Modeling of a reaction network and its optimization by genetic algorithm

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Abstract

Continuous endeavors are going on in many research works to find out the strategy to mathematically model and optimize complex reaction networks in order to maximize the main product and at the same time keeping the reactor dimensions within some acceptable limits. The aim of this work is to provide with a strategy for efficient modeling and optimization of reaction networks for reaction controlled processes. Genetic algorithm (GA) has been used for optimizing complex search spaces with multiple optima. Formation of styrene monomer from the ethylbenzene dehydrogenation, with several by-products in a fixed bed reactor, is taken as an example for this study. Two activation energies are found to be the best in term of maximizing styrene productivity.
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1. Introduction

Most of the times, a chemical product is generated out of a reaction network where more than one reaction occurs in parallel. Out of these reactions, only one reaction leads to the main product while the others lead to byproducts. While handling this kind of complex reaction network, one, therefore, can aim to find out permissible (meaning easy to implement in the process and economically feasible) operating conditions that can ensure maximum yield of the desired product. Dehydrogenation of ethylbenzene forms the styrene as the major product with mainly benzene and toluene as byproducts. The aim of this work is to find out permissible operating conditions for which styrene formation reaction network gets optimized in terms of the yield of the desired product keeping other operational constraints within the given bounds.

Modell [1] provides a very useful review about the total process and other valuable information related to process modeling like kinetic parameters, adsorption parameters etc. Carra and Forni [2] and Wenner and Dybdal [3] give some valuable experimental data that are very useful for validating model performance. Savoretti et. al. [4] represents some recent works on the related fields from which some valuable

information about the reactor design issues can be obtained. In terms of information about styrene formation from ethylbenzene and some relevant data, some other works are also very useful (Hermann et. al. [5], She and Ma [6], Bohm and Wenske [7]). From the above mentioned earlier works, some obvious lacunas are found as: (a) linearization of non-linear equations leading to high truncation errors while solving the ordinary differential equations (ODEs), (b) no attempt in reducing the number of the equations for better numerical accuracy, (c) lack of parametric sensitivity analysis for relatively uncertain parameters, (d) little consideration of process constraints, (e) tuning requirements of penalty parameters while using penalty function methods for handling constraints and (f) unavailability of proper optimization techniques (techniques used so far are known to get trapped into a local optima when the complicated objective function gives rise to multi-modality) and (g) inability in capturing many competitive peaks simultaneously in a functional space (objective function) of a multimodal function. In this present effort, linearization is avoided and the number of equations has been reduced for better numerical stability. For uncertain data like variations of activation energies for benzene and toluene, sensitivity analysis has been done to provide a gross idea about their effect on process performance. Throughout this work, an attempt has been made to work with industrial information as close as possible. As an example, overall conversion of ethyl-benzene has been used

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Nomenclature

A	cross sectional area of the reactor
b_i	adsorption coefficient ith component
b_{oi}	frequency factor for the ith component (1/atm)
E_i	activation energies for ith component
$E^{(i)}$	activation energy of ith chromosome
E^U, E^L	upper and lower limits for styrene activation energy
F	flow rate of reactants (kg mole/h)
$F^{(i)}$	fitness of ith chromosome
K_1	equilibrium constant for styrene formation
K_i	kinetic constants for ith component (kg mole/s kg$_{catal}$)
L	catalyst bed length (m)
L^U, L^L	upper and lower limits for reactor bed length
L_{Str}	length of binary strings for each of the decision variables
L_{Chr}	total length of a chromosome ($N_{Str} \times L_{Str}$)
N_{Str}	number of strings (equivalent to number of decision variables)
N_{Pop}	number of chromosome population in a generation
N_{Gene}	total number of binary zeros or ones in a generation ($L_{Chr} \times N_{Pop}$)
N_{Gen}	generation counter
$N_{Gen,max}$	number of maximum generation for convergence of the algorithm
P	total pressure
P_i	partial pressure for ith component (atm)
p_c	crossover probability
p_m	mutation probability
r_i	reaction rates for ith component (kg mole/s kg$_{catal}$)
$S^{(i)}$	ith string in a chromosome
SE	steam to ethylbenzene ratio
T	temperature in K
$T^{(i)}$	operating temperature of ith chromosome
T^U, T^L	upper and lower limits for operating temperature
X_i	conversions for ith component
Y_{EO}	initial ethylbenzene mole-fraction for the SE value 3.0
ϕ	overall conversion of ethylbenzene
ϕ^U, ϕ^L	upper and lower limits for overall conversion
ρ	density of bulk catalysts (kg/cu m)

as a constraint in our work. Industrial information say that 55–65% of conversion is available in actual process conditions. So an intentional attempt has been made to keep this range in between 50 and 75% and thus this parameter is used as a constraint fully defined by user. Genetic algorithm based optimization helped in extracting more features (e.g. finding simultaneously two suitable activation energies for styrene) in a multimodal search space as well as takes care of other lacunae mentioned earlier. Application of GA in styrene formation process (kinetic modeling) is definitely an advanced feature of this work.

In the first phase, modeling of the entire reactive system has been performed with the required considerations of kinetic constants, activation energies, adsorption coefficients, volume change etc. The reaction is assumed to take place on a fixed bed reactor with catalyst inside. The modeling exercise gives rise to some highly non-linear ODEs that can work within certain operating ranges. A Runge–Kutta type numerical scheme has been used to solve these non-linear ODEs. A large effort has been given to identify the actual operational zone in which model equations can work efficiently. The model predictions are tallied with some published data (simulated as well as experimental) from literature and found that the results are in good agreement.

In the second phase, the reaction network has been optimized with proper consideration of process constraints. Most of the earlier works use optimization techniques that suffer from the inherent problem of providing the initial guesses to the optimization algorithms to start with and constraints are handled using penalty function methods that itself suffer from the problem of tuning of penalty parameters. If the starting solution is guessed wrongly, these techniques converge to a completely deceiving trap of local optima and if the penalty parameter is not tuned properly, the optimization algorithms lead to a solution that is often not the true optimum. GA based evolutionary techniques are generally designed in such a manner that can take care of the problems stated earlier. Moreover, it is observed in many earlier works (e.g. Modell [1]) that selection of constraints is kept little flexible leading to further scope of optimization in this kind of reaction networks. In the methodology adopted here, activation energies and operating temperatures are taken as decision variables to find the suitable catalysts (in terms of activation energies) for which styrene productivity is maximum with an acceptable catalyst bed length and overall conversion.

1.1. About the process

In a fixed bed catalytic reactor, energy needed for the reaction is supplied by superheated steam (at about 720 °C). A stream of vaporized ethylbenzene also enters with the steam. Typically 2.5–3.0 kg of steam are required for each kilogram of ethylbenzene. Ethylbenzene conversion is typically 60–65% and styrene selectivity is greater than 90%.
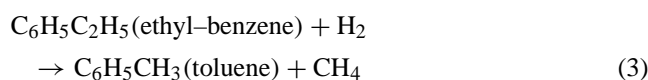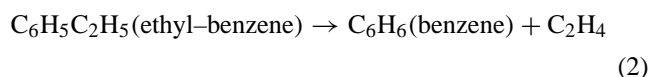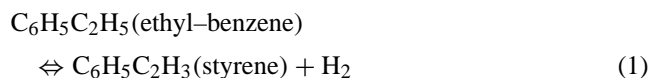
The three significant byproducts are toluene, benzene and hydrogen.

2. Formulation

2.1. Modeling aspects

2.1.1. Reactions
The main kinetic system can be described as

$$C_6H_5C_2H_5 (ethyl-benzene)$$
$$\Leftrightarrow C_6H_5C_2H_3 (styrene) + H_2 \qquad (1)$$

$$C_6H_5C_2H_5 (ethyl-benzene) \rightarrow C_6H_6 (benzene) + C_2H_4 \qquad (2)$$

$$C_6H_5C_2H_5 (ethyl-benzene) + H_2$$
$$\rightarrow C_6H_5CH_3 (toluene) + CH_4 \qquad (3)$$

2.1.2. Process and related issues
Data given by Bohm and Wenske [7], Carra and Forni [2] and Modell [1] with tubular reactors reveals that the rate is surface reaction controlled, adsorption and desorption are nearly in equilibrium and mass transfer is not the rate controlling process. Those papers has also shown very clearly that for total pressure more than 1 atm, partial pressure of ethylbenzene has little effect on the reaction kinetics. It has been observed that the reaction rate is increased by the order of 2 by changing the total pressure from 1 to 11 atm. Steam to ethylbenzene ratio is very important parameter as in high ratio, ethylbenzene gets diluted enough to cut the productivity and in low ratio, carbon poisoning of catalysts occurs. Actually steam reacts (water gas reaction) with deposited carbon to inhibit the probable poisoning. A study is made to see the effect of different equilibrium conversion of styrene with different steam to ethylbenzene ratio (SE ratio) as shown in the Fig. 1. From this figure it can be concluded that for a given temperature, there is higher styrene production for higher SE ratio or, in the other way, to obtain a constant conversion of styrene, lower temperature is required for higher SE ratio. In this context, a SE value of 3.0 has been chosen as it is widely used in most of the commercial processes. Some experiments showed [3] that the pressure drop is normally very less, therefore the pressure drop is neglected and a constant atmospheric pressure is assumed.

2.1.3. Equilibrium conversion
In order to bound the simulation with an upper theoretical limit as a theoretical as well as practical guidance, equilibrium styrene conversion is of great importance to be an upper limit. The equilibrium conversion can be expressed as follow [8]:

$$X_{1eq} = \frac{SE \pm [SE^2 + 4(1 + P/K_1)(1 + SE)]^{0.5}}{-2(1 + P/K_1)}; \qquad (4)$$
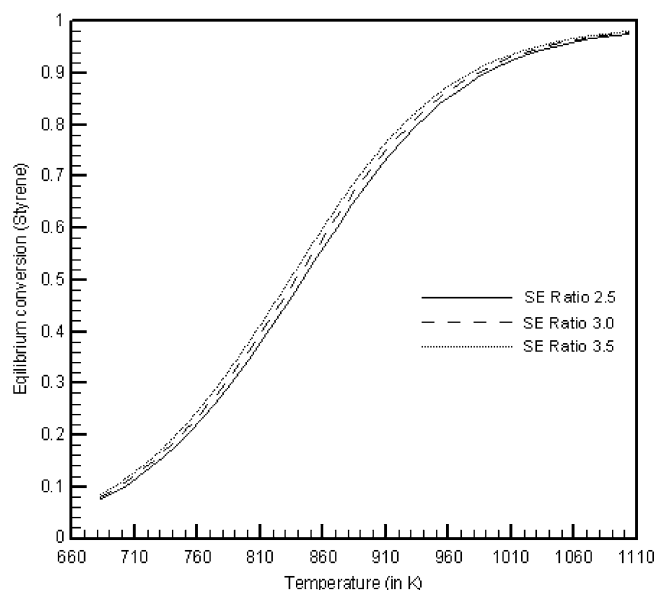

Fig. 1. Equilibrium conversion of styrene with temperature for different values of steam to ethylbenzene ratio (SE).

where

$$\log_e K_1 = 16.12 - \frac{15350.0}{T}$$

While simulating the reaction network for an activation energy and operating temperature, the upper value of the overall ethylbenzene conversion is almost same as X_{1eq} with an assumption that at equilibrium conversion level of styrene, other by-products are having almost zero concentrations.

2.1.4. Adsorption parameters
Modell [1] provides, the expressions of adsorption coefficients. The expressions are

$$b_E = 1.3363 \times 10^4 \times \exp - \frac{(-36.8195 + 0.05405 \times T)}{RT}; \qquad (5)$$

$$b_S = 1.0730 \times 10^5 \times \exp - \frac{(-36.8195 + 0.05405 \times T)}{RT}; \qquad (6)$$

where, the units of these coefficients are 1/atm. It is assumed that the heat of adsorption of styrene and ethylbenzene are equal. It has been found as well as theoretically perceived that the change in b_E with respect to the change in b_S is almost insensitive to temperature.

2.1.5. Kinetic parameters
The expressions of rate constants are in the Arrhenious form $k_i = k_{0i} \exp(-E_i/RT)$, where k_{0i} is the frequency factor and E_i is the activation energy. Mathematically k_1–k_3,

the kinetic constants for styrene, benzene and toluene reactions, respectively, are expressed as follows:

$$k_1 = 1.8191 \times 10^8 \times \exp\left(\frac{-191755.44}{RT}\right), \tag{7}$$

$$k_2 = 1.4901 \times 10^8 \times \exp\left(\frac{-212689.44}{RT}\right), \tag{8}$$

$$k_3 = 10.7737 \times 10^8 \times \exp\left(\frac{-91272.44}{RT}\right), \tag{9}$$

where, the units of those constants are g mole/min^{-1} g$_{catal}$.

Carra and Forni [2] have specified a type of catalyst that has 191755.44, 212689.44, 91272.24 (KJ/kg mole) as the activation energies for the styrene, benzene and toluene, respectively. From the kinetic constants, it can be concluded that styrene is the major product with respect to other products like benzene and toluene. But with the increase in temperature, the styrene productivity also increases, as the reaction is endothermic in nature. But one can't increase temperature to a large extent, as in higher temperatures, catalyst sintering may occur with a probable increase in byproduct concentrations. Typical temperature range in the commercially operating processes is 875.0–925.0 K.

2.1.6. Activation energies

Activation energies are one of the most uncertain parts of any analysis for styrene monomer formation, due to unavailability of experimental data. From Carra and Forni [2], Wenner and Dybdal [3], different sets of styrene activation energies with different frequency factors can be obtained which in turn shows the different variations of kinetic parameters for styrene reactions. Those different sets of activation energies with different frequency factors are useful enough to have an optimization search in those segments. A polynomial has been formed for the estimation of frequency factors (with respect to activation energies) in between few experimentally available data for activation energies and frequency factors. The activation energy range used in the simulations for styrene is 46055.0–238647.0 (KJ/kg mole) and the values of that for the benzene and toluene are 212689.44 and 91272.24 (KJ/kg mole), respectively.

2.1.7. Rate equations

From the equations, one can get the rate expressions for a surface reaction controlled process. The styrene reaction is a largely reversible one and all other reactions are largely irreversible reactions. As styrene is the major component, it can be assumed with no doubt that overall conversion can't be as high as 100% due to the reversible nature of styrene formation. The net rate expressions are

$$r_1 = \frac{k_1 b_E (P_E - P_H P_S / K_1)}{1 + b_E P_E + b_S P_S} \text{ (for styrene)} \tag{10}$$

$$r_2 = \frac{k_2 b_E P_E}{1 + b_E P_E + b_S P_S} \text{ (for benzene)} \tag{11}$$

$$r_3 = \frac{k_3 b_E P_E}{1 + b_E P_E + b_S P_S} \text{ (for toluene)} \tag{12}$$

where $K_1 = 16.12 - (15350.0/T)$; $K_1 \geq$ equilibrium constant;

$$P_{E0}\left[\frac{1 - (X_1 + X_2 + X_3)}{1 + \varepsilon(X_1 + X_2) + \varepsilon' X_3}\right]$$

$$P_H = P_{E0}(X_1 - X_3)$$

$$P_S = P_{E0} X_1$$

$$P_{E0} = P_0 y_{E0}$$

From stoichiometry, $\varepsilon = y_{E0}\partial$ (for reaction of styrene and benzene) and $\varepsilon' = 0.0$ (reaction for toluene; $\varepsilon' = y_{E0}\partial'$); these values are responsible for volume changes in the reactions.

$P_0 = 1.0$ atmosphere and all other pressures are the partial pressure of the respective components; y_{EO} = initial ethylbenzene mole-fraction for the SE value 3.0.

Subscripts E, H, S are for ethylbenzene, hydrogen and styrene, respectively.

Overall conversion is presented as $\phi = X_1 + X_2 + X_3$.

2.1.8. Mathematical modeling and solution

The process is a plug flow process with a catalyst bed length L. Thus the material balance results in three different equations for styrene, benzene, toluene and they are

$$\frac{dX_1}{dL} = \rho \frac{A}{F} r_1 \tag{13}$$

$$\frac{dX_1}{dL} = \rho \frac{A}{F} r_2 \tag{14}$$

$$\frac{dX_1}{dL} = \rho \frac{A}{F} r_3 \tag{15}$$

where ρ represents bulk density of the catalyst, A the cross sectional area of the reactor and F the ethylbenzene flow rate in. But one can see that the length, as a parameter, is not suitable for the equations as it is dependent on temperature as well as overall conversion. Thus overall conversion is a good independent variable to work with.

As $\phi = X_1 + X_2 + X_3$, it can be written like

$$\frac{dL}{d\phi} = \frac{F}{A\rho}\left(\frac{1}{r_1 + r_2 + r_3}\right). \tag{16}$$

Now

$$\frac{dX_1}{d\phi} = \frac{dX_1}{dL}\frac{dL}{d\phi} = \frac{r_1}{r_1 + r_2 + r_3}; \tag{17}$$

Similarly

$$\frac{dX_2}{d\phi} = \frac{r_2}{r_1 + r_2 + r_3} \tag{18}$$

$$\frac{dX_3}{d\phi} = \frac{r_3}{r_1 + r_2 + r_3}. \tag{19}$$

Table 1
Range of variance of temperature over the activation energies

Activation energy of styrene (KJ/kg mole)	Temperature range (K)
46055–87923	800–910
87923–125604	800–930
125604–238647	800–1000

Replacing r_1, r_2, r_3 with their respective expressions, last three equations result in highly nonlinear and mathematically complicated form. Actually X_2 can be expressed as $[\phi - (X_1 + X_3)]$ and replacing that in Eqs. (1) and (3), one can get only 2 equations instead of 3. After solving two

equations with respect to ϕ and different operating as well as system conditions, two variables like X_1 and X_3 can be evaluated. From X_1, X_3 and a value for a specific ϕ, X_2 value can be computed in a straightforward manner. For the complicated equations, reduction of the number of equations is always proved to be beneficial in terms of computational ease and accuracy.

The system of ODEs is solved by a RK type explicit technique. Walas [9] gives a short but well documented description about this method. During solving, a lot of effort has been given to identify the data domain where the model is more reliable as it is a hard truth that almost no model is valid for the entire domain of operations. After a detail

Table 2
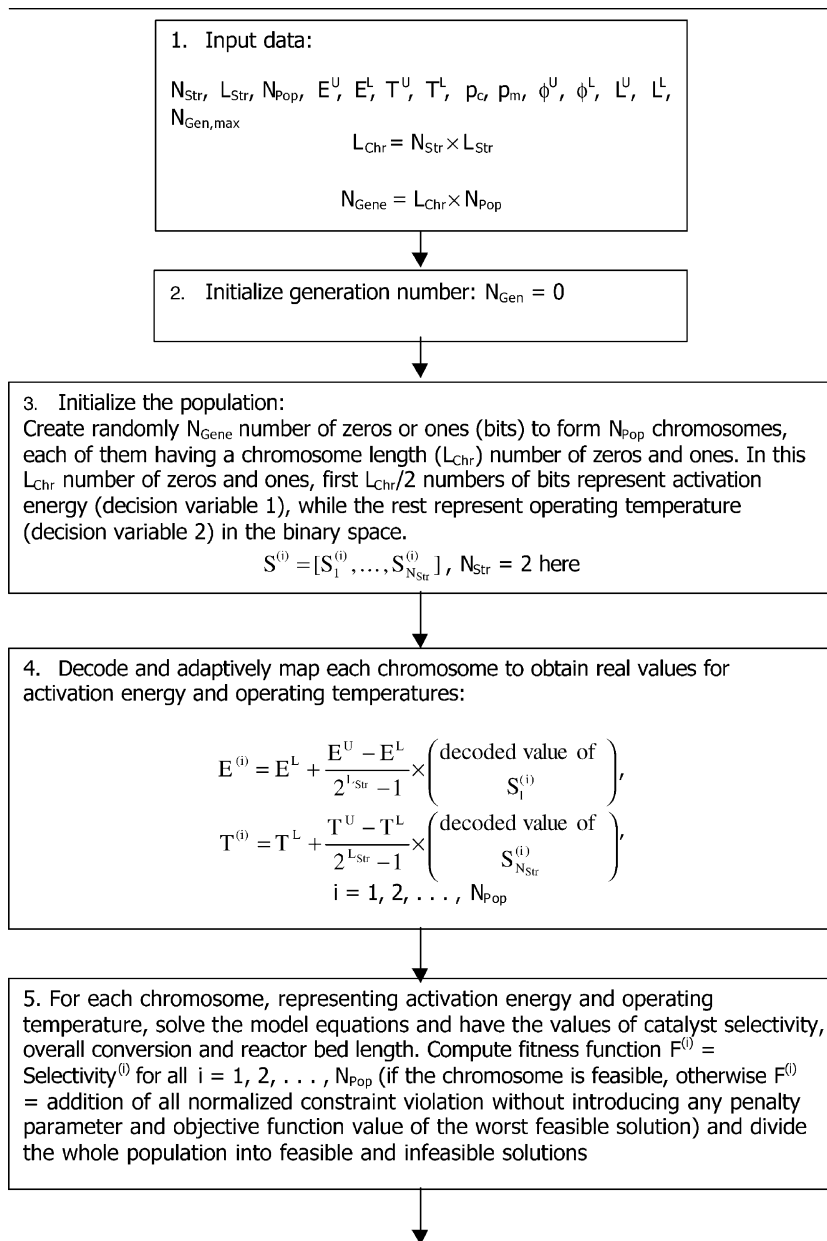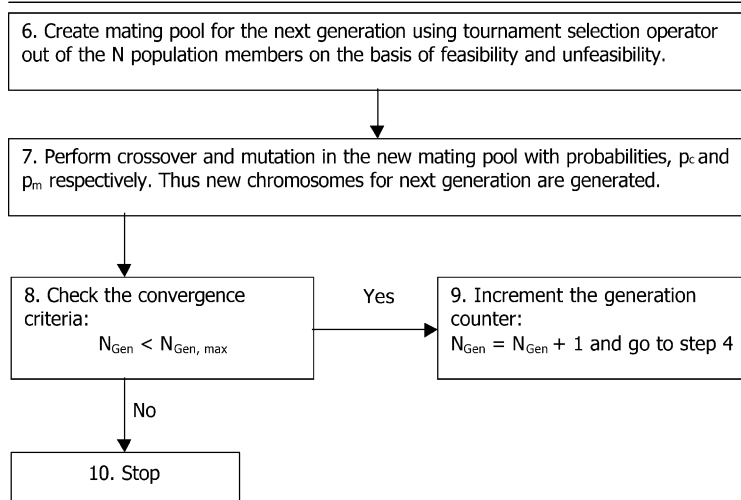Flowchart stating the working principle of binary GA

1. Input data:

N_{Str}, L_{Str}, N_{Pop}, E^U, E^L, T^U, T^L, p_c, p_m, ϕ^U, ϕ^L, L^U, L^L, $N_{Gen,max}$

$$L_{Chr} = N_{Str} \times L_{Str}$$

$$N_{Gene} = L_{Chr} \times N_{Pop}$$

2. Initialize generation number: $N_{Gen} = 0$

3. Initialize the population:
Create randomly N_{Gene} number of zeros or ones (bits) to form N_{Pop} chromosomes, each of them having a chromosome length (L_{Chr}) number of zeros and ones. In this L_{Chr} number of zeros and ones, first $L_{Chr}/2$ numbers of bits represent activation energy (decision variable 1), while the rest represent operating temperature (decision variable 2) in the binary space.

$$S^{(i)} = [S_1^{(i)}, \ldots, S_{N_{Str}}^{(i)}], \; N_{Str} = 2 \text{ here}$$

4. Decode and adaptively map each chromosome to obtain real values for activation energy and operating temperatures:

$$E^{(i)} = E^L + \frac{E^U - E^L}{2^{L_{Str}} - 1} \times \left(\begin{array}{c} \text{decoded value of} \\ S_1^{(i)} \end{array} \right),$$

$$T^{(i)} = T^L + \frac{T^U - T^L}{2^{L_{Str}} - 1} \times \left(\begin{array}{c} \text{decoded value of} \\ S_{N_{Str}}^{(i)} \end{array} \right),$$

$$i = 1, 2, \ldots, N_{Pop}$$

5. For each chromosome, representing activation energy and operating temperature, solve the model equations and have the values of catalyst selectivity, overall conversion and reactor bed length. Compute fitness function $F^{(i)} = $ Selectivity$^{(i)}$ for all $i = 1, 2, \ldots, N_{Pop}$ (if the chromosome is feasible, otherwise $F^{(i)}$ = addition of all normalized constraint violation without introducing any penalty parameter and objective function value of the worst feasible solution) and divide the whole population into feasible and infeasible solutions

Table 2 (*Continued*)

6. Create mating pool for the next generation using tournament selection operator out of the N population members on the basis of feasibility and unfeasibility.

7. Perform crossover and mutation in the new mating pool with probabilities, p_c and p_m respectively. Thus new chromosomes for next generation are generated.

8. Check the convergence criteria:

$N_{Gen} < N_{Gen, max}$

Yes

9. Increment the generation counter:

$N_{Gen} = N_{Gen} + 1$ and go to step 4

No

10. Stop

simulation study, it has been found that model is giving good results in the ranges given in Table 1.

2.2. Optimization aspects

Genetic algorithms (GAs) belong to the family of the optimization techniques that are inspired by the living nature. From the optimization point of view, they represent the random search techniques with a better kind of post search activities. They are robust in nature and applicable to wide range of problems. They are far away from the different kind of problems faced by traditional techniques while optimizing a system such as technique specific initial guess dependency, numerical as well as machine error while handling different orders of differentials, applicability only for either continuous or discrete optimization problems etc. Even GAs can converge in cases for which classical solutions come up with the problem of instability or do not converge at all. If the objective function space is multi-modal in nature, as found in case of most real world problems, it is very much advisable to use robust techniques like GAs for finding the global optimum as well as for finding multiple optima simultaneously.

The problem addressed in the present work can be formulated in the standard nonlinear programming (NLP) problem as follows:

$$\text{Max}_{E,T} \quad S$$
$$\phi^{L} \leq \phi \leq \phi^{U}$$
$$L^{L} \leq L \leq L^{U}$$
$$E^{L} \leq E \leq E^{U}$$
$$T^{L} \leq T \leq T^{U}$$

other mass balance equations

where, ϕ, L, E, T are overall conversion, catalyst bed length, activation energy and operating temperature, respectively

and superscript L and U denote the lower and upper limits of the above mentioned variables. In words, the selectivity of styrene (in presence of all other by-products i.e. toluene and benzene) is maximized for a set of activation energy and operating temperature while keeping the reactor bed length and overall conversion of the reaction network within specified upper and lower limits. Catalyst bed length and overall conversion are termed as constraints where as activation energy and operating temperatures are known as decision variables. An external user can provide the physical limits for these constraints as well as decision variables. The solution of the single objective optimization problem described above is obtained by adapting the binary coded GA. Details of this algorithm can be found in literature (Goldberg [10], Deb [11–13], Mitra et. al. [14]). A flowchart describing the working principle of GA is given in Table 2.

3. Results and discussions

The present work can cater two types of requirements: (1) one set of people who are having a catalyst with them, may require a change in operational parameters and/or change in catalyst bed length; (2) another set of people who may demand for the new catalyst with all new operating and design parameters.

First the model performance has been validated with experimental results of Carra and Forni [2], analysis of Modell [1] and they are in excellent numerical agreement (Table 3). This finding proves the validity of the model in the formation of styrene monomer.

Knowing that the model is very nonlinear, a contour is plotted (Fig. 2) to see the variability of product selectivity with activation energy and operating temperature. This plot clearly shows that, there are basically two activation energy candidates (one of the order of 124766 while the other is of

Table 3
Comparison of model accuracy with the available literature data

For the activation 191755.0 KJ/kg mole and temperature 985.5 K with
   60% overall conversion of ethylbenzene
   Modell analysis   Present analysis
     Selectivity (styrene): 92.86   Selectivity (styrene): 93.2
     Catalyst bed length (m): 0.02   Catalyst bed length (m): 0.02

For the activation 124766.0 KJ/kg mole and temperature 865.8 K with
   60% overall conversion of ethylbenzene
   Modell analysis   Present analysis
     Selectivity (styrene): 92.46   Selectivity (styrene): 91.95
     Catalyst bed length (m): 0.38   Catalyst bed length (m): 0.40

For the activation 233623.0 KJ/kg mole and temperature 933.0 K with
   60% overall conversion of ethylbenzene
   Modell analysis   Present analysis
     Selectivity (styrene): 93.61   Selectivity (styrene): 93.2
     Catalyst bed length (m): 0.066   Catalyst bed length (m): 0.069

For the activation 191755.0 KJ/kg mole and temperature 903.0 K with
   36% overall conversion of ethylbenzene
   Carra and Forni analysis   Present analysis
     Selectivity (styrene): 92.5   Selectivity (styrene): 92.8
     Catalyst bed length (m): NA   Catalyst bed length (m): 0.06

the order of 191755 in KJ/kg mole) that can get selected in the optimization study. Further the plot shows that for a lower temperature range, higher activation energy gets preference over the lower one whereas with increase in temperature, the situation starts behaving conversely. This becomes clearer by following the optimization results provided in the Table 4. These two peaks (one present at activation energy 124766 while the other is at 191755) are very competitive with each other. Any optimization technique that uses the optimization routine using some initial guess can be completely deceived by this terrain. Due to the sheer advantage of population based search procedure, GA is able to converge to the global optimum. The following data is used to run the GA based routines:

$$\phi^L = 55.0\%; \; \phi^U = 75.0\%; \; L^L = 0.001 \, \text{m}; \; L^U = 0.50 \, \text{m};$$

$$E^L = 46050.0 \, \text{KJ/kg mole}; \quad E^U = 238650.0 \, \text{KJ/kg mole};$$
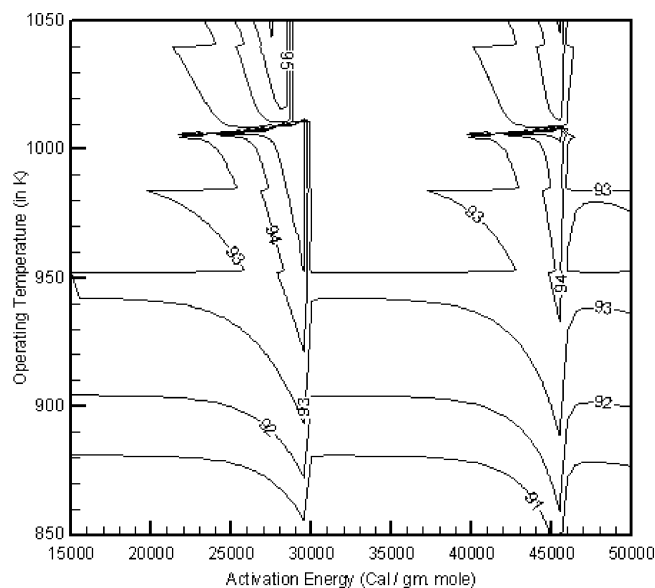$$T^L = 800.0 \, \text{K}; \; T^U = 1050.0 \, \text{K};$$

Fig. 2. Contour plot of styrene selectivity (%) over the optimizing range of operating temperature and activation energy.

$$N_{\text{Str}} = 2; \; L_{\text{Str}} = 25; \; N_{\text{Pop}} = 1000; \; p_c = 0.9;$$
$$p_m = 0.01 \; N_{\text{Gen,max}} = 1000$$

It is to be noted here that there was no requirement of tuning of penalty parameter in the methodology adopted here as tournament selection based GA approach handles constraints in a completely different manner (Deb [11]).

In modeling aspects, it has been said earlier that overall conversion (ϕ) is different in different cases with an upper bound guided by equilibrium considerations. Commercial processes like Dow chemicals claim that 60–65% conversion for ethylbenzene can be made possible. But in this case with the higher temperature, higher conversion is theoretically achievable. Keeping eyes on both the theoretical as well as practical aspects, an effort has been put to cover overall conversion values in between 55% to 75%. In all the tables, there are lists of data intentionally placed with the idea that the best-obtained value may not be practically feasible. With these lists of closely competing data, one can choose the suitable one for his case depending on his require-

Table 4
Optimum data for 191755 and 124766 KJ/kg mole activation energy of styrene

Activation energy of styrene (KJ/kg mole)	Temperature (K)	Overall conversion (%)	Length (m)	Percentage in product (styrene)	Percentage in product (benzene)	Percentage in product (toluene)
191754.3442	866.3625	55.4991	0.4479	92.5806	5.6089	1.8105
191753.0686	867.7358	55.9977	0.4420	92.6242	5.6101	1.7657
191754.3442	869.1168	56.4969	0.4363	92.6682	5.6093	1.7225
191753.0686	879.0048	59.9993	0.3967	92.9667	5.5833	1.4500
191754.3442	880.4391	60.4957	0.3913	93.0082	5.5761	1.4157
191754.3442	892.3871	64.4956	0.3479	93.3301	5.5012	1.1687
124765.1599	925.2391	73.9990	0.3001	94.3211	4.8326	0.8463
124765.1599	927.2347	74.4981	0.2987	94.3807	4.7844	0.8349
191754.3442	1041.7142	74.9997	0.0140	95.2028	3.8719	0.9254
124765.1599	929.2700	74.9976	0.2971	94.4404	4.7359	0.8237

ments. Table 4 gives the optimized values for different ϕ values.

From Table 4, it is clear that in 46050–238650 KJ/kg mole range of styrene activation energies, 191755 and 124766 values are the best values in terms of maximization of styrene production. From the analysis of Modell (1) and present work, it is very much clear that there is a strong trade-off between temperatures and the catalysts bed length. At a high temperature like 1041 K, the catalyst bed length is very less for the activation energy value 191755 KJ/kg mole. As catalyst bed length is of the order of only 0.20–0.40 m, by reducing length, one may not be benefited to large extent as, at the same time, the increment of temperature increases the operational liabilities of the process. Even making a catalyst bed length of much less dimension may be out of this feasibility range of manufacturing.

From this table, one can get an entirely new set of operating parameters like temperature, pressure, activation energy of styrene, catalyst bed length with an idea about the performance parameters like conversion of ethylbenzene, selectivity of styrene and other by-products. From Table 4, one can conclude the followings.

For a given activation energy and an overall conversion:

(1) reactor length decreases with the increase in temperature due to the fastness of reactions (Figs. 3 and 5);
(2) reactor length increases with the increase in overall conversion;
(3) reactor length increases with the increase in activation energy, as lowering activation energy at a given temperature means more extent of reactions;
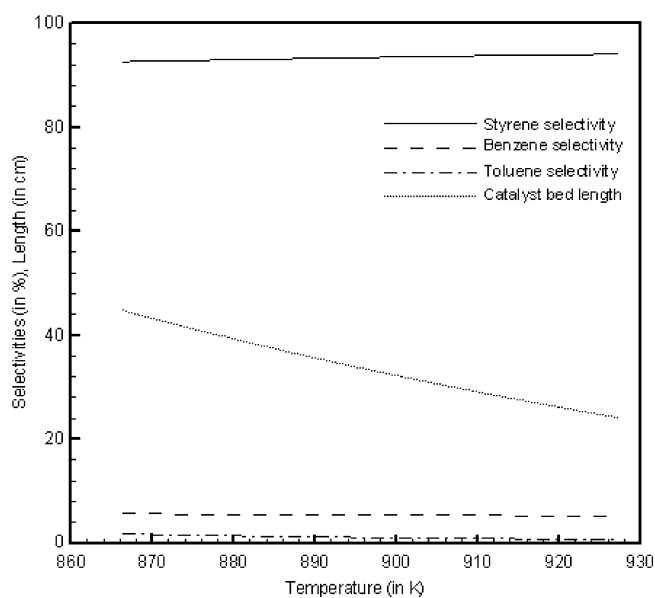(4) selectivity of styrene increases with increase in temperature (Figs. 3 and 5);

(5) selectivity of styrene decreases with the increase in length (Figs. 4 and 6).

But these types of relationships can be completely violated sometimes due to the coupled effect of all other parameters.

Less catalyst bed length than that of any values in Table 4, if desired, can be obtained just by changing the lower and upper limits of length constraint (making the range much less) and running the optimization routine once again with the new set of constraints. But one should keep in mind that if styrene productivity is the only concern, values presented in Table 4 are the best values in the total decision variable domain. Table 5 represents values that are coming out of lower range of catalyst bed length as a constraint.

Figs. 3–6 are presented to show the relationship of different process variables. For the 191755 KJ/kg mole activation energy of styrene, Fig. 3 (Fig. 5 for 124766 KJ/kg mole) shows the relationship among catalyst bed length and various selectivities (for styrene, benzene and toluene) with the temperature. Fig. 4 (Fig. 6 for 124766 KJ/kg mole) shows the change in selectivity of styrene with the catalyst bed length for the 191755 KJ/kg mole activation energy of styrene. Trends are quite common for all the figures; styrene selectivity increases with temperature and selectivity and other products are behaving oppositely. But the sensitivity for temperature is much less in all the cases. With less length, selectivity of styrene is high as in that case temperature is also high.

All the points above covered the issues of activation energy of styrene, as that is the major product. Appreciating the fact that styrene activation energy is undoubtedly the most important one to talk about, one can include benzene and toluene with styrene in order to get the complete picture. But frequency factors for benzene and toluene with different

Fig. 3. Change in selectivities and catalyst bed length with temperature for 191755 cal/g mole of styrene activation energy.
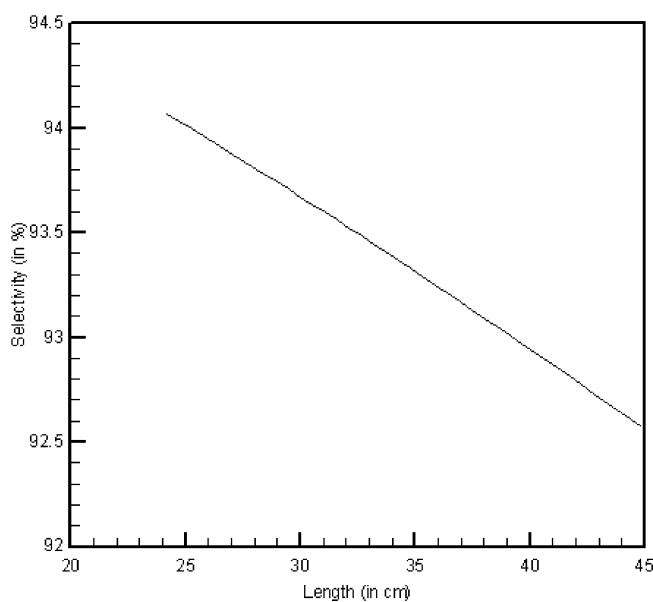

Fig. 4. Change in styrene selectivity with catalyst bed length for 191755 KJ/kg mole of styrene activation energy.

Table 5

Optimized data set with a catalyst bed length constraint (0.001–0.05 m)

Activation energy of styrene (KJ/kg mole)	Temperature (K)	Overall conversion (%)	Length (m)	Percentage in product (styrene)	Percentage in product (benzene)	Percentage in product (toluene)
209019.2846	866.3625	55.4991	0.0497	90.4392	9.0342	0.5266
209231.3885	867.7358	55.9977	0.0494	90.5251	8.9543	0.5206
109282.6761	869.1241	56.4996	0.0499	90.6105	8.8746	0.5149
193543.1872	870.5130	56.9993	0.0497	90.6938	8.7971	0.5092
173341.9754	874.7017	58.4916	0.0498	90.9347	8.5723	0.4929
193392.4134	876.1437	58.9999	0.0497	91.0141	8.4984	0.4876
174626.1127	893.9436	64.9976	0.0499	91.8636	7.7044	0.4320

Table 6

Effect on the optimum values for the percentage change in the activation energies of benzene and toluene, respectively

	Temperature (K)	Selectivity (%)	Conversion (%)	Length (m)
Benzene (E2): 212689 KJ/kg mole (in actual opti)				
Actual optimization with 191755 KJ/kg mole (styrene)	880.446	56.268	60.498	0.39120
+10% change in E2	880.446	55.764	60.498	0.40889
+5% change in E2	880.446	55.864	60.498	0.40542
−5% change in E2	880.446	57.660	60.498	0.33967
Actual optimization with 124766 KJ/kg mole (styrene)	893.944	60.597	64.997	0.31493
+10% change in E2	893.944	60.098	64.997	0.32873
Toluene (E3): 91272 KJ/kg mole (in actual opti)				
Actual optimization with 191755 KJ/kg mole (styrene)	880.446	56.268	60.498	0.39120
+10% change in E3	880.446	55.838	60.498	0.40681
+5% change in E3	880.446	55.993	60.498	0.40123
−5% change in E3	880.446	56.738	60.498	0.37373
Actual optimization with 124766 KJ/kg mole (styrene)	893.944	60.597	64.997	0.31493
−10% change in E3	893.944	61.556	64.997	0.28658
+10% change in E3	893.944	60.270	64.997	0.32428

activation energies are very rare to get. To have sensitivity analysis for benzene and toluene is the other alternative. Here the intention was to see how the optimized values change (Table 6) with the percentage change in the activation ener-gies of benzene and toluene. After this analysis, it is clear that even with a 10% change in their activation energies in-dividually, the change in optimum values are very less. It was expected as only the styrene activation energy affects
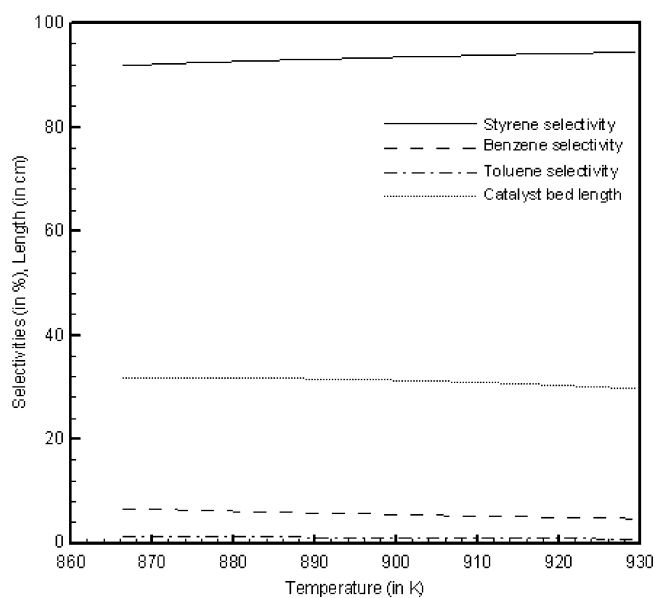

Fig. 5. Change in selectivities and catalyst bed length with temperature for 124766 KJ/kg mole of styrene activation energy.
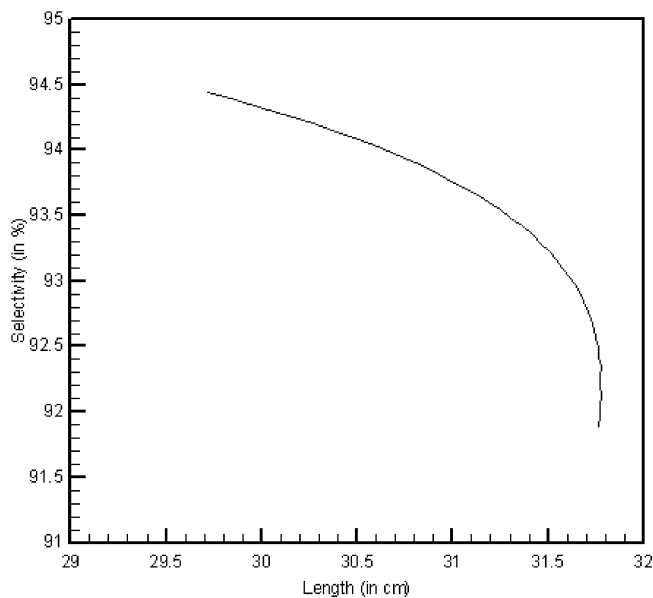

Fig. 6. Change in styrene selectivity with catalyst bed length for 124766 KJ/kg mole of styrene activation energy.

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the results substantially because of its major presence in the products. But with the data (for the variation of activation energies with frequency factors) available for benzene and toluene, one can even pick up those small changes in ultimate results. Also, now a days through molecular dynamics, one can think of a new type of catalyst design where only activation energy for styrene is different.

4. Conclusions

A detailed model is developed and solved for styrene formation reaction network from ethylbenzene with several byproducts associated with it. GA based optimization is carried out to maximize styrene selectivity using styrene activation energy and operating temperature as decision variables and bounds on catalyst bed length and overall conversion as constraints. A sensitivity study has been performed for the effect of change in byproduct's activation energies over the optimum performance of the process. It has been found that only two activation energies are undoubtedly the best in term of styrene formation. The variations of performance (i.e. styrene selectivity) with respect to different variables like temperature and overall conversions are studied. Issues like catalyst bed length, selectivity of the products are depicted as a function of process variables, which are giving a complete analysis for the process.

Acknowledgements

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