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Estimating the Parameters of the Arrhenius Equation through Genetic Algorithm Technique using Maleic Anhydride Synthesis as Study Case

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Abstract

The paper present a robust procedure to estimate the parameters set of the kinetic model, as the activation energy (E_i) and the pre-exponential factor (A_i), used in the calculation of the constant of Arrhenius (k_i) for the partial oxidation of benzene to maleic anhydride. This estimate is carried through Genetic Algorithms (*GAs*) with the purpose to minimize an objective function, that considers the error between real values operation supplied by literature, industrial units or laboratory scale reactors and the simulated theoretical values from the used model, so that a reliable adjusted kinetic model can be determined to be used in the reactor model to design and operational strategies development.

Keywords: kinetics, parameter estimation, optimization, genetic algorithms, fixed bed

1. Introduction

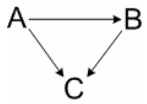
Maleic anhydride has numerous industrial uses and is of significant commercial interest worldwide. One of the synthesis routes for the production of maleic anhydride is based on the direct air oxidation of benzene over vanadium pentoxide catalyst (V_2O_5). An excess of air is applied, and a low benzene concentration must be utilized in order not to exceed the flammability limit of the mixture, but the reactant benzene cannot be recovered economically so the reactor must operate at high yields. Bearing this in mind, a pseudo-homogeneous bidimensional model for fixed bed catalytic reactors was developed taking into account variations in the physical properties of the fluid and their impact on the heat and mass transfer coefficients. The objective is to estimate the parameters set of the kinetic model, as the activation energy (E_i) and the pre-exponential factor (A_i), used in the calculation of the constant of Arrhenius (k_i). This estimate is carried through Genetic Algorithms (*GAs*) with the purpose to

minimize an objective function to be established, that considers the error between real values operation, values these that can be obtained from temperature or concentration reactor profiles for determined points throughout the reactor length, supplied by literature, industrial units or laboratory scale reactors, and the simulated theoretical values from the used model, so that a reliable adjusted kinetic model can be determined to be used in the reactor model to design and operational strategies development.

The genetic algorithms are based on the genetics and natural evolution principles of the species. The mechanism of the Genetic Algorithms technique occurs with successive modifications of the individuals or chromosomes (artificial structures) of population through the application of selection, crossover, and mutation operators. For the application of Genetic Algorithms in parameter estimation it is necessary to develop a suitable objective function based on the data from the reactor model and experimental values. The coding basic recommendations were considered. The interest of this work is to show that the Genetic Algorithms technique can be useful to estimating the parameters of the Arrhenius equation, obtaining good results so that with this accurate information operational improvements can be achieved when deterministic models are used. The results shown that, the whole procedure of kinetic data identification together with reactor model is a robust procedure, which allows the reactor to be operated at high level of performance.

2. Reaction Rates

The partial oxidation reaction rates of benzene to maleic anhydride with V_2O_5 catalyst consists on a system of parallel and series equations with a classical triangular reaction scheme:



where *A* and *B* are benzene and maleic anhydride, respectively, while *C* denotes the combustion products (CO, CO_2, H_2O).

The kinetic data were described in the works of Wohlfahrt and Emig (1980) and also by Westerink and Westerterp (1988) for the following system of reactions:

$$C_6H_6 + \frac{9}{2}O_2 \xrightarrow{k_1} C_4H_2O_3 + 2\,CO_2 + 2\,H_2O \quad (1)$$

$$C_6H_6 + \frac{15}{2}O_2 \xrightarrow{k_2} 6\,CO_2 + 3\,H_2O \quad (2)$$

$$C_4H_2O_3 + 3\,O_2 \xrightarrow{k_3} 4\,CO_2 + H_2O \quad (3)$$

There is no maleic anhydride, carbon dioxide and water in the reactor feed. Thus, $C_{AM,0} = C_{CO_2,0} = C_{H_2O,0} = 0$ and the conversion of the limiting reactant (benzene) is given by Westerink and Westerterp (1998):

$$\frac{F_{B,0} - F_B}{F_{B,0}} = \frac{F_{AM}}{F_{B,0}} + \frac{F_{CO_2}}{F_{B,0}} + \frac{F_{H_2O}}{F_{B,0}} = X_B = X_1 + X_2 + X_3 \tag{4}$$

The component molar flow rates of the reaction are calculated by:

$$F_B = F_{B,0}\left(1 - X_1 - X_2\right) \tag{5}$$

$$F_O = 0,21F_{Ar,0} - \left[F_{B,0}\left(\frac{9}{2}X_1 + \frac{15}{2}X_2 + 3X_3\right)\right] \tag{6}$$

$$F_N = 0,79F_{Ar,0} \tag{7}$$

$$F_{AM} = F_{B,0}\left(X_1 - X_3\right) \tag{8}$$

$$F_{CO_2} = F_{B,0}\left(2X_1 + 6X_2 + 4X_3\right) \tag{9}$$

$$F_{H2O} = F_{B,0}\left(2X_1 + 3X_2 + X_3\right) \tag{10}$$

The total molar flux rate is given by the above equation:

$$F_T = F_{B,0} + F_{Ar,0} + F_{B,0}\left(-\frac{1}{2}X_1 + \frac{1}{2}X_2 + X_3\right) \Rightarrow F_T = \sum_{i=1}^{6} F_i \tag{11}$$

with the ratio:

$$R_{Ar/B} = \frac{F_{Ar,0}}{F_{B,0}} \tag{12}$$

$$F_T = 1 + R_{Ar,B} + 1\left(-\frac{1}{2}X_1 + \frac{1}{2}X_2 + X_3\right) \tag{13}$$

The reaction equation rates are given by:

$$-r_1 = k_1 C_B C_O^{a1} = k_1 C_B \tag{14}$$

$$-r_2 = k_2 C_B C_O^{a2} = k_2 C_B \tag{15}$$

$$-r_3 = k_3 C_B C_O^{a3} = k_3 C_B \tag{16}$$

All the reactions are considered to be 1st order, due to the huge excess of air, and consequently, the oxygen. In this way, the oxygen concentration is considered constant. The reaction rate as a function of conversion can be obtained by using the relation above for concentrations, applied to multiple reactions (Fogler, 1999):

$$C_j = C_{T,0}\left(\frac{F_j}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right) \tag{17}$$

$$C_B = C_{B,0}\left[\frac{\left(1-X_1-X_2\right)}{1+y_{B,0}\left(-\frac{1}{2}X_1+\frac{1}{2}X_2+X_3\right)}\right]\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right) \tag{18}$$

$$C_{AM} = C_{B,0}\left[\frac{\left(X_1-X_3\right)}{1+y_{B,0}\left(-\frac{1}{2}X_1+\frac{1}{2}X_2+X_3\right)}\right]\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right) \tag{19}$$

where: $y_{B,0} = \frac{F_{B,0}}{F_{T,0}}$ and $C_{B,0} = y_{B,0}C_{T,0}$

3. Mathematical Model

The model developed for this work are based on the works of Jutan et al. (1977), Maciel Filho (1989) and Vasco de Toledo (1999), which incorporate the thermal capacities of the fluid and the solid, $(\rho C_p)_g$ e $(\rho C_p)_s$ respectively. This model incorporates in implicit form the presence of the solid, which allows overcoming the difficulties of representing the dynamic behavior of the fixed bed catalytic reactor satisfactorily, including the inverse response phenomenon, allowing for a fast and reliable analysis of the reactor performance.

The dynamic formulation of this model consists of partial differential equations derived from the balance of mass, energy, momentum and continuity equation, with the appropriate initial and boundary conditions. The model allows for variations in the physical properties, and their influence on the heat and mass transfer coefficients, as well as to variations in the temperature of the coolant, and reactor pressure, which are not normally considered in the literature. The following assumptions are made in the formulation of the model (Vasco de Toledo, 1999):

- The physical properties of the fluid (density, viscosity, thermal conductivity, heat capacity, reaction enthalpy, molecular weight, superficial velocity), and the coefficients of heat and mass transfer varies along the reactor length;
- Plug-flow velocity profile;

- Negligible axial dispersion;
- Flat temperature profile at the inlet of the bed;
- Uniform porosity.

A dynamic bi-dimensional model of the catalytic reactor is presented bellow.

- Mass Balance

$$\frac{\partial X_1}{\partial t} = \frac{D_{ef}}{R_t^2}\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial X_1}{\partial r}\right] - \frac{u_s}{L}\frac{\partial X_1}{\partial z} + \frac{q_{vo}\rho_B}{\varepsilon F_{B,0}} r_1 \tag{20}$$

$$\frac{\partial X_2}{\partial t} = \frac{D_{ef}}{R_t^2}\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial X_2}{\partial r}\right] - \frac{u_s}{L}\frac{\partial X_2}{\partial z} + \frac{q_{vo}\rho_B}{\varepsilon F_{B,0}} r_2 \tag{21}$$

$$\frac{\partial X_3}{\partial t} = \frac{D_{ef}}{R_t^2}\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial X_3}{\partial r}\right] - \frac{u_s}{L}\frac{\partial X_3}{\partial z} + \frac{q_{vo}\rho_B}{\varepsilon F_{B,0}} r_3 \tag{22}$$

where:

- X_1: Amount of benzene converted into the reaction (1) in relation the amount of fed benzene
- X_2: Amount of benzene converted into the reaction (2) in relation the amount of fed benzene
- X_3: Amount of maleic anhydride converted into the reaction (3) in relation the amount of fed benzene

- Energy Balance

$$\frac{\partial T}{\partial t} = \frac{\lambda_{ef}}{C_m R_t^2}\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial T}{\partial r}\right] - \frac{\varepsilon Cp_g \rho_g u_s}{C_m L}\frac{\partial T}{\partial z} + \frac{\rho_B}{C_m T_{ref}}\sum_{i=1}^{4} -\Delta H_{R_i} r_i \tag{23}$$

where: $C_m = \varepsilon(\rho_g Cp_g) + (1-\varepsilon)(\rho_s Cp_s)$

- Momentum Equation

$$\frac{\partial P}{\partial t} = -\frac{G_i}{\rho_g L}\left[\frac{\partial P}{\partial z} + \frac{G_i^2 L}{\rho_g D_p P_{ref} g_c} f\right] \tag{24}$$

- Continuity Equation

$$\frac{\partial}{\partial z}\left(\rho_g V_g\right) = 0 \tag{25}$$

- Coolant Fluid Equation for co-current flow

$$\frac{\partial T_R}{\partial t} = -\frac{u_R}{L}\frac{\partial T_R}{\partial z} + \frac{4U}{D_t \rho_R Cp_R}(T(1,z,t) - T_R) \tag{26}$$

with the following boundary conditions:

$$r = 0 \qquad \frac{\partial X}{\partial r} = \frac{\partial T}{\partial r} = 0 \quad \text{(simetry)} \tag{27}$$

$$r = 1 \qquad \frac{\partial X}{\partial r} = 0, \ \frac{\partial T}{\partial r} = B_{ih}\ (T_R - \ T(1,z,t)) \quad \text{(for all z)} \tag{28}$$

$$z = 0 \quad X = 0, \quad T = T_{fo}, \quad P = P_o, \quad T_R = T_{ro} \quad \text{(for all r)} \tag{29}$$

The solution procedure was based on the method of lines with the spatial variable discretization carried out by orthogonal collocation, Villadsen and Michelsen (1978) and Vasco de Toledo (1999). The integration was made through a GEAR type algorithm (Rice and Do, 1995; Vasco de Toledo, 1999), since the equations are stiff.

4. Reactor Optimization and Kinetic Data Identification

Genetic Algorithms (GAs) are general-purpose search techniques for able to solve complex problems, including those to identify kinetic parameters in a high non-linear function where more than one parameter is present. They are based on the genetics and natural evolution principles of the species. The GAs work through repeated modifications in an artificial structures population denominated of individuals (chromosomes or set of solutions) applying the selection, crossover, and mutation operators. The evaluation of optimization happens with an objective function (fitness) that determines the performance of the genetic process. The fitness could be understood as the capacity of the individuals to survive in a natural environment.

The problem consisted of maximizing an objective function taking into consideration the kinetic model together a detailed reactor model, based in a system of differential partial equations. With the reliable kinetic model it is possible to optimize the rector to match specific objectives.

5. Genetic Algorithms (GAs)

Genetic Algorithms are a family of computational models inspired by evolution. These algorithms are a procedure of research and optimization motivated by the principles of natural selection (Holland, 1992; Goldberg, 1989; Bäck et al., 2000). These are often viewed as function optimizers. In a strict interpretation, the genetic algorithm refers to a model introduced and investigated by John Holland. The primary

reasons for their success are their broad applicability, ease of use, and global perspective (Goldberg, 1989).

The GA initiate with a population of represented random solutions in some series of structures. After this first stage, a series of procedures (operators), are applied repeatedly, up to convergence is achieve. These operators are: coding, reproduction, crossover and mutation. These two last operators are used to create new and better populations. This procedure continues until a termination criterion defined in accordance with the necessities proposals for optimization of the problem. The determination of the parameters is made developing an objective function that can represent the problem in a suitable way. The application of the GA follows some steps as: coding, population size, evaluation – fitness, selection (reproduction), crossover and mutation.

5.1. Coding

There were two parameter coding schemes (floating point and binary), many selection schemes, and different types of crossover and mutation operators that have been investigated in previous GA works (Goldberg, 1989). For this application, the best choice of coding was binary form.

These studies were based in the Carroll's work (Carroll, 1996a). The parameters are discretized into a number of possibilities, but the chromosome length is based on the total number of possibilities in a binary format, e.g., 32 possibilities would be represented by a string of five 0's and 1's, whereas 16 possibilities would be represented by a string of four 0's and 1's. For this application, binary coding produced a total chromosome string length of 21. Again, the length of each parameter string is called the parameter length. For binary coding, each parameter is represented by a string of 0's and 1's in the total chromosome string; therefore, for binary coding, the parameter length is 5 for 32 possibilities and is 4 for 16 possibilities. During crossover with binary coding, the crossover point may occur in the middle of one the parameter strings; this allows the child to have a parameter string that is a mix of the parents parameter strings and, consequently, the child may have an allele (parameter value) between the two alleles of the parents. In floating point coding, the child must have a mix of the parents' alleles but cannot have alleles which are not present in the parents chromosome strings. Thus, in binary coding, more alleles (possible values of the parameters) are preserved as new generations are created.

The target is to create a representation of a parameter which allows its modification through the cut (division) in some position being these parts of the separate sequences in condition to be matched with others. A codified parameter is similar to a chromosome in genetics, in other words a modifiable carrier of information.

5.2. Population Size

In accord to Wehrens and Buydens (1998), the population size is determined by each particular case and normally is in the range of 20-500 are common. In general, when many parameters are optimized great populations are used, even so it does not exist definite rules. There are frequently limits for the number of evolutions (due to the time and computer bounder) that can be carried through. In many cases for a great number of evolutions, a small population is applied and vice-versa. When there is interest to obtain a set of "good" solutions instead of a single solution, executions are usually repeated with small populations. Some care must be considered to do not get premature conclusions when only one execution is carried out. Because of the random nature of the search, it is preferable to observe an average value in different executions. This study of optimization used population size of 20.

5.3. Evaluation – Fitness

The evaluation function (fitness) represents, in biological terms, the pressure exerted for the environment on the individuals, in other words, this function is representative of the problem to be analyzed and determines which of these individuals (parameters) of a determined population supplies better values (more adaptable) in the optimization (objective function). The best individuals can assume larger or smaller values that depend on the problem to be considered (maximization or minimization respectively). Application of the scheduling problem considers the series with better performance of fitness. The correct determination of the evaluation functions is the main task to carry out the optimization in an efficient way, preventing many executions and speeding the solution (Victorino, 2005).

5.4. Selection

Selection is the stage of a genetic algorithm in which the individuals are chosen from a population for later to be submitted to recombination (crossover) and mutation operators respectively. The selection is normally the first procedure applied in the population, and is carried out a choice of good individuals (series) and promotes a mating pool (reproduction). Some selection types are found in literature (Goldberg and Deb, 1991). The main idea is to select individuals that possess fitness values above the average of a current population and is duplicates and in mating pool. The more traditional selection methods are the proportional selection, roulette wheel, tournament and based in rank.

Expected value selection: the fitness of all the individuals in the population is summed, and then the expected probability of selection is based on the fitness of the individual divided by the total fitness of the population, i.e., $p_i = f_i \big/ \sum_i f_i$. The expected number of parents with chromosome set i for the new generation is simply np_i. This procedure will fill most of the parent slots, but there will be a fractional remainder of slots that are filled using the stochastic remainder sampling without replacement method (Goldberg, 1989). Random pairs of mates are then

chosen from this population of fit parents. Then, each pair of mates creates two children, e.g., one child could end up with chromosome set abcDE and the other with ABCde.

In this work was used the Tournament selection, where random pairs are selected from the population and the stronger (most fit) of each pair is allowed to mate. Each pair of mates creates one child, which has some mix of the two parents chromosomes according the method of crossover (discussed next). The process of selecting random pairs and mating the stronger individuals continues until a new generation of size *n* is repopulated.

Several other methods of selection can be applied in GA, such as elitist selection, bi-classist representative and for diversity. After the selection process, the selected individuals are submitted to the crossover and mutation operators described in the sequence. This operator is used to ensure that the chromosome set of the best parent generated to date is reproduced. After the population is generated, the GA checks to see if the best parent has been replicated; if not, then a random individual is chosen and the chromosome set of the best parent is mapped into that individual. Although this operator is not necessary, it was found to help prevent the random loss of good chromosome strings.

5.5. Crossover

This operator is applied in the series proceeding from mating pool (after the stage of selection), (Goldberg, 1989). In the same way that the reproduction operator, is found some different types of crossover operators applied to GA (Syswerda, 1989; Carroll, 1996b). In the majority of the operators, two series (individuals) are chosen from the mating pool randomly and a recombination is made, constructing two new individuals (recombining parts of the series relatives). This operator is considered the main operator of the genetic algorithms. It is regulated by an adjustable parameter for the user (crossover probability) normally the values that are used can be found in the range of 0.5-0.9. One of the most important is that one-point crossover cannot combine certain combinations of features encoded on chromosomes: schemata with a large defining length are easily disrupted. It is also possible that certain elements are not allowed to appear more than once. In that case, precautions have to be taken. Therefore, in previous years, several other crossover techniques have been used and will be discussed some of them here, as: two-point crossover, uniform crossover, partially mixed crossover and uniform order-based crossover.

In this study was used Single-point crossover and Uniform Crossover. The Single-point crossover the chromosome set of the first parent is mapped into the child, e.g., abcde. A crossover point is randomly chosen where the chromosome set of the second parent, ABCDE, overwrites the chromosome set of the first parent, e.g., one possible chromosome set for the child is abcDE, where the position between the c and D chromosomes is the randomly determined crossover point. For this study, the probability of a single-point crossover occurring, p_{cross}, was set at 0,6. Note that there

is a $1 - p_{cross}$ probability that the child would retain the entire chromosome set of the first parent. In the case with Uniform crossover is possible to obtain any combination of the two parents chromosomes, e.g., the child could end up with chromosome set aBcDe. For this study, the probability for a crossover occurring at each chromosome position was set at 0.6 (the same value used for single-point crossover). Note that it is possible that the child could retain the entire chromosome set of either parent, but in uniform crossover it is unlikely.

5.6. Mutation

The main target of this genetic operator is to promote new solutions (individuals) that cannot be generated by another form. The mutation introduces an element of the random research (some times called exploration) which has attention to focus in promising regions of the search space (exploitation). One more time the occurrence of this operator is determined by the user that can justify it with a mutation probability. Normally, the values that are used can be found in the range 0.001-0.05. In binary representations, normally, the random mutation is applied, where an individual of the current generation is chosen randomly by means of some method of selection or still the best individual of the population is taken (larger fitness), determining the percentage of genes that must be changed.

In this case jump mutation was used so that there is a small probability that one or more of the child's chromosomes will be mutated, e.g., the child ends up with chromosomes abcDM, where M was not a chromosome from either parent. The jump mutation produces a chromosome that is randomly picked to be in the range of the appropriate parameter, e.g., the parameter could jump from one side of the range to the other side. The probability of a jump mutation occurring for each chromosome was set equal to $1/n$, i.e., the inverse of the population size. The jump mutation operator was used in al of the GA work in this study.

The other form of mutation is Creep mutation, where another small probability mutation is that one or more of the child's parameters will be mutated by a single increment, e.g., the child ends up with chromosomes abcDF, where F was not a chromosome from either parent, but is only one increment away from parent 2’s chromosome value of E. The creep mutation produces a parameter value that is randomly picked to be larger or smaller, so long as it remains in the range of the appropriate parameter, i.e., the parameter could creep one increment up or down from one of the parents values. The probability of a creep mutation occurring for each chromosome was set equal to $1/n$, i.e., the inverse of the population size (a probability of $1/n$ was chosen for the same reason it was used for jump mutations).

6. Strategies of Optimization

The objective is to estimate the parameters set of the kinetic model, as the activation energy (E_i) and the pre-exponential factor (A_i), used in the calculation of the constant of Arrhenius (k_i). This estimate is carried through algorithms optimization as, for example, Genetic Algorithms with the purpose to minimize an objective function to be established, that considers the error between real operational values, obtained from temperature or concentration reactor profiles for determined points throughout the length of the reactor supplied by literature, and simulated values from the model. With is procedure is possible to determine the kinetic model taking into account all the observable phenomena taking place in the reactor allowing the use of real operational data. In Table 1 are presented the design and operation reactor data.

Table 1 – Data set of the fixed bed catalytic reactor.

Design Parameters		**Operation Parameters**	
Reactor Length	3.0 m	Gas Feed Temperature	760.15 K
Shell Diameter	0.030 m	Coolant Feed Temperature	760.15 K
Tube Diameter:	0.025 m	Feed Air/Benzene Ratio	75.0
Pellet Diameter	0.0025 m	Inlet Pressure	2.0 atm
Tube thickness:	0.000889 m	Gás Mass Velocity	9000.0 $kg.m^{-2}.h^{-1}$
Solid Thermal Conductivity	7.0 $kcal.m^{-1}.h^{-1}.K^{-1}$	Coolant Velocity	150.0 $m.h^{-1}$
Bed Density	900.0 $kgcat.m^{-3}$	Initial Benzene Concentration	0.000467 $kmol.m^{-3}$
Bed Porosity	0.47	Feed Benzene Molar Flow	0.002262 $kmol.h^{-1}$

In Table 2 are shown the kinetic parameters of reaction rate, with the maximum and minimum values.

Table 2 - Westerink, E. J., Westerterp, K. R., 1988)

Parameters	**A_i**	**$A_{i\ MAX}$**	**$A_{i\ MIN}$**	**Ea_i (Ea/R)**	**$Ea_{i\ MAX}$(Ea/R)**	**$Ea_{i\ MIN}$(Ea/R)**
k_1 ($m^3.kg_{cat}^{-1}.s^{-1}$)	4.280×10^3	4.360×10^3	4.200×10^3	-1.2660×10^4	1.280×10^4	1.250×10^4
k_2 ($m^3.kg_{cat}^{-1}.s^{-1}$)	7.010×10^4	7.150×10^4	6.950×10^4	-1.5000×10^4	1.560×10^4	1.440×10^4
k_3 ($m^3.kg_{cat}^{-1}.s^{-1}$)	2.600×10^1	2.680×10^1	2.530×10^1	-1.0800×10^4	1.160×10^4	1.030×10^4

The Arrhenius's Equation was linearized in accordance with Rodionova and Pomerantsev (2003), the procedure is presented in the sequence:

$$k_i = k_0 \exp\left(\frac{Ea_i}{T}\right),\ T = [K] \tag{30}$$

Defining,

$$k_0 \rightarrow q = \ln(k_0) \tag{31}$$

Substituting in (1),

$$k_i = \exp\left(q - \frac{Ea_i}{T}\right) \tag{32}$$

Making,

$$T \rightarrow X = \frac{Ea_i}{T} \qquad \text{and} \qquad b = \frac{Ea_i}{Ea_0} \tag{33}$$

Obtaining:

$$k_i = \exp\left(q - bX\right) \tag{34}$$

The genetic code based on the code developed by Carroll (1996a,b) was coupled with the reactor model. The genetic code possesses the following characteristics: binary code; uses the elitism; search in niches and selection by tournament. More details can be found in the site http://cuaerospace.com/carroll/html). This genetic algorithm (GA) code is written in FORTRAN.

6.1. Parameters of Control of the Genetic Algorithms

The selected values for the GA parameters are given in Table 4. The parameters to be optimized were codified with the binary form, based and adapted of many published literature works (Carroll, 1996a,b; Deb, 1998; Goldberg, 1989). In the Table 3 shows genetic parameters that are used in the optimization.

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Table 3 - Control parameters of genetic algorithms utilized in the optimization.

Size Population	Parameters (Variables)	Crossover (Uniform Crossover)	Mutation Rate (Jump Mutation)	Creep Mutation (Rate)	Generations (Maximum Number)
20	6	0.5	0.01	0.02	100

The GAs parameters were chosen based on extensive simulation not shown in this work.

6.2. Objective Function

In this work the objective function is related the average and simulated temperature. The representation of this function is:

$$f = \frac{\sum_{i=1}^{N} (T_{Avg} - T_{Sim})^2}{N} \tag{35}$$

Where, T_{Avg} and T_{Sim} are the average and simulated axial temperature respectively, this values are in Kelvin (K).

In the Figure 1, the optimization reactor flowchart is presented and this is based in the Carroll's code and that it is used in this work.

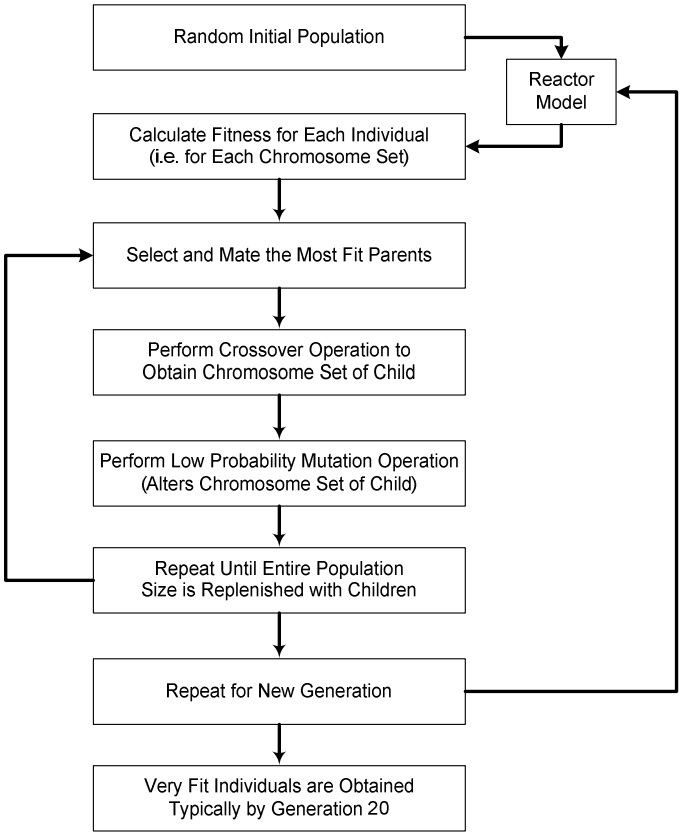

Figure 1 – Flowchart of Genetic Algorithm optimization reactor, based in Victorino (2005).

7. Results

The kinetic parameters of reaction rate used from the literature together with the estimated values obtained with the optimization procedure are presented in the Table 4:

Table 4 - Kinetic parameters of reaction rate from the literature (Westerink, E. J. and Westerterp, K. R., 1988) and estimated values.

	Literature values		**Estimated values**	
Parameters	**A_i**	**Ea_i (Ea/R)**	**A_i**	**Ea_i (Ea/R)**
k_1 ($m^3.kg_{cat}^{-1}.s^{-1}$)	4,280 x 10^3	- 1,2660 x 10^4	4,3198 x 10^3	- 1,2539 x 10^4
k_2 ($m^3.kg_{cat}^{-1}.s^{-1}$)	7,010 x 10^4	- 1,5000 x 10^4	6,9543 x 10^4	- 1,5072 x 10^4
k_3 ($m^3.kg_{cat}^{-1}.s^{-1}$)	2,600 x 10^1	- 1,0800 x 10^4	2,530 x 10^1	- 1,1545 x 10^4

The steady state simulated temperature profile with the estimated kinetics parameters are compared to temperature profile obtained using the kinetics parameters from the literature as illustrated in Figure 2:

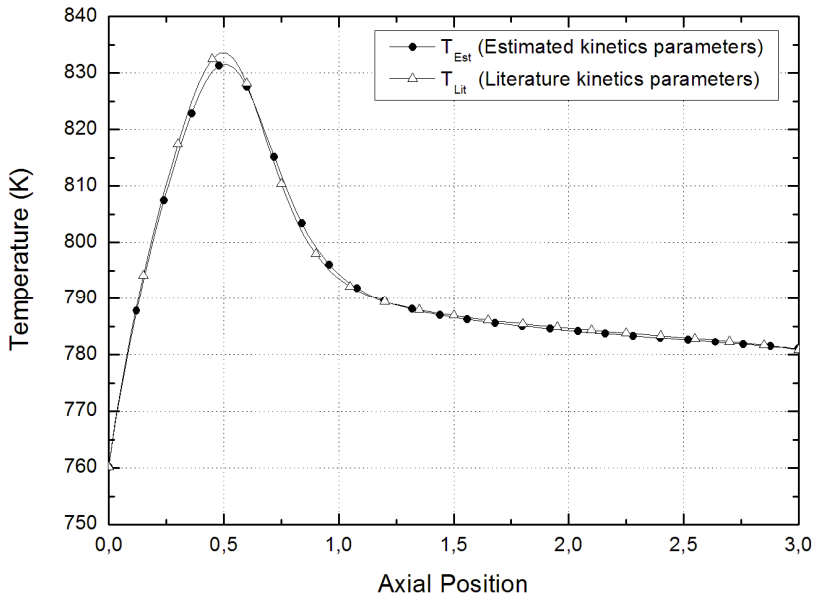

Figure 2 – Axial temperature profile along the reactor length.

As can be seen a very good adjust was obtained taking into account the available data. The same procedure was used with an industrial set of data either for temperature and concentration and very good results were obtained in terms of parameter fitting. It is worthwhile mentioning that is more adequate to deal with the thermal profiles instead of concentrations ones to achieve a good parameter estimation. The industrial data were not shown explicitly in this work for sake of confidentiality.

8. Conclusions

A suitable procedure to identify kinetic parameters using large scale industrial units data is proposed. It is based on the use of a detailed deterministic model for the reactor coupled with a kinetic model with the parameters led freely to be determined. An objective function based on the minimization of the difference of the real operation and simulated data from the model is generated and the whole problem is solved using Genetic Algorithms. The procedure allows the use of real profile of either temperature or concentration but the former are more easily obtained form industrial units. The whole procedure showed to be robust so that is a good tool to deal be used to find out kinetic data from industrial reactors.

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