









TABLE I. DETAILS OF THE PHASE STABILITY, PHASE EQUILIBRIUM AND REACTIVE PHASE EQUILIBRIUM PROBLEMS USED IN THIS STUDY

Code	System	Feed conditions	Thermodynamic models	Global optimum
<b>T7</b>	$C_1 + C_2 + C_3 + C_4 + C_5 + C_6 + C_{7-16} + C_{17+}$	$n_F = (0.7212, 0.09205, 0.04455, 0.03123, 0.01273, 0.01361, 0.07215, 0.01248)$ at 353K and 38500kPa	Phase stability problem with SRK EoS with classical mixing rules.	-0.002688
<b>T8</b>	$C_1 + C_2 + C_3 + iC_4 + C_4 + iC_5 + C_5 + C_6 + iC_{15}$	$n_F = (0.614, 0.10259, 0.04985, 0.008989, 0.02116, 0.00722, 0.01187, 0.01435, 0.16998)$ at 314K and 2010.288kPa	Phase stability problem with SRK EoS with classical mixing rules.	-1.486205
<b>T9</b>	$C1 + C2 + C3 + C4 + C5 + C6 + C7 + C8 + C9 + C10$	$n_F = (0.6436, 0.0752, 0.0474, 0.0412, 0.0297, 0.0138, 0.0303, 0.0371, 0.0415, 0.0402)$ at 435.35K and 19150kPa	Phase stability problem with SRK EoS with classical mixing rules.	-0.0000205
<b>G4</b>	$C_1 + H_2S$	$n_F = (0.9813, 0.0187)$ at 190K and 4053kPa	Phase equilibrium problem with SRK EoS with classical mixing rules.	-0.019892
<b>G6</b>	$C_2 + C_3 + C_4 + C_5 + C_6$	$n_F = (0.401, 0.293, 0.199, 0.0707, 0.0363)$ at 390K and 5583kPa	Phase equilibrium problem with SRK EoS with classical mixing rules.	-1.183653
<b>G7</b>	$C_1 + C_2 + C_3 + C_4 + C_5 + C_6 + C_{7-16} + C_{17+}$	$n_F = (0.7212, 0.09205, 0.04455, 0.03123, 0.01273, 0.01361, 0.07215, 0.01248)$ at 353K and 38500kPa	Phase equilibrium problem with SRK EoS with classical mixing rules.	-0.838783
<b>G8</b>	$C_1 + C_2 + C_3 + iC_4 + C_4 + iC_5 + C_5 + C_6 + iC_{15}$	$n_F = (0.614, 0.10259, 0.04985, 0.008989, 0.02116, 0.00722, 0.01187, 0.01435, 0.16998)$ at 314K and 2010.288kPa	Phase equilibrium problem with SRK EoS with classical mixing rules.	-0.769772
<b>R4</b>	A1+A2 ↔ A3+A4 (1) Acetic acid (2) n-Butanol (3) Water (4) n-Butyl acetate	$n_F = (0.3, 0.4, 0.3, 0.0)$ at 298.15K and 101.325kPa	Reactive phase equilibrium problem with UNIQUAC model and ideal gas. $\ln K_{eq} = 450/T + 0.8$	-1.10630
<b>R7</b>	A1+A2 ↔ A3	$n_F = (0.52, 0.48, 0.0)$ at 323.15K and 101.325kPa	Reactive phase equilibrium problem with Margules solution model. $K_{eq} = 3.5$	-0.653756

*D. Details of numerical implementation and performance metrics used for testing the algorithms*

All thermodynamic problems and the different optimization algorithms were coded in the MATLAB® technical computing environment. MAKHA was developed and coded by the authors. The code for CS was obtained from MATLAB file exchange server as uploaded by their developers and used as is. Parameters were tuned using preliminary calculations and are shown in Table II. Each problem was solved 30 times independently and with different random initial seeds to determine the reliability of the optimization algorithms. Calculations were performed for a certain number of iterations and then stopped. This maximum value for the number of iterations was different for different algorithms. The maximum

values were selected to give the same number of function evaluations at the end of the run.

The methods were evaluated according to the reliability and efficiency for finding the global optimum. The efficiency is determined by recording the number of function evaluations NFE for each optimization algorithm, where a low value of NFE means a higher efficiency. Note that NFE is an unbiased indicator of the computational costs required by a certain algorithm and is independent on the host hardware. In this work, we present a different reliability metric: a plot of the average best value against the number of function evaluations. The best values are averaged over all the runs and plotted against NFE, which is calculated at each iteration. Since the NFE needed for each iteration differ amongst the optimization methods, the plot of average best value against NFE is a good

indication of reliability versus efficiency of the optimization method.

TABLE II. PARAMETERS FOR THE STOCHASTIC METHODS

Method	Parameters	
	Symbol	Value
MAKHA	c	-1
	d	-1
	$D^{\max}$	[0.001,0.02]
	$C_t$	0.5
	$V_f$	0.02
KHA	$W_f$	0.1
	$D^{\max}$	0.8
	$C_t$	0.5
	$V_f$	0.02
	$N^{\max}$	0.01
	$w_f$	[ 0.1,0.9]
MA	$w_N$	[ 0.1,0.9]
	a	0.00001
	c	-1
	d	1
CS	$N_c$	10
	p	0.25

#### IV. RESULTS AND DISCUSSION

The results are presented in two different ways. For each problem, the mean best values are plotted versus NFE for each of the four algorithms. Three of these plots, one for each problem category, are shown here as representatives of the results. The minimum NFE required to reach a certain tolerance from the known global minimum for each problem were calculated and presented in Table III. A detailed discussion of the results follows.

##### A. Phase stability problems

Problem T7 is a nine-variable phase-stability problem that is extremely difficult to solve. The means of the minimum values obtained by all methods were not close enough to the global minimum except for CS, which was able to find the global minimum down to a tolerance of  $10^{-7}$ . MAKHA outperformed both MA and KHA and was able to find the global minimum down to a tolerance of  $10^{-5}$ . Fig. 2 shows how the two original problems, MA and KHA, were trapped in a local minimum, and only MAKHA and CS, were able to reach the global minimum.

Problem T8 is also a difficult phase-stability problem. KHA outperformed both MAKHA and CS in solving this problem down to a tolerance of  $10^{-5}$ . However, none of the algorithms was able to get closer to the global minimum within the total NFE run in our study, as illustrated by the NFE values of Table III.

Problem T9 is the last of the three phase stability problems. Even though, KHA was again the most efficient algorithm down to a tolerance of  $10^{-5}$  but it failed to go any further. MAKHA was more reliable down to  $10^{-6}$  and CS was the most reliable to down to  $10^{-7}$  tolerance level.

For the phase stability problems, CS is clearly the most reliable method. It may not be as efficient in its initial approach to the global minimum as other methods but it outperforms the rest in terms of finding the global minimum. However, the hybridization of MA and KHA resulted in an improvement in reliability as MAKHA was more reliable than the two original algorithms.

##### b) Phase equilibrium problems

Problem G4 is a two-variable phase equilibrium problem that is relatively easy to solve. However, KHA seemed to have been trapped in a local minimum and was unable to find its global minimum, within a tolerance of  $10^{-5}$ , as shown in Figure 3. MA performed better than KHA but it was inefficient and was unable to reach the global minimum at the  $10^{-7}$  level. MAKHA and CS were reliable and efficient in solving this problem.

Despite the fact that KHA was not able to solve adequately problem G4, it was superior in solving problem G6 down to  $10^{-6}$  tolerance level. It was not able to solve it any further to the end of the runs. Again, MAKHA and CS were more reliable in solving this problem. For Problem G7, MAKHA again was more reliable than the original two algorithms. G8, on the other hand, was the only problem that MAKHA was less reliable than KHA in its solution. MA was not able to reach the global minimum at any tolerance level. CS was the most reliable problem but less efficient than KHA.

The convergence profiles of the four phase equilibrium problems (G4, G6, G7 and G8) indicated that CS is the most reliable of all algorithms as it was the only one to be able to solve all problems down to the  $10^{-7}$  tolerance level. MAKHA has shown better reliability than the two original algorithms but less efficient than KHA at the higher tolerance levels.

##### c) Reactive phase equilibrium problems

Regardless of the number of variables, the reactive phase equilibrium problems are more difficult than the non-reactive phase equilibrium problems, because the chemical reaction equilibria constraints must be satisfied. Problem R4 was successfully solved down to the  $10^{-5}$  tolerance level by CS, which was also able to converge to the global minimum at the  $10^{-7}$  level. MAKHA performed better than MA and KHA but all of them were not able to arrive even at a level of  $10^{-4}$  from the global minimum.

Problem R7 is a good indication of the significance of this study. Even though both MA and KHA failed completely in solving this problem, MAKHA was able to converge to the global minimum down to the  $10^{-7}$  tolerance level. Its performance was similar to that of CS as shown in Figure 4.

#### V. CONCLUSIONS

In this study, we have developed a hybrid optimization algorithm that combines feature from MA and KHA. The developed algorithm was used to solve nine difficult phase stability and phase equilibrium problems. Its performance was compared against the two original algorithms and CS, which is considered the most reliable algorithm for solving this type of problems. These thermodynamic problems were systematically

solved by the different metaheuristics and the results were tracked and compared. The results clearly show that MAKHA is more reliable than the original two algorithms. Even though CS is still the most reliable of all tested optimization methods, MAKHA's performance was close second.

REFERENCES

[1] I. Fister Jr., X.S. Yang, I. Fister, J. Brest, D. Fister, *Elektrotehniški Vestnik*, 2013, 80, 116-122.  
 [2] A. Bonilla-Petriciolet, G.P. Rangaiah, J.G. Segovia-Hernández, *Fluid Phase Equilibria*, 2011, 300, 120-134.  
 [3] A. Bonilla-Petriciolet, J.G. Segovia-Hernández, *Fluid Phase Equilibria*, 2010, 289, 110-121.  
 [4] H. Zhang, J.A. Fernández-Vargas, G.P. Rangaiah, A. Bonilla-Petriciolet, J.G. Segovia-Hernández, *Fluid Phase Equilibria*, 2011, 310, 129-141.  
 [5] S.E.K. Fateen, A. Bonilla-Petriciolet, G.P. Rangaiah, *Chemical Engineering Research and Design*, 2012, 90, 2051-2071.  
 [6] J.A. Fernandez-Vargas, A. Bonilla-Petriciolet, J.G. Segovia-Hernandez, *Fluid Phase Equilibria*, 2013, 353, 121-131.  
 [7] V. Bhargava, S.E.K. Fateen, A. Bonilla-Petriciolet, *Fluid Phase Equilibria*, 2013, 337, 191-200.  
 [8] A. O. Elnabawy, S.E.K. Fateen, and Adrian Bonilla-Petriciolet, *Industrial & Engineering Chemistry Research* 2014 53 (6), 2382-2395  
 [9] S.E. K. Fateen and A. Bonilla-Petriciolet, *The Scientific World Journal*, 2014, 2014, Article ID 374510  
 [10] S.E.K. Fateen and A. Bonilla-Petriciolet, "A note on effective phase stability calculations using a Gradient-Based Cuckoo Search Algorithm" *Fluid Phase Equilibria*, 2014, In press.  
 [11] H. Zhang, A. Bonilla-Petriciolet, G.P. Rangaiah, *The Open Thermodynamics Journal*, 2011, S1, 71-92.  
 [12] Zhao R, Tang W, "Monkey algorithm for global numerical optimization", *Journal of Uncertain Systems*, 2008, 2:165-176.  
 [13] Gandomi AH, Alavi AH, "Krill herd: a new bio-inspired optimization algorithm", *Communications in Nonlinear Science and Numerical Simulation*, 2012, 17:4831-4845.  
 [14] X.S. Yang, S. Deb, In *Proceedings of World Congress on Nature & Biologically Inspired Computed*, India, 2009, 210-214.  
 [15] I. Aghababaei, M.M. and M. Farsangi, *International Journal on Technical and Physical Problems of Engineering*, 2012. 4(2): p. 13-17.

TABLE III. MINIMUM NFE FOR THE AVERAGE BEST VALUE TO REACH 1E-3, 1E-4, 1E-5, 1E-6, AND 1E-7 FROM THE KNOWN GLOBAL MINIMUM

Metaheuristic	$\epsilon$	Phase equilibrium thermodynamic problem								
		T7	T8	T9	G4	G6	G7	G8	R4	R7
MAKHA	1E-3	<b>34222</b>	4336	602	61	302	482	94579	<b>53152</b>	21659
	1E-4	<b>81217</b>	91869	1505	61	453	6266	140649	$\infty$	56507
	1E-5	167495	148237	33712	<b>1037</b>	604	81458	168562	$\infty$	62799
	1E-6	$\infty$	$\infty$	140868	5002	1057	117126	$\infty$	$\infty$	64372
	1E-7	$\infty$	$\infty$	$\infty$	9150	52246	$\infty$	$\infty$	$\infty$	82159
KHA	1E-3	$\infty$	<b>1000</b>	<b>302</b>	<b>41</b>	<b>152</b>	<b>242</b>	<b>1364</b>	$\infty$	$\infty$
	1E-4	$\infty$	<b>1364</b>	<b>706</b>	<b>41</b>	<b>305</b>	<b>1376</b>	<b>2365</b>	$\infty$	$\infty$
	1E-5	$\infty$	<b>2183</b>	<b>4847</b>	$\infty$	<b>509</b>	<b>48599</b>	<b>3184</b>	$\infty$	$\infty$
	1E-6	$\infty$	$\infty$	$\infty$	$\infty$	<b>917</b>	$\infty$	<b>5004</b>	$\infty$	$\infty$
	1E-7	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	<b>25843</b>	$\infty$	$\infty$
MA	1E-3	$\infty$	$\infty$	82000	820	6150	13120	$\infty$	$\infty$	$\infty$
	1E-4	$\infty$	$\infty$	274700	820	12300	$\infty$	$\infty$	$\infty$	$\infty$
	1E-5	$\infty$	$\infty$	$\infty$	14760	22550	$\infty$	$\infty$	$\infty$	$\infty$
	1E-6	$\infty$	$\infty$	$\infty$	70520	38950	$\infty$	$\infty$	$\infty$	$\infty$
	1E-7	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$
CS	1E-3	41120	17820	7400	120	1700	7840	21780	16100	<b>11120</b>
	1E-4	84000	35460	11400	120	3700	25440	45540	<b>32700</b>	<b>20400</b>
	1E-5	<b>113760</b>	60660	59400	1240	5100	54240	76860	<b>52700</b>	<b>30640</b>
	1E-6	<b>135520</b>	$\infty$	<b>95400</b>	<b>2760</b>	6900	<b>96800</b>	111060	<b>71700</b>	<b>41200</b>
	1E-7	<b>157920</b>	$\infty$	<b>135000</b>	<b>4120</b>	<b>24700</b>	<b>144480</b>	151740	<b>90300</b>	<b>53040</b>

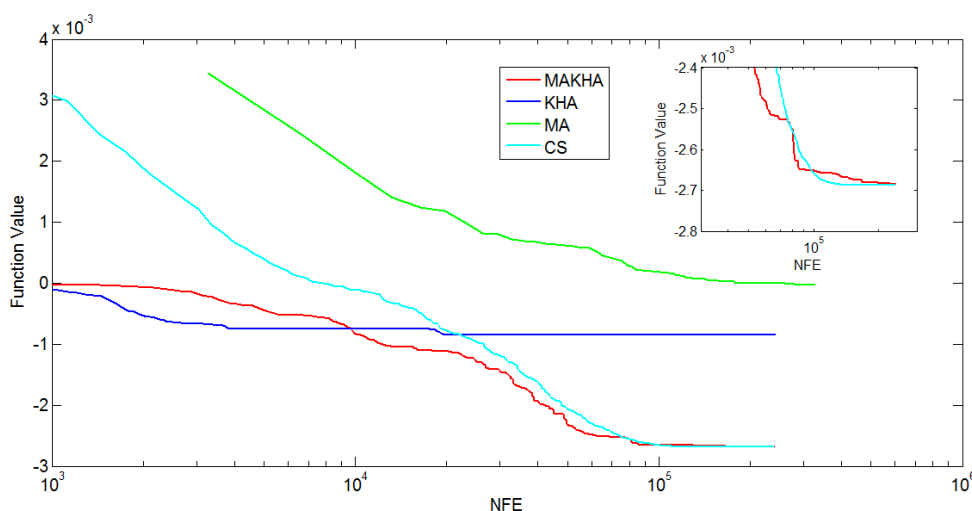


Fig. 2. The evolution of the mean best value calculated via the four metaheuristics versus NFE for problem T7

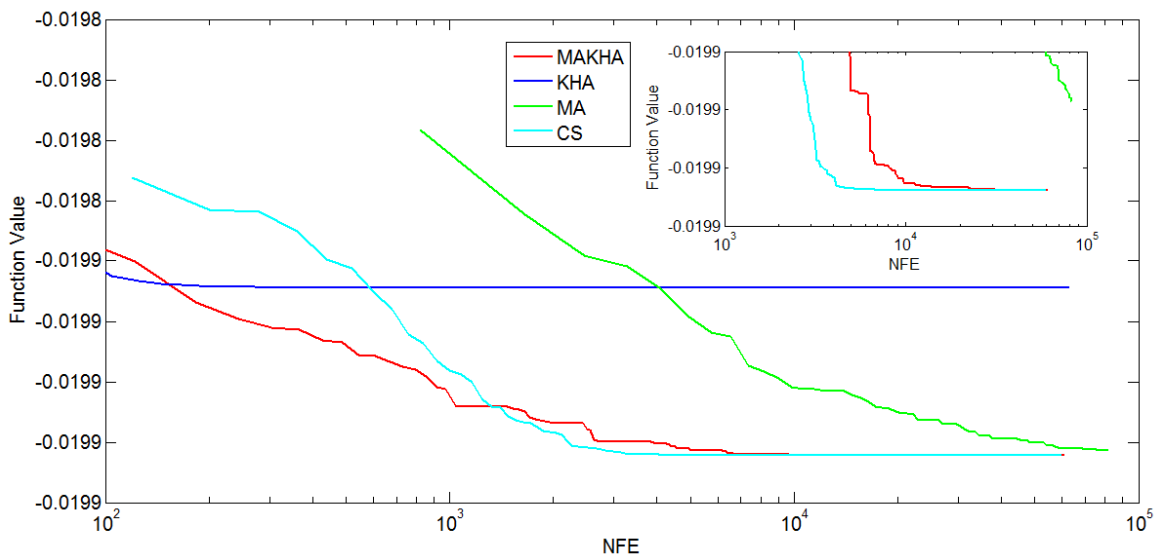


Fig. 3. The evolution of the mean best value calculated via the four metaheuristics versus NFE for problem G4

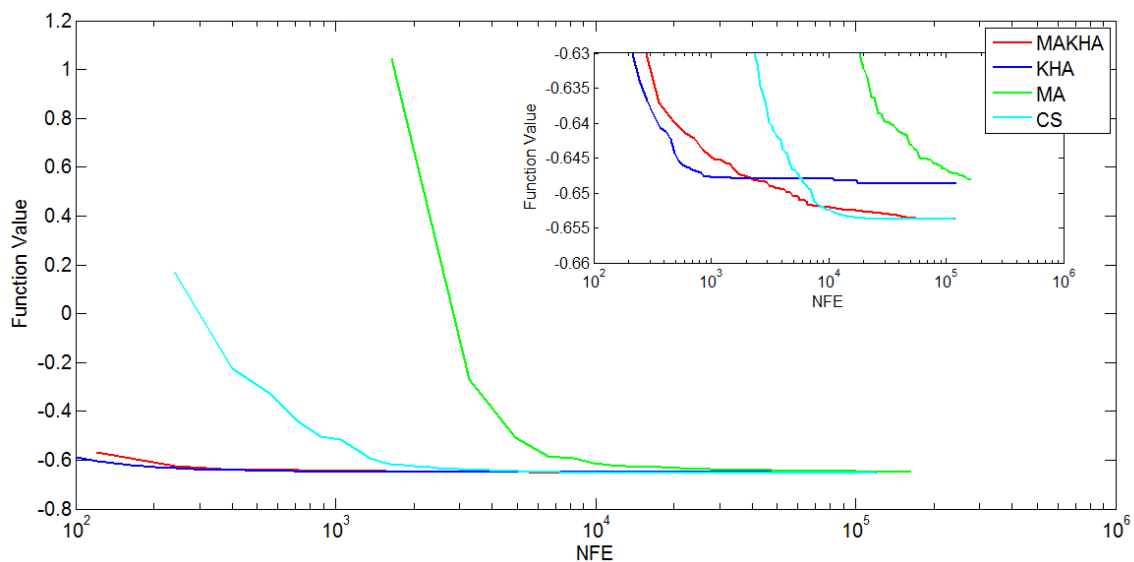


Fig. 4. The evolution of the mean best value calculated via the four metaheuristics versus NFE for problem R7