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Improving the Performance of a Catalytic Membrane Reactor via Stochastic Optimization

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Abstract – *Dehydrogenation of ethyl benzene and hydrogenation of nitrobenzene are coupled in the catalytic shell and tube membrane reactor to enhance the conversion and yield of the dehydrogenation reaction. The reactor system needs to be optimized to achieve the maximum benefit. Six process variables are selected as decision variables, which are; ethyl and nitrobenzene molar flow rate, pressure and temperature on shell and tube side. The flow rate of ethyl benzene can be considered as the effective variable on the nitrobenzene conversion and styrene yield. Optimization technique is the powerful tool to generate several new designs and sets of operating conditions. This reduces the risk of experimental runs and the expanded cost on the design and operation. The optimal operating conditions could enhance the yield of styrene within the range of (51 to 99.6%) and conversion of nitrobenzene within range of (35.7 to 79.6%) compared to the previous works which were within range of (49 to 98%) for styrene yield and (21 to 79%) for nitrobenzene conversion at the same range of operating conditions. For highly nonlinear membrane reactor, the global stochastic genetic optimization algorithm has been found more suitable than the deterministic methods. The reliability of the search can be increased by the adaption of the genetic operators.*

Keywords: *Genetic Algorithm, Membrane Reactor, Optimization*

I. Introduction

The demand for higher conversion, high yield and selectivity of the desired reaction products had led to new ingenious configuration and design of reactors. In this regards, multifunctional reactors where reactions combined with separation have received much attention [1]. Membrane reactors are one of such type of multi-functional reactors. A membrane reactor is a plug-flow reactor that contains an additional structure of some porous material within it.

This porous inner cylinder is the membrane that gives the membrane reactor its name**.** Membrane reactors are combined reaction with separation to increase conversion. Membrane reactors are commonly used in the dehydrogenation reactions where only one of the products (molecular hydrogen) is small enough to pass through the membrane.

This raises the ion for the reaction, making the process more economical. A catalytic membrane reactor (CMR) has a membrane that either has been coated with or is made of a material that contains catalyst, which means that the membrane itself participates in the reaction [2]. Hence the membrane reactor can be used to achieve conversions greater than the original equilibrium value [3].

The production of styrene from ethyl benzene is one of the process that can be held in (CMR) and although the high production of this type of reactor opportunities remain for further improvement of the productivity, electivity and yield of the process that can reduce costs and generate additional revenue using optimization. [4]

A number of earlier studies on the optimization of the styrene process were in fact single objective optimizations reported by Sheel and Crowe [5].

They used Rosenbrocks' multivariable search technique to optimize a profit function with steam temperature, steam rate, and bed length as the decision variables. The results show that existing reactors operation can be improved and that the performance of the steam-injected reactor is better than that of the adiabatic reactor.

In recent years, multiobjective optimization has a great attention. It includes the generation of multiple Pareto-optimal solutions that give the decision maker or expert a global perspective about trade-offs between conflicting objectives, the ability to optimize functions without requiring information about function derivatives [6]. Yee et al. [7] were the first to use multiobjective optimization to determine the optimal design and operating conditions for both adiabatic and steam-injected industrial styrene reactors.

They selected a non-dominated sorted genetic algorithm (NSGA) with productivity, selectivity, and yield as the objectives and four decision variables namely the temperature of ethyl benzene, steam to ethyl benzene ratio, pressure and initial molar flow rate of ethyl benzene.

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Babu et al. [8] also used multiobjective differential evaluation (MODE) algorithm to optimize the styrene reactor, and the results are compared with those obtained from the non-dominated sorting genetic algorithm (NSAG).The parato set based on the new algorithm was found to be much better than that obtained by the NSGA.

Abdollahi et al. [9] carried a multiobjective optimization of three radial flow reactors in series through an oxidative reheat process using the Levenberg-Marquardt algorithm.

The objective variables were the yield and selectivity of styrene. For catalytic membrane reactors, a multiobjective optimization problem was studied by Cheng e tal [10] for a methanol reactor and a hydrogen production reactor. The elitistNSGA-∏ algorithm was used to obtain the optimal solution. The problem was solved to evaluate the effect of key membrane characteristics like membrane thickness and membrane area per unit length. Gujarathi and Babu [11] reported another multiobjective optimization study of the adiabatic and steam-injected styrene reactors using MODE, with the temperature of steam going into the reactor as an additional decision variable. Their results indicated that some improvement was required in the MODE algorithm because it was unable to generate a pareto domain with a diverse set of non-dominated solutions in the case of the optimization of styrene yield and productivity.

Salim Fettaka [12] used the dual population evolutionary algorithm (DPEA) to circumscribe the pareto domain of two and three objective optimization case studies for three different configurations of the reactor: adiabatic, steam-injected and isothermal reactor model in styrene production. He found that the DPEA led to pareto domains for which the spread of each objective covers a wider range of values of non-dominated solutions compared to those reported by Yee et al. [7] and Babu et al. [8]

(Mousavi, et al., 2012) [13] proposed a A pseudo-homogeneous model with artificial neural network model to achieve the prof iles of ethyl benzene conversion, styrene yield and selectivity through the length of catalytic bed reactor. Good agreement was found between model results and industrial data

Also, mathematical models for predicting the fractional conversion of ethyl benzene and yields of products in a catalytic membrane reactor for the dehydrogenation of ethyl benzene were developed by Akpa, [4]. The mathematical models developed consisted of nonlinear simultaneous differential equations which were solved numerically using the 4 order Runge-kuta algorithm.

The models were subsequently used to simulate the effects of feed inlet temperature, feed molar ratio of steam and ethyl benzene and inlet pressure on the reactor performance. Aboghander et al [14] studied the optimization of auto thermal membrane reactor coupling the dehydrogenation of ethyl benzene to styrene with the hydrogenation of nitrobenzene to aniline.

The two conflicting objective functions, namely: the yield of styrene on the dehydrogenation side and the conversion of nitrobenzene on the hydrogenation side, are considered. The total number of the decision variables considered in the optimization problem is 12, representing a set of operating and dimensional parameters. The problem is solved numerically by two deterministic multiobjectives approaches: the normalized normal constraint (NNC) method and the normal boundary intersection (NBI) method. The resulting sets of pareto optimal solutions obtained by both techniques are shown to be identical.

I.1. Motivation and the Focus of This Work

The reactor system needs to be optimized to achieve the maximum objectives (nitrobenzene conversion and styrene yield). The reliability of an optimization process depends on the formulation of the objective functions, selection of the decision variables and the selection of the proper optimization search technique.

The present membrane reactor process is highly nonlinear so; the advanced stochastic genetic algorithm (GA) is more suitable than the deterministic methods that were used in previous work.

II. Description of the Process

In the present work, the dehydrogenation of ethyl benzene and hydrogenation of nitrobenzene are coupled in the catalytic shell and tubes membrane reactor (Fig. 1). The specifications of the reactor membrane are given in Table I.

Ethyl benzene is continuously dehydrogenated; styrene, hydrogen, and secondary products like benzene and toluene are produced. Hydrogen produced in the outer shell diffuses through the hydrogen-selective membranes to the inner compartment under the influences of the difference in hydrogen partial pressures on the two sides.

Inside the tubes, the diffused hydrogen encounters nitrobenzene and steam in the presence of the palladium catalyst, where it reacts in an irreversible exothermic hydrogenation reaction. Heat produced by this reaction was transferred from the tube compartment through the hydrogen-selective membrane walls to the shell compartment where it provides the endothermic heat of the dehydrogenation of ethyl benzene.

TABLE I
SPECIFICATIONS OF THE MEMBRANE REACTOR VOLUME

Shell side	Tube side
Net diameter=3.0 m	Diameter of tube=0.048 m
Cross-sectional area=3.0 m^2	Total cross section area=3.31 m^2
Length of reactor=4.0 m	Thickness of tube=0.003m
Number of shell=1	Number of tubes=1270
The shellis manufactured from carbon steel (304L) and the inner surface is coated with 30nm of F2O3.	The membrane tube is the composite wall having the stainless steel layer coated by the thin layer (20nm) of palladium. The thickness of hydrogen permeation is 20 nm.

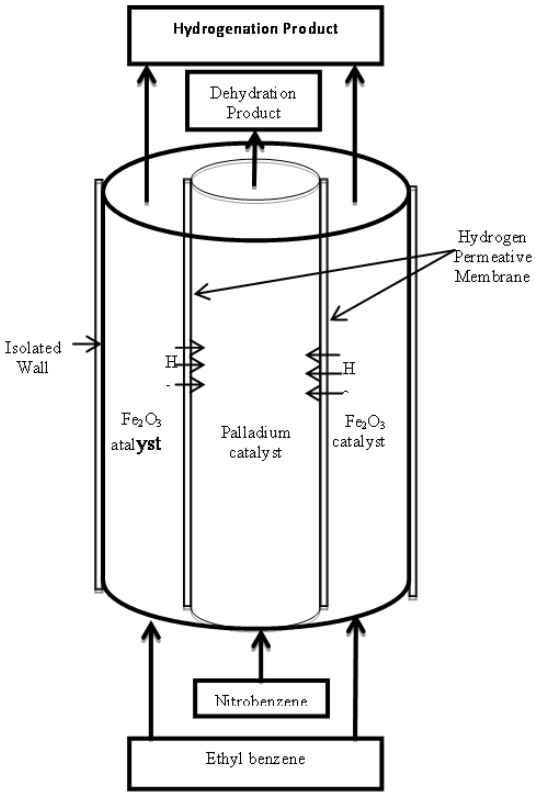

Fig. 1. Schematic diagram of auto thermal dehydrogenation/ hydrogenation catalytic membrane reactor

The transfer of hydrogen from the shell compartment to the tube compartment, while heat flows in the opposite direction, promotes the formation of more styrene.

The conversion of nitrobenzene and yield of styrene are calculated from the following equations:

Conversion of nitrobenzene (Xnb)=(Moles of nitrobenzene reacted per moles of nitrobenzene fed) (1)

or:

$$Xnb = (Nnbi - Nnbo)/ (Nnbi)$$

On the other hand:

yield of styrene (Yst) =(Moles of styrene produced per moles of ethylbenzene fed) (2)

or:

$$Yst = Nst/Neb$$

II.1. Formulating of the Objective Functions

In the present work six effective process variables are selected as decision variables based on Aboghander's results. Furthermore, if such optimization scheme is used for process control, these process variables can be used as manipulated variables rather than the design variables used by Aboghander [14].

These decision variables are:

1. Molar flow rate of ethyl benzene.
2. Feed temperature on shell side.
3. Feed pressure on shell side.
4. Molar flow rate of nitrobenzene.
5. Feed temperature on tube side.
6. Feed pressure on tube side.

The objectives have been correlated with these decision variables depending on the available data obtained by Aboghander [14]. By using the advanced nonlinear model estimation (Quasi-Newton method) with the aid of static program (version 10) the nonlinear empirical equations are obtained:

$$\text{Maximize } Xnb = 0.188\, Neb^{0.52}\, Ts^{-0.217} \cdot Ps^{-0.182} Nnb^{-0.5} Tt^{-0.222}\, Pt^{-0.037} \quad (3)$$

$$\text{Maximize } Yst = 0.043\, Neb^{-0.792} Ts^{0.343} Ps^{0.011} Nnb^{0.022} Tt^{0.343}\, Pt^{0.188} \quad (4)$$

where:

Ps, Pt: Pressure of component i on shell and tube sides, [bar].

Ts, Tt: Temperature on shell and tube sides, [K].

subject to inequality constraints:

$$\begin{aligned} 7.5 &\le Neb \le 11.0 \\ 776.0 &\le Ts \le 820.0 \\ 2.0 &\le Ps \le 4.0 \quad (5) \\ 0.0015 &\le Nnb \le 0.004 \\ 776.0 &\le Tt \le 820.0 \\ 0.7 &\le Pt \le 4.0 \end{aligned}$$

III. Results

The conflicting effect of the feed molar flow rate of ethyl benzene one of the styrene yield and nitrobenzene conversion is illustrated in Fig. 2.

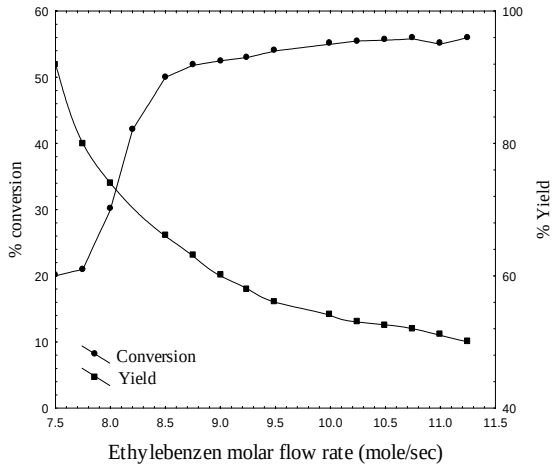

Fig. 2. Effect of ethyl benzene flow rate on yield of styrene and conversion of nitrobenzene

The styrene yield decreases with the ethyl benzene flow rate increase while the nitrobenzene conversion is increased. The effects of the dehydrogenation feed temperature (shell side) on styrene yield and nitrobenzene conversion are explained in Fig. 3.

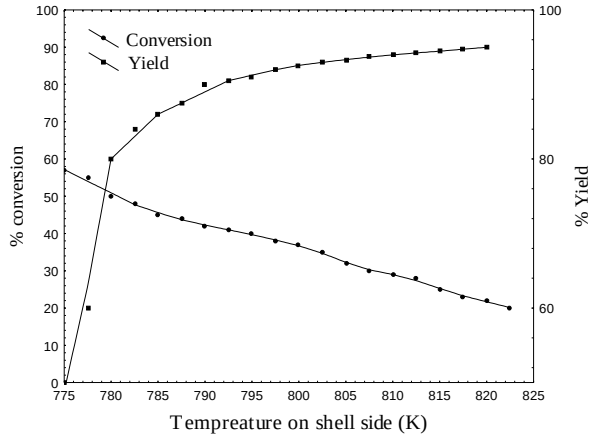

Fig. 3. Effect of feed temperature on shell side on yield of styrene and conversion of nitrobenzene

The temperature shows a conflicting effect on both objectives: as the feed temperature increases the styrene yield increases whereas the nitrobenzene conversion decreases. The feed pressure on the dehydrogenation side also shows a conflicting effect on both objectives as shown in Fig. 4. As the feed pressure increases, the styrene yield increases, but the nitrobenzene decreases.

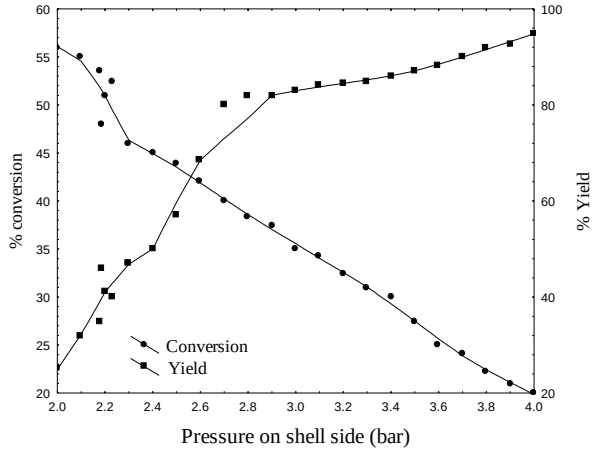

Fig. 4. Effect of feed pressure on shell side on yield of styrene and conversion of nitrobenzene

The effect of the feed molar flow rate of nitrobenzene on both objectives is plotted in Fig. 5. As the molar flow of nitrobenzene on the hydrogenation feed stream increases, the styrene yield increases. The effect of the feed temperature of the hydrogenation(tube) side on both objectives is the same as that of the dehydrogenation side and is plotted in Fig. 6. Fig. 7 illustrates the effect of the pressure of the hydrogenation (tube) side on the objectives. As the pressure increases the styrene yield increases while the nitrobenzene conversion decreases.

IV. Discussion

The yield decreasing of styrene with increasing flow rate of ethyl benzene shown in Fig. 2 is because when the molar flow rate of ethyl benzene increases, hydrogen is produced, then the side reactions become significant leading to reduce the product of styrene while the conversion of nitrobenzene on the other side of the membrane is increased as a result of increasing the hydrogen product.

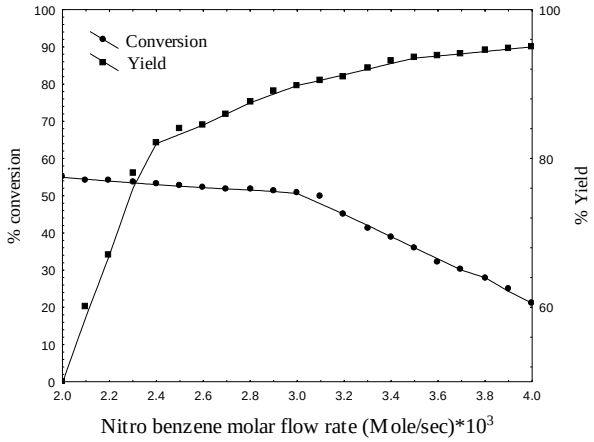

Fig. 5. Effect of nitrobenzene flow rate on yield of styrene and conversion of nitrobenzene

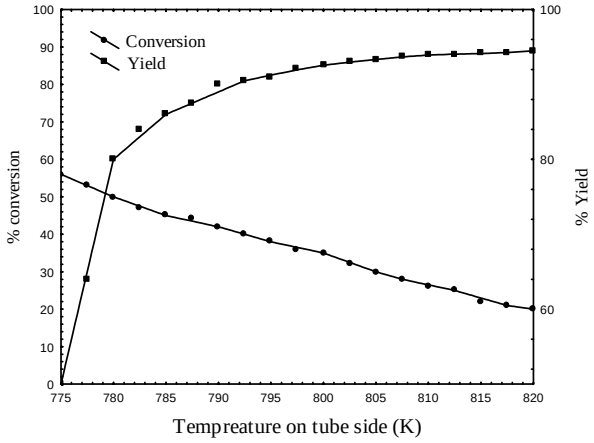

Fig. 6. Effect of feed temperature on tube side on yield of styrene and conversion of nitrobenzene

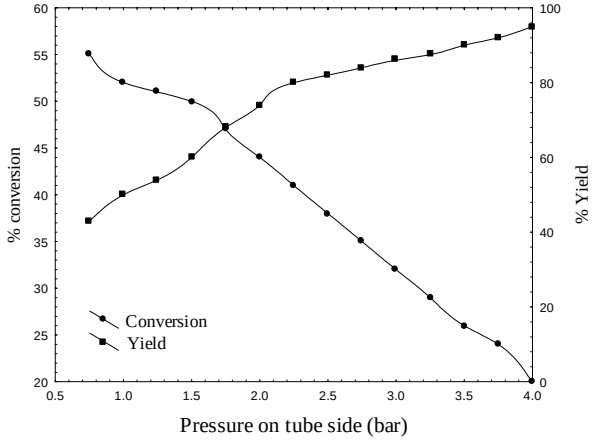

Fig. 7. Effect of feed pressure on tube side on yield of styrene and conversion of nitro benzene

Abogander [14] attributed the decreasing of yield of styrene to that as the molar flow rate of ethyl benzene increases, the rates of the side reactions become significant because their reaction rates are directly proportional to the partial pressure of ethyl benzene. The styrene yield approaches the limit of 93% when shell side temperature increase as shown in Fig. 3 because the forward reaction producing styrene is favors by high temperatures as well as the heat from the hydrogenation chamber transferred from the hydrogenation reaction. Although this phenomenon helps breaking the endothermality of the dehydrogenation side, producing a high styrene yield, it also creates a drop in temperature on the hydrogenation side, leading to low nitrobenzene conversion. The reduction of nitrobenzene conversion with increasing feed pressure occurs because increasing the feed pressure creates a significant driving force for the transfer of hydrogen from the dehydrogenation side to the hydrogenation side leading to higher styrene yields.

However, as the styrene is produced on the dehydrogenation side, the temperature drops, creating a significant temperature gradient between the two compartments and helping to transfer more heat from the hydrogenation side, which reduces the nitrobenzene conversion, similar results obtained with the work of Akpa [4].

Increasing the molar flow rate of nitrobenzene in the feed stream of the hydrogenation side leads to higher yield of styrene; this is because of large heat transfer between the two compartments. However, the heat transfer has a negative effect on the conversion of nitrobenzene as it reduces the temperature inside the tubes, causing the hydrogenation reaction to take place at a lower temperature.

Also, the increase of molar flow rate of nitrobenzene causes an unfinished reaction which reduces the nitrobenzene conversion [14]. As the temperature of the hydrogenation side increases, more heat is produced on this side due to the reaction.

However, the heat produced transfers across the membrane to break the endothermality inside the dehydrogenation side, resulting in a high styrene yield and a lower conversion of nitrobenzene due to a lower production of aniline on the hydrogenation side. The increase in rate of dehydration (endothermic reaction) is also shown by the work of Mousaive et al [13].

The intersection points between the conversion and yield curves, which appear in Figures 2-7, represent the local optimal values of the process. Equations (3) & (4) describe and confirm mathematically these effects of the decision variables on the objectives.

The negative sign of the power indicates to negative effect, while the positive sign indicates to positive effect on the objectives. The interaction between the decision variables is high as shown in equations (3) & (4). Also, one can conclude that molar flow rate of ethyl benzene is the effective variable on the conversion of nitrobenzene and yield of styrene.

GA is a global search algorithm based on mechanics of natural selection starting from population of points.

The multiobjective GA is implemented for the two conflicted functions (Eqs. (3) & (4)) with the inequality constraints (Eq. (5)). For more reliability; the operators of the GA (Table II) are adapted to obtain the best optimal results.

Fig. 8 shows the operators/results of the GA search. The solution has a range of optimal (pareto) results and generates (30) chromosomes. Each chromosome represents a possible solution to the problem and the population of chromosomes represents the set of the possible solutions [15].

However, 30 sets of new designs and operating conditions could be obtained for the membrane reactor. This can reduce the risk of experimental runs and the cost of the design and operation. The decision makers can select the appropriate one as shown in Table III.

The maximum values of objectives are; 79.6% for nitrobenzene conversion and 99.6% for the yield of styrene, while 80% and 70% of styrene yield and ethyel benzene conversion respectively gained using a mathematical model made by Akla [4]. The optimum results of the multiobjective technique can be improved regarding to the current operating conditions [16].

TABLE II
ADAPTED OPERATORS OF THE MULTIOBJECTIVE GA

Operator	Type and values
Population type	Double vector
Population size	80
Selection function	Tournament
Crossover function	Intermediate
Crossover fraction	0.7
Mutation function	Adaptive feasible
Migration direction	Both
Migration fraction	0.2
Hybrid function	Fgoalattain
Number of chromosome	30
Number of generation	175
Function tolerance	1.0E-6

TABLE III
SELECTED OPTIMAL/MAXIMUM VALUES

Decision variables	Optimal values	Optimal values
Molar feed of ethyl benzene(mole/s)	10.8	8.0
Feed temperature on shell side(K)	777.8	819.4
Feed pressure on shell side(bar)	2.2	3.8
Molar feed of nitrobenzene(mole/s)	0.002	0.003
Feed temperature on tube side(K)	777.3	818.6
Feed pressure on tube side(bar)	0.8	3.7
Maximum Objectives	NB conversion=0.796	ST yield=99.6

Since the objective functions (Eqs. (3) & (4)) are highly nonlinear then the number of generations is high, which is equal to (175) as explained in Table II.

The optimal values of process variables enhance the performance of the membrane reactor as shown in Table III.

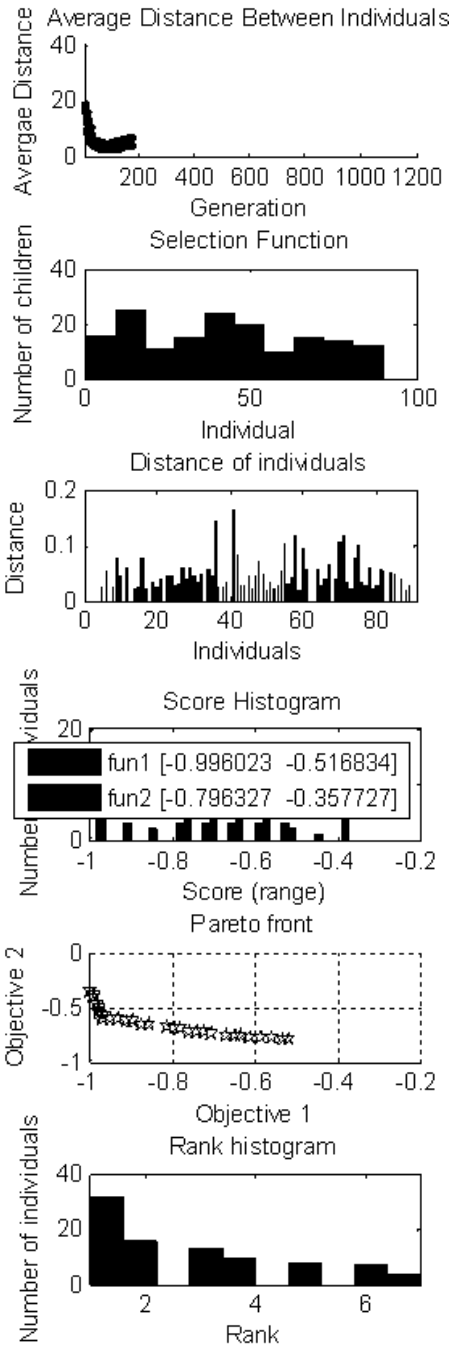

Fig. 8. Results/solutions of multiobjective genetic algorithm

The optimization results have reasonable improvements when compared with that of the previous work that used the deterministic methods as shown in Table VI. Also, comparing the optimum values in Table III with other workers, Mousavi, et al [13] stated that the inlet temperature between 850 °C to 950 °C is the best temperature to get the highest conversion and selectivity in his mathematical model.

The success of the present optimization technique depends on the good formulation of the objective function, best selection of the decision variables and the selection of the appropriate operators of the GA [17].

TABLE VI
COMPARISON WITH THE PREVIOUS WORK

Author	Optimization method	Nitro benzene conversion	Styrene yield
Aboghander etal.2010	Multiobjective (NNC&NBI)	0.211-0.796	0.49-0.98
Present work	Multiobjective GA	0.357-0.796	0.51-0.996

V. Conclusion

This paper presented the global stochastic multiobjective genetic algorithm as a method for the optimization of multiple conflicting design objectives of a catalyst membrane reactor of styrene production. The objectives were the maximization of the styrene yield and nitrobenzene conversion. It was found that this method led to a pereto of 30 set of new designs and operating conditions for this membrane reactor. The maximum values of objectives are; 79.6% for nitrobenzene conversion and 99.6% for the yield of styrene. The selection of process variables as decision variables is more reasonable than that of the design variables, in this method the molar flow rate of ethyl benzene has been found the effective decision variable in the hydrogenation and dehydrogenation side.In order to compare our proposed method with previously published results [14], the multiobjective GA gives reasonable improvement in styrene yield and nitrobenzene conversion.

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