calculations at high pressures using the enhanced simulated annealing algorithm. *Chemical Engineering Science*, Vol. 55, No. 17, 3451-3459.
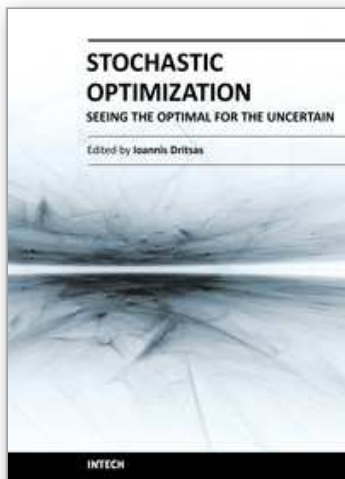
Stochastic Optimization - Seeing the Optimal for the Uncertain

Edited by Dr. Ioannis Dritsas

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