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MULTI-OBJECTIVE OPTIMIZATION OF SYNDIOTACTIC POLYMERIZATION OF STYRENE USING GENETIC ALGORITHM TECHNIQUE

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ABSTRACT: - The optimal control policies for the syndiotactic polymerization of styrene over silica supported metallocene catalyst, have been determined using a multiobjective optimization technique. Kinetics model (KM) and genetic algorithms (GA) were tested as tools for modeling and optimization of syndiotactic polystyrene (sPS) synthesis process. The dependence between the main parameters of the process and working conditions were modeled by using KM. To verify the KM, syndiotactic polymerization of styrene over silica supported metallocene catalyst was conducted. The validation results show that the KM predicts best polymerization reactor performance with an average absolute error less than 15%. The KM is then included into an optimizing control scheme, which uses a genetic algorithm solving technique and a multiobjective function in a scalar form. Genetic algorithms based methodology provides accurate results, computing optimal values of decision variables, which lead to the maximum rate of polymerization and the desired value for molecular weight. The validation results in these optimum values are valid and the average absolute error less than 5 % of all responses.

Keywords*:* Multiobjective optimization, Genetic algorithms, Kinetics model, Polystyrene, Syndiotactic Polymerization.

1- INTRODUCTION

Syndiotactic polystyrene (sPS) is a new polymeric material of industrial relevance, the high crystallization rate and the high melting point (270°C), make this polymer a crystalline engineering thermoplastic material with potential applications [1]. Syndiotactic polystyrene was first synthesized by Ishihara [2], using a soluble titanocene compound, and activated by methylalumoxane (MAO). Several styrene polymerization were carried out with supported metollocene catalyst, prepared by reaction of silica gel with MAO and then with metallocene catalyst [3, 4].

The optimization approach can have a significant effect on the polymer manufacturing process and economics. Polymer production facilities focus attention on improving the product quality and cost reductions [5]. In general, polymerization process optimization is naturally multi-objective, since it normally has several objectives that are often conflicting and non-measurable, which must be adjusting simultaneously. Therefore, solving such a problem cannot be devoid of difficulties, starting with the objective function formulating. It then proceeds with the choice of working procedure and the result selection from several options [6].

Multi-objective optimization can be defined as the problem of finding a vector of decision variables, which satisfies the constraints and optimizes a vector function whose elements represent the objective functions. In such cases, instead of obtaining a unique optimal solution, a set of equally good optimal solutions is usually obtained. There are referred to as Pareto sets [7]. A decision maker can choose any one of these non-dominant optimal solution based on additional information [8]. So one can consider that the multi-objective optimization is carried out in two phases: an objective or mathematical phase and a subjective or decision – making phase. Some examples of the vectorial approach of the multi-objective optimization for polymerization reactors are given in [8, 9].

Recently, new numerical algorithms have become widely established due to the fast-paced progress in the availability of the computing technology. In particular, there is a newly found interest in the optimization techniques based on evolutionary algorithms, especially genetic algorithms (GA). Genetic algorithms have been successfully employed in a wide range of multi-objective problems because of their flexibility, global perspective and minimal requirements [10, 11].

Regarding the use of genetic algorithms in chemical process engineering, particularly in polymer reaction engineering, two research directions are the most popular within the scientific community: a) increasing the performance of algorithms that are already in use or enhancing their capabilities; b) applying genetic algorithms for different chemical process optimization. All the relevant work in this field has been surveyed the papers of Coello [12], Deb [6] and Coello [13] where both the advantages and disadvantages of different types of GA have been analyzed.

Chakravarthy et al. [14] and Lee et al. [15] were the first to adapt simple GA, and used it to optimize polymer production using decision variables that are continuous functions of time. The optimization of the bulk polymerization of methyl methacrylate isstudied using the temperature history, to minimize the reaction time in a batch reactor, while simultaneously requiring the attainment of the design values of both the final monomer conversion and the number average chain length of the polymer product [14].

The genetic algorithms for an industrial ethylene reactor with a multi-objective optimization technique is applied to find a scope for further improvements and to detect a range of optimal solutions. They discussed in detail the effects of design and operating variables on the optimal solutions, and the generated results were compared with industrial data [16].

Furtuna et al. [17] applied neural network and genetic algorithm for a polysiloxane synthesis process. The algorithm provided optimum reaction conditions (reaction temperature, reaction time, amount of catalyst, and amount of co-catalyst), which maximize the reaction conversion and minimize the difference between the obtained viscometric molecular weight and the desired molecular weight. The used of the neural network made it also suitable to the multi-objective optimization of processes for which the amount of knowledge was limited.

Sharifi, et al. [18] has been developed a genetic algorithm as an optimization procedure to predict the phase behavior of polymer solutions. The phase equilibrium diagrams of binary and ternary polymer solutions have been determined using the appropriate form of Flory–Huggins free-energy function for polymer solutions. The algorithm has been used to predict the phase behavior of the two polymer–solvent–non solvent systems as polystyrene-butanone-methanol and polystyrene-butanone-propanol at three different temperatures and results show good agreement with the experimental observations.

This paper presents the use of kinetics model (KM) and genetic algorithms (GA) as tools for modeling and optimization applied to the syndiotactic polymerization of styrene. The objective function for the polymerization system is the minimization of the final reaction time, which leads to higher polymerization rate. The other objective included in the same function is the minimization of the polydispersity index of the polymer product. The rate of polymerization and molecular weight distributions were modeled by using KM. Then, the KM is included into an optimizing control scheme, which uses a GA solving technique and a multiobjective function in a scalar form.

2. EXPERIMENTAL WORK

To verify the kinetics model (KM), batch syndiotactic polymerization of styrene over silica supported metallocene catalyst was carried out at the laboratory scale.

2.1. Materials

Styrene (Aldrich) was vacuum distilled over calcium hydride and activated alumina was used to remove inhibitor from the monomer. n-Heptane (Fisher Scientific) was used as a diluent and it was purified by 75 g of activated type 4 A molecular sieves in nitrogen atmosphere. $IndTiCl_3$ (Indenyltitaniumtrichloride) (Aldrich) and methylaluminoxane (MAO, Aldrich) were used as-supplied without further purification. Silica gel Davison 952, (Aldrich,) was used as a catalyst support.

2.2.Preparation of silica supported catalysts

As shown in Figure (1), into 100 ml two neck round bottom flask, 0.056 gram $IndTiCl_3$ followed by 43 ml MAO (10 wt %) in toluene solution was added. The mixture was stirred at 25 °C for 30 min. The $IndTiCl_3$/MAO mixture was then transferred into another flask containing one gram of silica gel, dehydrated at 600 °C using a syringe while constantly stirred. The mixture was stirred then for 5 h. The solvent was evaporated at room temperature and a red free-flowing powder was obtained. The catalyst was stored in desiccators until used. The Al and Ti loadings measured by inductively coupled plasma emission spectroscopy (ICP) were 1.31×10^{-3}mol Al/g catalyst and 2.74×10^{-4} mol Ti/g catalyst, respectively.

2.3. Polymerization reaction

Styrene polymerization experiments were carried out using a 250 mL reactor equipped with a cooling jacket and stainless steel agitator under nitrogen atmosphere. Predetermined amounts of monomer, solvent, catalyst, and MAO were charged into the reactor. After polymerization, the reaction mixture was removed from the reactor, washed with excess amount of acidified methanol 10 Vol % of hydrochloric acid, and dried. Since the reactor has no provisions for sampling during the polymerization, the polymer yield vs. time profiles were obtained by conducting the individual experiments with same reaction conditions but terminated at different reaction times. The polymerization rate values were determined by numerically differentiating a polymer yield vs. time curve. The number and weight average molecular weight were determined by gel permeation chromatography (GPC) with trichlorobenzene (TCB) using PLgel® 10μm MIXED-B column. Table 1 shows the 30 experimental design matrix based on center composite design application (CCD)[19], with its corresponding responses for the rate of polymerization (Rp), degree of polymerization (Dp), and poly dispersity index (PDI).

3. KINETICS MODEL (KM)

The polymerization kinetics model is a key to understand and predict the properties of the produced polymer, thus it is a very important part of the modeling of polymerization reactor. To predict the polymerization rate behaviors in our experiments, we consider the following reaction kinetic model as shown in Table 2, where C_o is the potent catalyst site and C* is the activated site. MAO is methylaluminoxane cocatalyst. M_c is the monomer concentration at the catalyst surface. L_n and D_n are the live and dead polymer chains of length n respectively. D* is the deactivated catalyst site. k_j represents the reaction rate constant for each corresponding reaction [20].

The rate of polymerization (R_p) is proposed due to the consumption of monomer concentration as well as the catalyst deactivation to follow the following form:

$$R_p = k_p[M]_c[C^*] \tag{1}$$

where k_p is the propagation rate constant, $[M]_c$ represents the monomer concentration at the catalytic active sites in the solid phase and $[C^*]$ is the concentration of active catalyst sites.

In a heterogeneous reaction system such as considered in this work, it is possible that the monomer concentration in the bulk liquid phase $[M]_b$ may not be same as that in the solid phase $[M]_c$. The non- linear rate dependence of polymerization rate on monomer concentration is often observed in other catalyzed polymerization processes such as ethylene slurry polymerization with metallocene catalysts [21].

To analyze the non-linear rate dependence on monomer concentration, we propose that the monomer concentration in the solid phase (liquid-swollen polymer phase) is nonlinearly related to the monomer concentration in the bulk liquid phase. This can be illustrated using Langmuir isotherm monomer partition equation. In ethylene or propylene polymerization in liquid slurry phase with transition metal catalysts, monomer partition occurs between the bulk liquid phase and the solid polymer particle phase [22]. In this case, we employ a similar empirical correlation for the partition of styrene between the bulk liquid phase $[M]_b$ and the solid phase $[M]_c$:

$$[M]_c = \frac{K_1[M]_b}{1 + K_2[M]_b} \tag{2}$$

According to Eq. (2), the monomer concentration in the solid phase increases linearly with the bulk phase concentration at low $[M]_b$ but it approaches the saturation value i.e., $[M]_{sat}=K_1/K_2$ at high $[M]_b$. If we adopt the form given by Eq. (2), the polymerization rate is expressed as:

$$R_p = k_p[M]_c[C^*] = \frac{k_pK_1[M]_b}{1 + K_2[M]_b}[C^*] \equiv \frac{k_p'[M]_b}{1 + K_2[M]_b}[C^*] \tag{3}$$

where $k_p' \equiv k_pK_1$ represents the effective propagation rate constant.

Another factor that can contribute to the decrease in the polymerization rate is catalyst deactivation. Although the site deactivation mechanisms and kinetics are not well understood for most of the transition metal catalyzed olefin polymerization processes, first-order deactivation kinetics has been generally well accepted [11]. If we assume the first-order deactivation kinetics, the polymerization rate equation can be expressed as follows:

$$R_p = \frac{Mws\, k_p'[M]_b}{\rho_c(1 + K_2[M]_b)}[C^*]_o e^{-k_d t} \qquad (g\, sPS/cat.h) \tag{4}$$

where k_d is deactivation rate constant.

To calculate the polymer molecular weight distributions represented by degree of polymerization (Dp) and poly dispersity index (PDI), moment of live and dead polymer chain equations are needed, the mass balance equations for catalyst concentration ($[C^*]$), monomer concentration ($[M]_c$) and moments of the live (λ_L) and the dead polymer (λ_D) described the kinetic model of the polymerization process as shown in Table 3. Where [L] is the total live polymer concentration and $[L] = \lambda_{Lo}$.

Number average (M_n) and weight average molecular weights (M_w) of the polymer can be calculated from the moment's live and the dead polymer (λ_L) and (λ_D) of the molecular weight distribution (MWD). The number average chain length is the ratio of the first moment to the zeros moment of MWD and the weight average chain length is the ratio of the second moment to the first moment of MWD. M_n and M_w of the polymer are obtained by multiplying theses chain lengths with the molecular weight of unit monomer using the following equations:

$$M_n = \left[\frac{\lambda_{L1} + \lambda_{D1}}{\lambda_{Lo} + \lambda_{Do}}\right] Mws \approx \frac{\lambda_{D1}}{\lambda_{Do}} Mws \tag{5}$$

$$M_w = \left[\frac{\lambda_{L2} + \lambda_{D2}}{\lambda_{L1} + \lambda_{D1}}\right] Mws \quad \approx \frac{\lambda_{D2}}{\lambda_{D1}} Mws \tag{6}$$

The degree of polymerization (DP) and poly dispersity index (PDI) is given by:

$$DP = \frac{M_n}{Mws} = \frac{\lambda_{D1}}{\lambda_{Do}} \tag{7}$$

$$PDI = \frac{M_w}{M_n} = \frac{\lambda_{D2}\lambda_{Do}}{\lambda_{D1}^2} \tag{8}$$

Where (Mws) represents the molecular weight of styrene. Notice that in Eqs. (5) and (6), the contributions of live polymers to overall molecular weight averages are ignored because the concentrations of live polymers are far smaller than the concentration of dead polymers.

The propagation rate constant (k_p) and K_2 were estimated using non-linear least squares regression (MATLAB package, Ver. 6.5) by test Eq. (3). Then, the deactivation rate constant (k_d) was predicted by test Eq. (4) using the same method. On other hand, the monomer chain transfer rate constant (k_{tM}), and the β-hydrogen elimination rate constant ($k_{t\beta}$) were investigated form the instantaneous average degree of polymerization represented by the following equation [23].

$$\overline{Dp} = \frac{R_p}{R_t + R_d} = \frac{k_p [M]_c\, [\lambda_{Lo}]}{k_{tM}[M]_c[\lambda_{Lo}] + k_{t\beta}[\lambda_{Lo}] + k_d[\lambda_{Lo}]} \tag{9}$$

Where R_p is the chain propagation rate, R_t is the total chain transfer rates, and R_d is the site deactivation rate.$[\lambda_{Lo}]$ represents the total active site concentration i.e. $[\lambda_{Lo}]=[C^*]+\sum_{n=1}^{\infty}[\lambda_{Ln}]$. Eq. (9) can be rearranged to:

$$\frac{1}{\overline{\overline{Dp}}} = \frac{k_{tM}}{k_p} + \frac{k_{t\beta} + k_d}{k_p}\frac{1}{[M]_c} = \frac{k'_{tM}}{k'_p} + \frac{K_2(k_{t\beta} + k_d)}{k'_p} + \frac{k_{t\beta} + k_d}{k'_p}\frac{1}{[M]_b} \tag{10}$$

Where$k'_{tM} \equiv K_1 k_{tM}$ It should be pointed out that the molecular weight averages measured experimentally are cumulative molecular weight values at specific sampling times. Eq. (10) indicates that by plotting 1/ Dp against 1/ $[M]_{bo}$, we can estimate the k_{tM}, and $k_{t\beta}$rate constant values.

All kinetic rate parameters were estimated for experimental runs carried out at different temperatures, the Arrhenius law was applied to estimate activation energies and pre-exponential factors. As a result, the kinetic parameters for styrene polymerization over silica supported metallocene catalyst in the batch reactor are shown in equations below:

$$k'_p = 3.72 * 10^2 e^{\left(\frac{-9416.4}{RT}\right)} \qquad \left(\frac{L}{mol.h}\right) \tag{11}$$

$$K_2 = 1.4 * 10^{-3} e^{\left(\frac{-14730.7}{RT}\right)} \qquad \left(\frac{L}{mol}\right) \tag{12}$$

$$k_d = 6.0 * 10^{-3} e^{\left(\frac{-14033.2}{RT}\right)} \qquad (h^{-1}) \tag{13}$$

$$k_{t\beta} = 9.43 * 10^{-6} e^{\left(\frac{-1553.8}{RT}\right)} \qquad (h^{-1}) \tag{14}$$

$$k'_{tM} = 12.5 * 10^8 e^{\left(\frac{-3488.9}{RT}\right)} \qquad \left(\frac{L}{mol.h}\right) \tag{15}$$

Where (R = 1.987 cal K^{-1} mol^{-1})

4. GENETIC ALGORITHM OPTIMIZATION

The objective of this part is to obtain the optimum conditions of the kinetic model (KM) variables using the genetic algorithm (GA) technique to achieve maximum polymerization reactor performance. The GA technique is used to optimize the KM. A different population size was employed, whose initial values were random numbers with a uniform distribution between the lower and upper limit of the parameters involved in the polymerization process.

A roulette wheel selection technique was implemented [24]. In this strategy the parents are selected proportional to their fitness. The probability of an individual *i* to be chosen is:

$$P_i = \frac{F_i}{\sum_{j=1}^{n} F_j} \tag{16}$$

Where F_i is fitness of individual *i* and *n* is the number of individuals in the population. Since roulette wheel is basically a stochastic process, there is a good chance that the individual with best fitness is selected both as mother and father. Thus, in order to diminish the loss of genetic diversity, we imposed that the two parents be different individuals, given a uniform random number b $\in[0, 1]$.

$$C = b.M + (1-b).F \tag{17}$$

or

$$C = b.F + (1-b).M \tag{18}$$

Where C is the real value chromosome of the child, and M and F are the chromosome of the parents.

After a new individual has been created, a mutation was performed on it. Given the chosen solution encoding, we employed a uniform mutation, that randomly changes a gene to a uniform random value from i interval: x_i =U (min_i, maxi) .The interval we used was (0.03 - 0.1), where x_i represents the current value of the gene.

The models mass balance equation give the following set of ordinary differential equations:

$$\frac{dz}{dt} = f(z,u,t) \qquad z(t_o) = z_o \tag{19}$$

Where z(t) is the state variable vector defined, for polymerization process, by

$$z = [[C^*], [M]_b, \lambda_{Lo}, \lambda_{L1}, \lambda_{L2}, \lambda_{Do}, \lambda_{D1}, \lambda_{D2}] \tag{20}$$

And u(t)is the control variable vector, corresponding to the monomer concentration, catalyst concentration and temperature as:

$$u(t) = [[M]_b, [C^*], T] \tag{21}$$

An admissible control input u(t) should be formed in such a way that the performance indices, the objective function (J) defined by the following equation, is minimized:

$$\text{Min J } [u(t)] = w_{PDI}.PDI_f + w_{Rp}.\left(\frac{1}{1+Rp_{nf}}\right) + w_{Dpn}.\left(1-\frac{Dp_{nf}}{Dp_{nd}}\right)^2 \tag{22}$$

Subject to:

$$\frac{dz}{dt} = f(z,u,t) \quad \text{and} \quad u_{min} \le u(t) \le u_{max} \tag{23}$$

Where w is weighting factors, PDI_f, $Rp_{nf}$and Dp_{nf} are the actual values of PDI, Rp and Dp corresponding to the final reaction time t_f, Dp_{nd} are the desired values of degree of polymerization at t =t_f,An important objective function of the polymerization system is the minimization of the final reaction time, which leads to higher polymerization rate. The other objective included in the same function is the minimization of the polydispersity index of the polymer product. This ensures good physical properties of the polymer manufactured. The constraint on D_{pn} leads to the production of polymer having desired properties, because several physical properties of polymers are related to their values of D_{pn}.

Genetic algorithms are based on the mechanism of natural selection and genetics. They start with an initial setoff solutions, called population, each solution in the population being called a chromosome. The chromosomes are evolved through successive iterations, called generations, by the genetic operators (selection, crossover and mutation) that mimic the principle of natural evolution.

The optimization procedure includes the kinetics model (KM) is solved with a genetic algorithm. The fitness function of the GA is the scalar objective function (Eq. 22). Genetic algorithm provides, after an iterative calculus, the optimal values for decision variables ($[M]_b$, [C], T, t), which are the inputs for the kinetics model and, also, the weights for the objective function. With these inputs, the kinetics model computes the responses Rp, Dp and PDI and the last one will by compared with desired values. If the two values are identical or the difference between them is very small, we can conclude that the task of the optimization, represented by minimum of the objective function, is achieved. The details of the algorithm are presented in Figure 2.

A simple genetic algorithm with real value encoding for the chromosomes was used. The stop GA condition corresponds to the point where the maximum number of generations has been executed. Population size, number of generations, crossover probability, mutation probability and weighting factors are known as the control parameters of genetic algorithm. The values of these parameters must be specified before the execution of GA and they depend on the nature of the objective function. The GA parameters ranges are summarized in Table 4.

5. RESULTS AND DISCUSSION

5.1. Kinetics model validation

Model validation is important to ensure that the developed model is able to predict the polymerization reactor performance accurately. Kinetics model (KM) is validated by undergoing confirmation run experiments, using the set of experiments that conducted based on CCD application (Table 1).Based on the predicted kinetics parameters, predicted rate of polymerization and molecular weight distribution analysis as well as the predicted Dp and PDI, the KM able to predict the polymerization reactor performance for the rate of polymerization (Rp), degree of polymerization (Dp) and poly dispersity index (PDI).Tables 5 summarize the experimental and predicted results for Rp, Dp and PDI under different polymerization condition. The validation results show that within the experimental rang; the kinetics model was capable in predicting Rp, Dp and PDI within less than 15% error, i.e. the total average absolute error % for Rp, Dp and PDI are 11.23% , 13.35 and 14.87 respectively.

5.2. Genetic algorithm results

A good process model is a necessary prerequisite for application of the optimal control strategy. Thus, the kinetics model was selected to predicate the optimum polymerization operational conditions and the catalyst properties using the genetic algorithm (GA) technique. To optimal control problem supposes the determination of the maximum polymerization rate (Rp) and the desired degree of polymerization (Dp_{nd}), minimum polydispersity index (PDI) in a minimum polymerization reaction time (t). The GA as well as the kinetic model is implemented in Matlab M-Function program (Version 7.10.0.499), as specific functions were programmed for each phase of the genetic algorithm.

Table 6 contains optimizations performed with different values for GA parameters in order to determine the best set for the actual polymerization process. We imposed the value for Dp =1000, thus we keep in mind the objective of the optimization: to obtain a maximum Rp and the imposed value for Dp equal the desire value degree of polymerization with minimum polydispersity index (PDI) in a minimum polymerization reaction time (t). The optimization results of Table 6, show that Run (5) given appropriate parameters of GA used to solve the proposed optimization problem are: Population size = 50, Generation Number = 100, Crossover rate = 0.6and Mutation rate = 0.03, due to Dp calculated with optimal decision values is close to desire value of polymerization degree (Dp_{nd}) with high value of Rp and the minimum values of PDI and objective function J.

Table 7 presents supplementary optimization results obtained for different values imposed to degree of polymerization (Dp). In most of the runs, Dp calculated with optimal decision values is close to desire value with high values of Rp and minimum value of PDI, which means that one of the optimization goals is reached. Run 1 in Table 7 does not represent an acceptable result. Tests with different values of GA parameters do not improve it; a better value for polymerization rate and PDI is obtained along with a worse value for Dp. This is the general rule of the multi-objective optimization with conflicting partial objectives, where a compromise between the possible solutions is realized.

Model validation is important to be performed once optimization has been conducted. The goal is to check the results of the response experimentally, in order to ensure that the suggested optimum conditions are valid. The methods and experimental procedures conducted are similar to previous experiments presented in previous section for consistency. Three optimum solutions (Run 5 in Table 6, run 2 and 3 in Table 7) were selected for each response to validate it.

Table 8 show the summary results of experimental data and predicted KM at different optimal values of control variables ($[M]_{bo}$, $[C]_o$, T, t), as well as the maximum rate of polymerization with desired value of Dp and minimum PDI. Based on the results in Table 8, the optimum results are shown in Run (2), i.e. initial monomer concentration ($[M]_{bo} = 2.91$ mol/L), initial catalyst concentration ($[C]_o = 1.88*10^{-4}$ mol/L), polymerization temperature ($T=67^oC$) and polymerization time (t=25 min), these results gives the maximum rate of polymerization (Rp= 338.2 g sPS/g cat.h) and the desired value of polymerization degree (Dp=705.8) with minimum poly dispersity index (PDI=2.28). The validation results at these optimum values are valid and the average absolute error less than 5 % for all responses.

6. CONCLUSIONS

In this paper we developed and tested the modeling and optimization capacities of simple topologies and simple working strategies for kinetics model and genetic algorithms. For the syndiotactic polystyrene synthesis, these techniques provide a useful tool to easy find the reaction conditions to obtain a polymer with desired molecular weight and high polymerization rate. The genetic algorithm solves the optimization problem, while the kinetics model constitutes the model included in the optimization procedure, computes rate of polymerization and molecular weight that are used in the objective function of the optimization procedure, with the goal to maximize polymerization rate and to obtain a desired value for the molecular weight.

Nomenclature

$[C]_o$	Initial catalyst concentration	mol/L
$[M]_b$	Monomer concentration in the bulk liquid phase	mol/L
$[M]_c$	Monomer concentration at the catalytic active sites	mol/L
C*	Concentration of active catalyst sites	mol/L
D*	Deactivated catalyst site	-
D_n	Total dead polymer concentration	mol/L
Dp	Degree of polymerization	-
Dp_d	Desired values of polymerization degree	-
Dp_f	Actual values of degree of polymerization at final time	-
ka	Activation rate constant	1/s
k_d	Deactivation rate constant	1/s
kp	Propagation rate constant	L/mol.s
k_{tM}	Termination rate constants	L/mol.s

$k_{t\beta}$	β-hydrogen elimination rate constant	1/s
L_n	Live polymer chains of length n	
T	Temperature	^oC
t	Time	min
t_f	Final reaction time	min
ρ_c	Catalyst density	Kg/m^3
λ_{Lk}	Kth-moment of the live polymer	mol/L
λ_{Lo}	Total concentration of live polymer	mol/L

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Table (1): Reaction conditions and experimental data of styrene polymerization

Run	Variable				Response		
	$[M]_{bo}$ (mol/L)	$[C]_o$ (mol/L)	T (^oC)	t (min)	Rp (gsPS/gcat.h)	Dp (-)	PDI (-)
1	1.90	1.5	60	37.5	98.42	905.61	3.13
2	4.00	1.5	60	37.5	151.47	1624.84	2.42
3	1.90	2.1	60	37.5	137.89	698.4	3.40
4	4.00	2.1	60	37.5	223.21	1322.42	2.64
5	1.90	1.5	80	37.5	91.05	874.8	2.75
6	4.00	1.5	80	37.5	141.37	1463.35	2.11
7	1.90	2.1	80	37.5	133.94	585.67	2.82
8	4.00	2.1	80	37.5	192.77	1175	2.23
9	1.90	1.5	60	92.5	55.94	979.81	2.97
10	4.00	1.5	60	92.5	85.50	1683.66	2.28
11	1.90	2.1	60	92.5	78.35	654.84	3.27
12	4.00	2.1	60	92.5	119.75	1300.99	2.46
13	1.90	1.5	80	92.5	50.78	863.51	2.59
14	4.00	1.5	80	92.5	83.27	1481.01	2.08
15	1.90	2.1	80	92.5	73.67	559.64	3.01
16	4.00	2.1	80	92.5	121.26	1109.03	2.39
17	0.84	1.8	70	65.0	62.94	620.01	3.24
18	5.06	1.8	70	65.0	159.42	1579.69	1.88
19	2.95	1.2	70	65.0	67.91	1261.13	2.25
20	2.95	2.4	70	65.0	176.42	933.83	2.72
21	2.95	1.8	50	65.0	96.51	960.35	3.71
22	2.95	1.8	90	65.0	98.86	747.25	3.30
23	2.95	1.8	70	10.0	243.18	1236.77	2.94
24	2.95	1.8	70	120	82.36	1268.8	3.10
25	2.95	1.8	70	65.0	118.8	1013.16	2.41
26	2.95	1.8	70	65.0	124.3	1129.56	2.90
27	2.95	1.8	70	65.0	129.6	1135.64	3.02
28	2.95	1.8	70	65.0	132.8	1151.92	3.03

29	2.95	1.8	70	65.0	133.1	1149.99	3.04
30	2.95	1.8	70	65.0	132.9	1151.27	2.98

Table (2): Kinetic mechanisms of styrene polymerization over metallocene catalyst

Description	**Reaction**
Catalyst activation	$C_o + MAO \xrightarrow{ka} C^*$
Propagation	$C^* + M_c \xrightarrow{kp} L_1$ $L_n + M_c \xrightarrow{kp} L_{n+1}$
Chain transfer to monomer	$L_n + M_c \xrightarrow{ktm} D_n + L_1$
β-hydrogen elimination	$L_n \xrightarrow{kt\beta} D_n + C^*$
Catalyst deactivation	$C^* \xrightarrow{kd} D^*$, $L_n \xrightarrow{kd} D^*$

Table (3): Rate and moment equations of styrene polymerization over metallocene catalyst

$$\frac{d[C^*]}{dt} = -k_d[C^*] - k_p[C^*][M]_c + k_{t\beta}\lambda_{Lo}$$

$$\frac{d[M]_c}{dt} = -k_p[L][M]_c - k_{tm}[L][M] \approx -k_p[L][M]_c$$

$$\frac{d\lambda_{Lo}}{dt} = k_p[C^*][M]_c - k_{t\beta}\lambda_{Lo} - k_d\lambda_{Lo}$$

$$\frac{d\lambda_{L1}}{dt} = k_p[C^*][M]_c + k_p\lambda_{Lo}[M]_c + k_{tm}\,[M]_c(\lambda_{Lo} - \lambda_{L1}) - k_{t\beta}\lambda_{L1} - k_d\lambda_{L1}$$

$$\frac{d\lambda_{L2}}{dt} = k_p[C^*][M]_c + k_p[M]_c(2\lambda_{L1} + \lambda_{Lo}) + k_{tm}\,[M]_c(\lambda_{Lo} - \lambda_{L2}) - k_{t\beta}\lambda_{L2} - k_d\lambda_{L2}$$

$$\frac{d\lambda_{Do}}{dt} = k_{t\beta}\lambda_{Lo} + k_d\lambda_{Lo} + k_{tm}\lambda_{Lo}[M]_c$$

$$\frac{d\lambda_{D1}}{dt} = k_{t\beta}\lambda_{L1} + k_d\lambda_{L1} + k_{tm}\lambda_{L1}[M]_c$$

$$\frac{d\lambda_{D2}}{dt} = k_{t\beta}\lambda_{L2} + k_d\lambda_{L2} + k_{tm}\lambda_{L2}[M]_c$$

Table (4): Genetic algorithm parameters used in models optimization

GA Parameters	**Values**
Population size	30-300 individuals
Number of generations	50-500
Crossover probability	60-90 %
Mutation probability	1-3 %
Number of children / crossover	1
Weight factor for PDI (w_{PDI})	1
Weight factor for Rp (w_{Rp})	1
Weight factor for Dp (w_{Dpn})	50

Table (5): Summary of experimental and predicted KM for polymerization rate data

Run	Rp (gsPS/gcat.h)			Dp (-)			PDI (-)		
	Exp. Data	**KM Predicted Data**	**Absolute Error(%)**	**Exp. Data**	**KM Predicted Data**	**Absolute Error(%)**	**Exp. Data**	**KM Predicted Data**	**Absolute Error(%)**
1	98.42	105.54	7.23	905.60	995.81	9.96	3.13	3.46	10.4
2	151.47	159.06	5.01	1624.8	1760.1	8.33	2.42	2.60	7.50
3	137.89	154.93	12.3	698.40	862.59	23.5	3.74	4.49	20.6
4	223.2	238.36	6.79	1322.4	1417.9	7.22	2.64	2.88	8.99
5	91.05	116.85	28.3	874.80	1038.3	18.7	2.98	3.58	20.3
6	141.37	155.04	9.67	1463.3	1670.2	14.1	2.11	2.28	7.97
7	133.94	168.03	25.4	585.67	756.57	29.2	2.93	3.74	27.5
8	192.77	218.10	13.1	1175.0	1440.2	22.6	2.23	2.81	25.6
9	55.94	65.89	17.7	979.81	1040.8	6.23	2.97	3.32	11.9
10	85.50	90.72	6.11	1683.6	1831.3	8.77	2.28	2.47	8.40
11	78.35	85.36	8.95	654.84	768.65	17.4	3.27	3.47	6.05
12	119.75	131.43	9.75	1300.9	1374.1	5.62	2.77	3.11	12.2
13	50.78	58.86	15.9	863.51	1034.7	19.8	2.80	3.42	21.9
14	83.27	88.46	6.23	1481.0	1708.2	15.3	2.08	2.19	5.49
15	73.67	83.07	12.7	559.64	614.88	9.87	3.06	3.89	27.2
16	121.26	151.61	25.0	1109.0	1410.0	27.2	2.39	2.78	16.2
17	62.94	72.01	14.4	620.01	722.44	16.5	3.24	3.83	18.3
18	159.42	172.91	8.46	1579.6	1699.2	7.57	1.88	2.02	7.35
19	67.91	81.36	19.8	1261.13	1599.2	26.8	2.25	2.59	15.3
20	176.42	202.35	14.0	933.83	1053.3	12.8	2.72	3.26	19.8
21	96.51	106.85	10.7	960.35	1065.2	10.9	3.71	4.41	18.7
22	98.86	122.45	23.8	747.25	1014.2	35.7	3.30	4.53	37.1
23	243.18	261.49	7.53	1236.77	1355.9	9.64	2.94	3.46	17.7
24	82.36	85.04	3.26	1268.8	1413.1	11.3	3.10	3.31	6.77
25	118.8	133.25	12.1	1013.16	1106.8	9.25	2.41	2.65	9.95
26	124.3	133.25	7.2	1129.56	1106.8	2.01	2.44	2.65	8.69
27	129.6	133.25	2.82	1135.64	1106.8	2.53	2.36	2.65	12.1
28	130.7	133.25	1.94	1151.92	1106.8	3.91	2.36	2.65	12.5
29	130.5	133.25	2.11	1149.99	1106.8	3.75	2.35	2.65	12.7
30	130.31	133.25	2.26	1151.27	1106.8	3.86	2.39	2.65	10.9
	Average Absolute Error		**11.23**	**Average Absolute Error**		**13.35**	**Average Absolute Error**		**14.87**

Table (6): Optimization with different values for the GA parameters

Run	GA parameters	Control variable	Responses obtained by KM	Optimum response by GA
1	Pop. = 30 Gen. No. = 100 Cross. rate = 0.9 Mut. rate = 0.03	$[M]_{bo}$ =2.71 mol/L $[C]_o$ = 1.97 mol/L T = 62°C t = 39 min	Rp = 311.8 Dp =1018.6 PDI = 3.34	J = 0.0205 Dp_{nd} = 1000
2	Pop. = 50 Gen. No. = 100 Cross. rate = 0.9 Mut. rate = 0.03	$[M]_{bo}$ =2.33 mol/L $[C]_o$ = 2.48 mol/L T = 78°C t = 28 min	Rp = 297.2 Dp =994.5 PDI = 2.38	J = 0.0049 Dp_{nd} = 1000
3	Pop. = 300 Gen. No. = 100	$[M]_{bo}$ =2.96 mol/L $[C]_o$ = 1.57 mol/L	Rp = 288.6	J = 0.0074 Dp_{nd} = 1000

	Cross. rate = 0.9 Mut. rate = 0.03	$T = 71^{o}C$ t = 27 min	Dp =1008.9 PDI = 2.81	
4	Pop. = 50 Gen. No. = 200 Cross. rate = 0.9 Mut. rate = 0.03	$[M]_{bo}$ =3.11 mol/L $[C]_{o}$ = 2.04 mol/L $T = 75^{o}C$ t = 34 min	Rp = 321.2 Dp =989.4 PDI = 2.49	J = 0.0087 Dp_{nd} = 1000
5	Pop. = 50 Gen. No. = 100 Cross. rate = 0.6 Mut. rate = 0.03	$[M]_{bo}$ =2.62 mol/L $[C]_{o}$ = 1.51 mol/L $T = 64^{o}C$ t = 23 min	Rp = 334.7 Dp =1003.9 PDI = 2.26	J = 0.0037 Dp_{nd} = 1000
6	Pop. = 50 Gen. No. = 100 Cross. rate = 0.9 Mut. rate = 0.1	$[M]_{bo}$ =2.39 mol/L $[C]_{o}$ = 2.56 mol/L $T = 81^{o}C$ t = 36 min	Rp = 257.5 Dp =1012.3 PDI = 3.43	J = 0.0114 Dp_{nd} = 1000

Table (7): Optimization with different values for Rp, Dp, PDI

No.	GA parameters	Control variable	Responses obtained by KM	Optimum response by GA
1	Pop. = 50 Gen. No. = 100 Cross. rate = 0.6 Mut. rate = 0.03	$[M]_{bo}$ =2.42 mol/L $[C]_{o}$ = 1.67 mol/L $T = 56^{o}C$ t = 29min	Rp = 257 Dp =523 PDI = 2.93	J = 0.1097 Dp_{nd} = 500
2	Pop. = 50 Gen. No. = 100 Cross. rate = 0.6 Mut. rate = 0.03	$[M]_{bo}$ =2.91 mol/L $[C]_{o}$ = 1.88 mol/L $T = 67^{o}C$ t = 25 min	Rp = 338.2 Dp =705.8 PDI = 2.23	J = 0.0065 Dp_{nd} = 700
3	Pop. = 50 Gen. No. = 100 Cross. rate = 0.6 Mut. rate = 0.03	$[M]_{bo}$ =2.73 mol/L $[C]_{o}$ = 2.19 mol/L $T = 71^{o}C$ t = 31 min	Rp = 323.5 Dp =1502 PDI = 2.28	J = 0.0032 Dp_{nd} = 1500
4	Pop. = 50 Gen. No. = 100 Cross. rate = 0.6 Mut. rate = 0.03	$[M]_{bo}$ =2.46 mol/L $[C]_{o}$ = 1.91 mol/L $T = 69^{o}C$ t = 23 min	Rp = 296.1 Dp =2006 PDI = 2.64	J = 0.0038 Dp_{nd} = 2000

Table: (8): Summary of experimental data and predicted KM for Rp, Dp and PDI at different optimum values of control variables.

Run	**Optimum variables**				**Rate of polymerization (Rp)**		
	M_o (mol/L)	**C_o *10^4 (mol/L)**	**T (°C)**	**t (min)**	**Experimental Data**	**KM Predicted Data**	**Absolute Error (%)**
1	2.62	1.51	64	23	320.4	334.7	4.46
2	2.91	1.88	67	25	324.3	338.2	4.29
3	2.73	2.19	71	31	307.7	323.5	5.13
Run	**Optimum variables**				**Degree of polymerization (Dp)**		
	M_o (mol/L)	**C_o *10^4 (mol/L)**	**T (°C)**	**t (min)**	**Experimental Data**	**KM Predicted Data**	**Absolute Error (%)**
1	2.62	1.51	64	23	959.6	1003.9	4.62
2	2.91	1.88	67	25	681.4	705.8	3.58
3	2.73	2.19	71	31	1431.2	1502	4.95
Run	**Optimum variables**				**Poly dispersity index (PDI)**		
	M_o (mol/L)	**C_o *10^4 (mol/L)**	**T (°C)**	**t (min)**	**Experimental Data**	**KM Predicted Data**	**Absolute Error (%)**
1	2.62	1.51	64	23	2.37	2.26	4.64
2	2.91	1.88	67	25	2.33	2.23	4.29
3	2.73	2.19	71	31	2.41	2.28	5.39

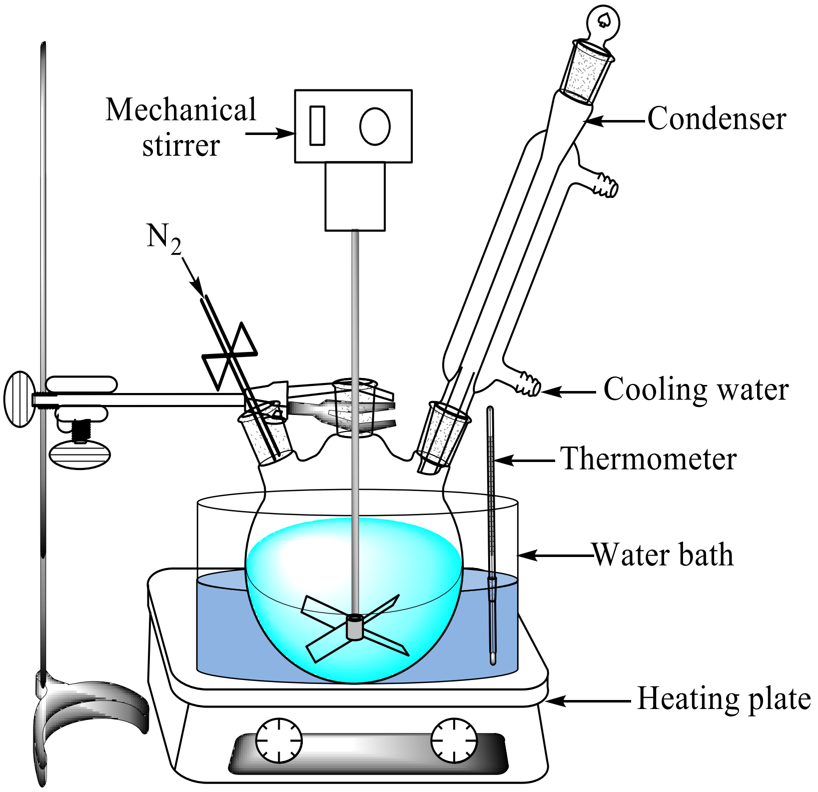

Fig. (1): Schematic diagram for Preparation of silica supported catalyst

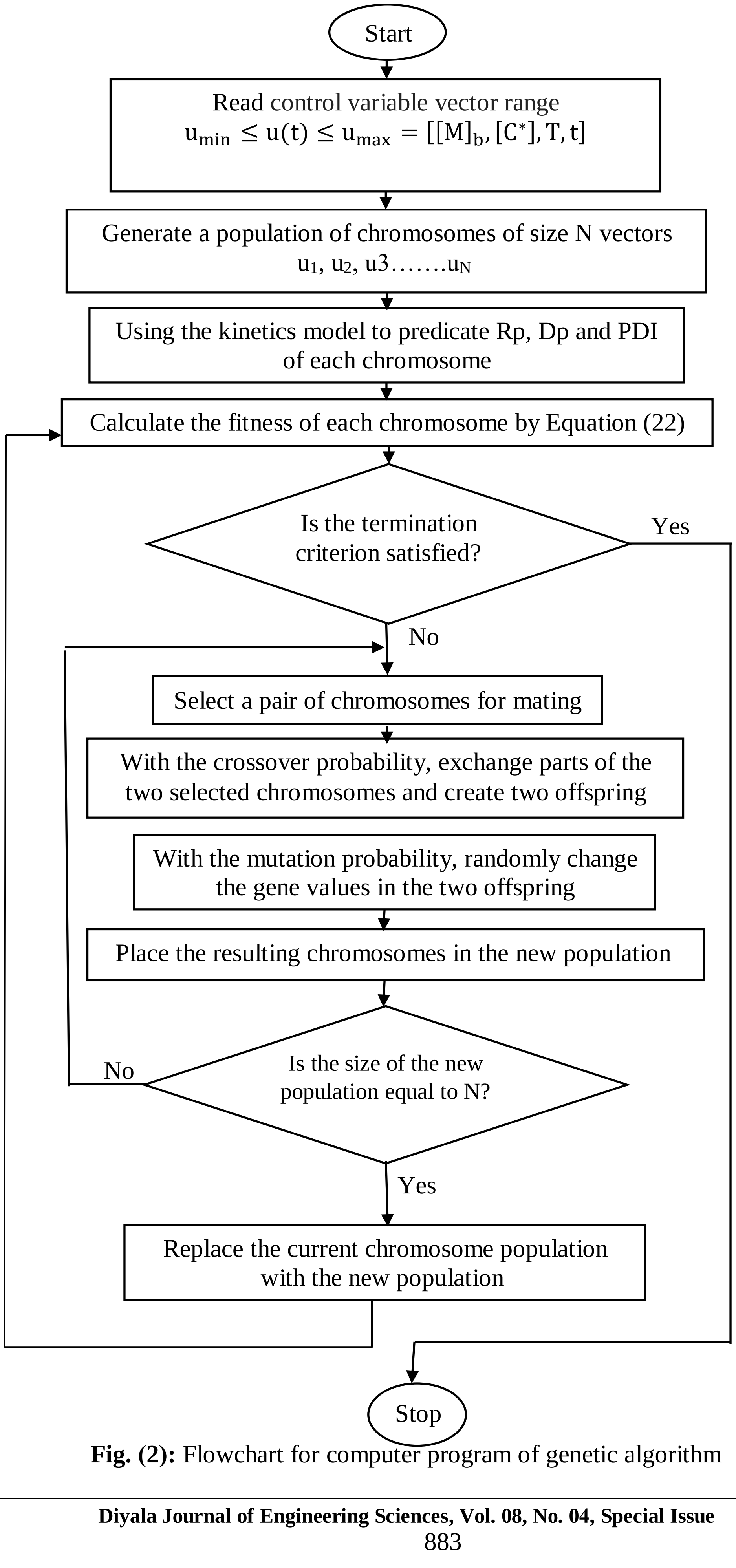

Fig. (2): Flowchart for computer program of genetic algorithm

اختيار الأمثل متعددة الأهداف لبلمرة الستايرين التناسقية باستخدام تقنية الخوارزمية الجينية

الخلاصة:

تم استخدام تقنية اختيار الأفضل متعدد الأهداف لتحديد الضروف المثلى لبلمرة الستايرين التناسقية. حيث تم اختبار نموذج حركية التفاعل وتقنية الخوارزمية الجينية لنمذجة واختيار الافضل لعملية بلمرة الستايرين. للتحقق من هذه النموذج، تم إجراء بلمرة الستايرين التناسقية المدعمة بالعامل المساعد المحمل على السيلكا. أظهرت النتائج أن نموذج حركية التفاعل يتوقع أفضل أداء لمفاعل البلمرة وبنسبة خطأ اقل من 10% وبالتالي، تم اعتماده في إيجاد أفضل الظروف التشغيلية باستخدام تقنية الخوارزمية الجينية, حيث كانت أفضل النتائج تعطي الحد الأقصى لمعدل البلمرة و القيمة المطلوبة من درجة البلمرة مع الحد الأدنى من مؤشر التشتت المتعدد وبنسبة خطاء اقل من 2% .