Optimization of Ammonia Synthesis Reactor using Genetic Algorithm

Behnam Hosseinzadeh, Mohammad T. Sadeghi[a]

[a] Process Simulation and Control Research Lab., Department of Chemical Engineering, Iran University of Science and Technology (IUST), Narmak 16844, Tehran, Iran sadeghi@iust.ac.ir

Abstract- In this paper Genetic Algorithm was employed as a powerful method for optimization of an industrial ammonia synthesis reactor. The reactor consists of four adiabatic catalytic fixed beds equipped with three quench flows and an internal heat exchanger on its top. The optimization problems were defined based on plant data obtained from an operational ammonia reactor at Khorasan petrochemical complex, Bojnurd-Iran. An optimum ratio of H_2/N_2 was obtained from numerical solution of the problem in which Micro Genetic Algorithm was employed. However, Simple Genetic Algorithm was used to find the quench flow rates configuration. The results for mathematical model show that the estimated optimum condition can improve the overall product yield by 4.5%.

Keywords: Optimization, Modeling, Genetic Algorithm, Ammonia Synthesis Reactor.

1. Introduction

Ammonia is the second largest synthetic chemical product. More than 90 % of the world consumption is manufactured from the elements nitrogen and hydrogen in a catalytic process originally developed by Fritz Haber and Carl Bosch [1] using a promoted iron catalyst. Discovered by Alwin Mittasch [2] Ammonia is the initial chemical material for a variety of industries. It is used in production of chemical fertilizers, explosive materials, polymers, acids and even cooler systems. About 1.6 % of the world consumption of fossil energy (not including combustion of wood) goes into the production of ammonia. In developing countries, ammonia is generally one of the first products of industrialization. As 85 % of world nitrogen consumption is for fertilizers it might be expected that ammonia production should develop approximately in proportion to the growth of world population [3]. Optimization can play an important role

providing an insight of the industrial plants. Hence, optimization of ammonia unit is very important to investigate the appropriate operation modes for the unit. Ammonia synthesis loop is the most important part of this unit and a better understanding of its bottleneck can led us to enhance the operation yield at higher level.

2. Ammonia Synthesis Loop

In ammonia production plant, the synthesis loop is located after the syngas production and purification units. Ammonia synthesis process takes place in high pressure and high power multi cycle compressors are used to supply the required pressure. The Kellogg synthesis reactor incorporated in this loop is of vertical type with four beds, three quenches and an internal heat exchanger. In addition to the mentioned heat exchanger, the quench gas flow is also used for control of temperature of beds. The input feed to the reactor, is first divided into two parts before entrance. One part is considered as feed and the other part is considered as quench flow. The feed, after entering the reactor, passes through the empty spaces of the beds as well as the reactor walls and gets slightly heated. When reaching to the end of the reactor, it passes through the shell of the internal heat exchanger and its temperature reaches 715 K. Tubes of the heat exchanger contain the output gas from the forth bed. Quench gas is used to control the inlet temperature of the beds.

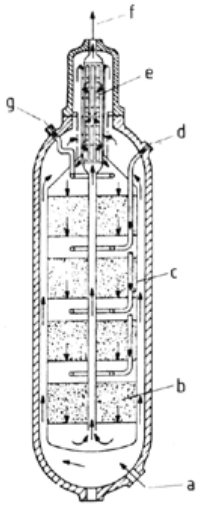

Fig.1 Ammonia Synthesis Reactor - Kellogg method [11]

Figure 1 depicts the schematic diagram of a Kellogg vertical reactor. When the gas passes the first bed and the reaction is occurred, its temperature increases and reaches 774.5 K. After leaving the first bed, quench flow is injected and the two flows are mixed and enter the second bed. This process is occurred between second, third and fourth beds. After the forth bed, the syngas flows through the heat exchanger warming up the inlet feed flow. The catalyst of this reactor is magnetic ferro-oxide.

3. Mathematical Model

Temperature and concentrations of the species are obtained through modeling of the synthesis reactor. However, validation of the model is only plausible at the end of each bed since industrial data are not usually available along the length of the bed. The following assumptions have been applied in modeling the reactor:

1. One-dimensional coordinate has been considered along the bulk flow
2. Negligible mass and heat diffusion, as the fluid velocity is very high in industrial scale
3. Constant density
4. Uniform concentration and temperature on catalyst surface and bulk of the gas
5. The effects of diffusion resistance in catalyst, temperature gradient and catalyst internal concentration have been taken into account in the equations by a coefficient.

3.1 Material balance (Molar) [2, 3]

Considering an element with height of Δx and cross section area equal to the bed area following equation can be written:

$$(uCA|x - uCA|x + \Delta x) + A\Delta x(R_{NH_3})\eta = 0 \quad (1)$$

Dividing both sides of the equation by $A\Delta x$ and $\Delta x \rightarrow 0$, results in the following:

$$u\frac{dc}{dx} + \left(-r_{NH_3}\right)\eta = 0 \quad (2)$$

This equation can be written based on the nitrogen conversion percentage shown by Z as below:

$$\frac{dZ}{dx} = \frac{\eta r_{NH_3}}{2\frac{F^0_{N_2}}{A}} \quad (3)$$

In which the term $\frac{F_{N_2}^0}{A}$ is the initial molar flow of N_2.

3.2 Reaction Rate [3, 4, 5, 6, 7, 8]

In order to calculate the rate of reaction, modified Temkin equation offered by Dyson and Simon in 1968 has been employed [4]

$$R_{NH_3} = 2k\left[K_a^2 a_{N_2}\left(\frac{a_{H_2}^3}{a_{NH_3}^2}\right)^{\alpha} - \left(\frac{a_{NH_3}^2}{a_{H_2}^3}\right)^{1-\alpha}\right] \quad (4)$$

In which:

α: Constant which takes a value from 0.5 to 0.75 in literature[8].

k: Rate constant for reverse reaction in: $N_2 + 3H_2 \rightarrow 2NH_3$

K_a*:* equilibrium constant

a_i*:* Activity

Activation can be written in terms of activation coefficient as below:

$$a_i = \frac{f_i}{f_i^0} \quad (5)$$

f_i^0: Reference fugacity. If the reference fugacity is considered to be 1 atm, then:

$$a_i = \frac{f_i}{1} = f_i = y_i \phi_i P \quad (6)$$

In this equation f_i is the fugacity coefficient and P is the total pressure.

Following relations are based on the experimental data for fugacity coefficient of hydrogen, nitrogen and ammonia [4].

$$\phi_{H_2} = \exp\left\{e^{(-1.69657+0.0142)P} - e^{(-0.13657-1.87)P^2} + 500\left[e^{(-0.011957-1.841)}\right]\left(e^{\frac{P}{300}}\right)\right\} \quad (7)$$

$$\phi_{N_2} = 0.93431737 + 0.2028538\times 10^{-2}T + 0.298596\times 10^{-2}P - 0.270727\times 10^{-6}T^2 + 0.4778207\times 10^{-6}P^2$$

(8)

$$\phi_{NH_3} = 0.1438996 + 0.2028538\times 10^{-2}T - 0.4487672\times 10^{-3}P - 0.1142945\times 10^{-5}T^2 + 0.2761216\times 10^{-6}P^2$$

(9)

T is in Kelvin and P in atmosphere units.

The relation for reverse ammonia synthesis reaction is base on Arrhenius equation as:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \qquad (10)$$

k: Arrhenius coefficient equal to 8.849×10^{14}

E: Activation energy, which varies with temperature and its mean value is $40765\frac{kcal}{kmol}$

R: Gas constant

Gillespie and Beattie in 1930 have developed the following equation to calculate the equilibrium constant [9].

$$\log K_a = -2.691122\log T - 5051925\times10^{-8}T + 1.848863\times10^{-7}T^2 + \frac{20001.6}{T} + 2.689$$

(11)

3.3 Effectiveness Factor [3, 4, 10]

In order to investigate the effects of temperature and density for the catalyst interior and the difference between these parameters with those of the catalyst surface, an effectiveness factor called η has been defined.

The general form of the equation defining the effectiveness factor has been given below [10].

$$\eta = b_0 + b_1T + b_2Z + b_3T^2 + b_4Z^2 + b_5T^3 + b_6Z^3 \qquad (12)$$

The above equation is in terms of T and conversion percentage. The coefficients of this equation for three different pressures have been depicted in table 1[4].

Table1. Coefficients of the correction factor polynomial in terms of pressure

Pressure (bar)	b_0	b_1	b_2	b_3	b_4	b_5	b_6
150	-17.539096	0.07697849	6.900548	-1.08279×10^{-4}	-26.42469	4.927648×10^{-8}	38.937
225	-8.2125534	0.03774149	6.190112	-5.354571×10^{-5}	-20.86963	2.379142×10^{-8}	27.88
300	-4.6757259	0.02354872	4.687353	-3.463308×10^{-5}	-11.28031	1.540881×10^{-8}	10.46

3.4 Energy balance

Energy balance is investigated on the same element on which mass balance has been considered.

Accumulation = Consumed Energy – Produced Energy + Output Energy – Input Energy

In steady state, the accumulation is zero therefore:

$$A\{\rho u C_p T|x - \rho u C_p T|x+\Delta x\} + A\Delta x(-\Delta H_r)R_{NH_3}\eta = 0 \qquad (13)$$

Dividing the above equation by $A\Delta x$ and $\Delta x \rightarrow 0$, results:

$$\rho u C_p \frac{dT}{dx} + (-\Delta H_r) R_{NH_3} \eta = 0 \quad (14)$$

3.5 Heat Capacitance

The following equation is used to determine the heat capacitance:

$$C_{Pi} = 4.184(a_i + b_i T + c_i T^2 + d_i T^3) \quad \left(\frac{kj}{kmol}\right) \quad (15)$$

Table2. Coefficients of the heat capacitance polynomial

Component	a	b×10^2	c×10^5	d×10^5
H_2	6.952	-0.04567	0.09563	-0.2079
N_2	6.903	-0.03753	0.193	-0.6861
CH_4	4.75	1.2	0.303	-2.63
Argon	4.9675	----	----	----

Shah has developed an equation for determination of ammonia heat capacity which was used in the model [11, 12]

$$C_{P_{NH_3}} = 4.184\left\{\begin{array}{c} 6.5846 - 0.61251 \times 10^{-2}T + 0.23663 \times 10^{-3}T^2 - \\ 1.5981 \times 10^{-9}T^3 + 96.1678 - 0.067571P + (0.2225 + \\ 1.6847 \times 10^{-4}P)T + (1.289 \times 10^{-4} - 1.0095 \times 10^{-7}P)T^2 \end{array}\right\} \quad \left(\frac{kj}{kmolK}\right) \quad (16)$$

3.6 Reaction Heat

Elnashaie has developed a relation in 1981 for calculation of reaction heat as following: [13]

$$\Delta H_r = 4.184\left\{\begin{array}{c} -\left[0.54526 + \frac{846.607}{T} + \frac{439.734 \times 10^6}{T^3}\right]P - 5.34658T - \\ 0.2525 \times 10^{-3}T^2 + 1069197 \times 10^{-6}T^3 - 9157.09 \end{array}\right\} \quad \left(\frac{kj}{kmol}\right) \quad (17)$$

3.7 Pressure Drop [14, 15, 16]

In order to calculate the pressure drop inside the beds, Ergun equation has been applied. This relation for a one dimensional flow is as below [15, 16]

$$\Delta P = -\mu \nabla^2 u = \frac{150(1-\varepsilon)^2}{\varepsilon^3} \times \frac{\mu u}{d_p^2} - 1.75 \frac{1-\varepsilon}{\varepsilon^3} \times \frac{\rho u^2}{d_p} \quad (18)$$

As most of the industrial data along the beds are not available, the model is tested based on the above values at the end of each bed. Applying mass, energy and momentum balances on an

element, derive the mathematical model. Considering all the points and discussions raised in the previous sections, the set of three differential equations are derived as below:

$$\begin{cases} \frac{dx}{dw} = \frac{\eta r_{NH_3}}{2F_{N_2}/_A} \\ \rho u C_p \frac{dT}{dx} + (-\Delta H_r) r_{NH_3} \eta = 0 \\ \frac{dP}{dx} = -\mu \nabla^2 u = -\frac{150(1-\varepsilon)^2}{\varepsilon^3} \times \frac{\mu u}{d_p^2} - 1.75 \frac{1-\varepsilon}{\varepsilon^3} \times \frac{\rho u^2}{d_p} \end{cases} \quad (19)$$

The 4th order Runge Kutta approach is used to solve the above set of equations. As this set of equations is stiff, pressure drop equation is first taken out of the set and the new set with two equations is solved using Runge Kutta numerical method. At each stage of the numerical solution, pressure drop is calculated by means of the temperature and concentration derived from that stage and in this case the three parameters i.e. temperature, pressure and conversion rate are determined.

4. Simulation results

Results taken from simulation are compared with industrial data. Input conditions are as below

Reactor input temperature: 650 K

Reactor input pressure: 150 bar

Desired temperature for input gas flow to the first bed: 715 K

Input flow rate to reactor: $20.83 \frac{kg}{hr}$

Table3 presented input compositions of feed.

Table3. Input compositions of feed

Component	Mole fraction
y_{0,N_2}	0.2099
y_{0,H_2}	0.6331
y_{0,NH_3}	0.0209
y_{0,CH_4}	0.1040

$y_{0,Ar}$	0.0320

The mathematical heterogeneous model involves of a system of partial differential equations solved in steady state mode. These equations are discretized with respect to axial coordinate to 105 nodes along the reactor. Mathematical model was obtained by elimination of all time-derivatives in the original ordinary differential equations in each node of the reactor. These algebraic equations are solved with "Rung - Kutta" method. Results of simulation are shown in Fig. 2 and 3 for profiles of temperature and ammonia concentration along the reactor.

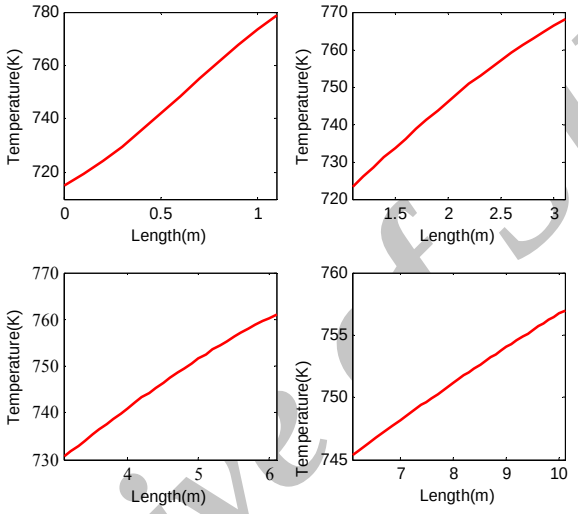

Fig. 2 Temperature profile of ammonia synthesis reactor

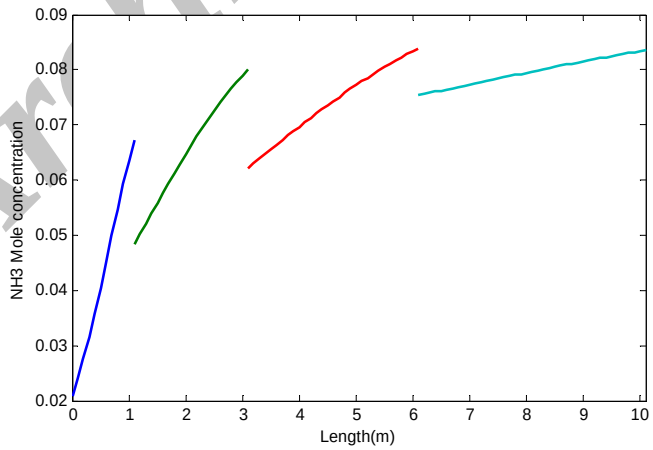

Fig. 3 NH_3 concentration along the reactor beds predicted by simulation

Table 4 illustrates the comparison of simulation results and plant data obtained from an operational ammonia reactor in Khorasan petrochemical complex at Bojnurd-Iran.

Table.4 Comparison of simulation results and Khorasan petrochemical complex

	First bed's Temperature(K)		Second bed's Temperature(K)		Third bed's Temperature(K)		Fourth bed's Temperature(K)	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Simulation	715	778.6	723.3	767.9	730.6	761.1	745.3	757.0
Plant data	715	774.5	721.6	763	728.7	754.5	738.6	748.3

5. Optimization and results

Ammonia synthesis reactor of Khorasan petrochemical complex at Bojnurd-Iran was chosen as a case study. The product yield at operational condition was $2.19730 \times 10^2 \ \frac{ton}{year}$. Therefore, all of the results were compared with operation condition. In this study, the optimization of reactor was investigated in two approaches, optimal quench configuration approach and optimal H_2/N_2 ratio approach. Mathematical model was used to evaluate objective function.

a. Optimal quench configuration approach

From a theoretical point of view, there is an optimal temperature profile along the ammonia synthesis reactor, which maximizes ammonia production rate. The objective function was to maximize the ammonia production rate. Then, optimization problem was formulated as below:

Maximize $P = f \times y_{NH_3} \times M_{av}$ (20)

Subject to: $Q1+Q2+Q3=41.52$

(21)

$$700 < T_{syngas} < 780 \quad (22)$$

The focus of this work is to maximize the product yield of reactor regarding to constant rate of quenches and temperature of syngas 700-780 for prevention of catalyst destruction. The optimization of the reactor was carried out using the simple GA parameters presented by Goldberg [18], summarized in Table 5.

Table.5 Genetic algorithm parameters used to find optimal quench configuration

Number of population	100
Selection method	Roulette
Crossover fraction	.95
Mutation fraction	.05
Elitism	0

The termination criterion adopted was to reach a high assigned number of generations, set on 250 iterations. Table 6 shows the optimization results for SGA. Results show that for increasing of the product yield of reactor first and second quench rate should be increased and so third quench rate is decreased. Figure 4 shows the temperature profiles of syngas along the beds and regarding to figure 4 temperature on syngas don't violate the in equally constraint.

Table.6 Optimal quench configuration predicted by SGA

Inlet temperature to first bed	713.49 K
First quench rate	17.14 kg/s
Second quench rate	18.50 kg/s
Third quench rate	5.85 kg/s
Predicted product yield	222.030 ton/year

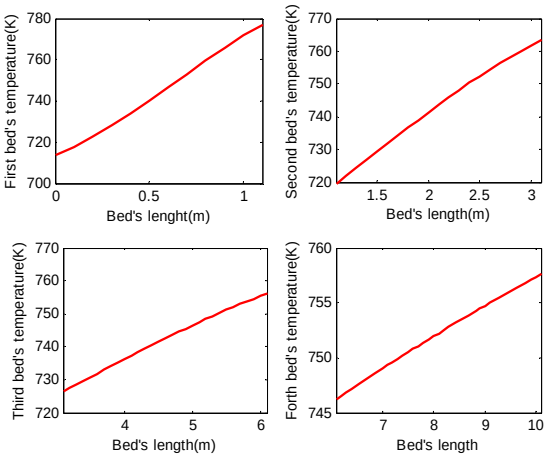

Fig. 4 Temperature profile of ammonia synthesis reactor with new quench configuration

Figure 5 shows the NH_3 concentration along the reactor beds with new quench configuration. Ammonia synthesis reaction is exothermic reaction so decreasing of inlet temperature and increasing of first and second quench rate caused the increasing of the NH3 concentration in first 3 beds.

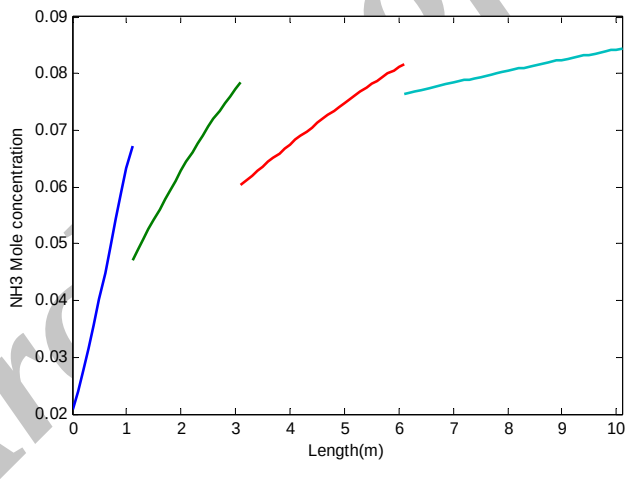

Fig.5 NH_3 concentration along the reactor beds with new quench configuration

b. Optimal H_2/N_2 ratio approach

Because of complexity and unimodality of objective function, optimal H2/N2 ratio should be determined with μGA. A simple genetic algorithm (SGA) works with a serially implemented binary coded population of size N, with a generation to generation evolution based on reproduction, with crossover (rate of crossover, C) and mutation (rate of mutation, M). Just as in

the SGA, the μGA works with binary coded populations and are implemented serially. The major difference between SGA and the μGA comes in the population choice. In the μGA structure proposed by Krishnakumar[19], the population size is fixed at N=5.

Optimization problem was formulated as below:

$$Maximize\ P = f \times y_{NH_3} \times M_{av} \qquad (23)$$

Subject to: $y_{H_2} + y_{N_2} = 0.8431$

H_2/N_2 ratio presented in literature is 2.5 – 3 and in operational reactor this ratio is about 3. μGA parameters presented by Krishnakumar, summarized in Table 7.

Table.7 Genetic algorithm parameters used to find optimal quench configuration

Number of population	5
Selection method	Tournament
Crossover fraction	.95
Mutation fraction	.09
Elitism	1

Optimal ratio of H2/N2 is 2.778 and this new ratio can improve the product yield by 1.5%.

Conclusion:

Optimization of an operational ammonia synthesis reactor at Khorasan petrochemical complex, Bojnurd-Iran was performed in this research using Genetic Algorithm as a powerful method. Numerical solution of the optimization problem applying Micro Genetic Algorithm shows that an optimum ratio of H_2/N_2 is 2.778. Moreover, Simple Genetic Algorithm was employed to find the quench flow rates configuration. Simulation results show an improvement of the overall product yield by 4.5% when optimum conditions are applied.

References

[1] R.W. Missen, C.A. Mims, B.A. Saville, "Introduction to Chemical Reaction Engineering & Kinetics", Wiley, 1999.
[2 J. Morud, "The dynamics of Chemical Reactors Whit Heat Integration", PhD thesis, 1995.
[3] S. S. Elnashaie, M. E. Abashar and A. S. Al. Ubaid, "Simulation and Optimization of an Industrial Ammonia Reactor", Ind. Eng, chem. Res, Vol. 27, pp. 2015, 1988.
[4] D.C. Dyson and J.M. Sicon. "A Kinetic Expression with Diffusion Correction for Ammonia Synthesis on Industrial Catalyst", Ind. Eng. Chem. Fundamental, Vol. 7, No. 4, pp. 605, 1986.
[5] P.P. Singh and N. Saraf "Simulation of Ammonia Synthesis Reactor", Ind. Eng. Chem. Process Des. Dev, Vol. 18, No.3, pp. 304, 1979.
[6] P. Stoltze and J. K. Norshov, "An Interpretation of the High-pressure Kinetics of Ammonia Synthesis Based on a Microscopic Model" J. Catal, Vol. 110, pp. 1, 1988.
[7] L. D. Gaines, "Optimal Temperatures for Ammonia Synthesis Converters", Ind. Eng. Chem, process Des. Dev, Vol. 16, No. 3, pp. 381, 1977.
[8] A. Nielsen, "An investigation on Promoted Iron Catalysts for the Synthesis of Ammonia", 3rd Ed, Jul. Gjellerups, Copenhagen, 1968
[9] L. J. Gillespie, J. A. Beattie, Phys. Rev., Vol. 36, pp. 734, 1930
[10] L. D. Gaines, "Ammonia Synthesis Loop Variables Investigated By Steady-State Simulation", Chem. Engng Sci, Vol. 34, pp. 37, 1970.
[11] B. Elverse, S. Hawkins, W. Russey, G. Schulz, "Ullman's Encyclopedia of Industrial Chemistry", 5th Ed, Vol. A2, 1993.
[12] M. J. Shah, "Control Simulation in Ammonia Production", Ind. Eng. Chem., Vol 59, No 1, 72, 1967.
[13] A.T. Mahfouz, S.S. Elshishini, and S.S.E.H. Elnashaie, "Steady-State Modelling and Simulation of an Industrial Ammonia Synthesis Reactor – I. Reactor Modeling ", Modeling Simulation & control, B, ASME press, Vol. 10, No. 3, pp. 1, 1987.
[14] S.S.E. H. Elnashaie and S.S. Elshishini, "Modeling, Simulation, and Optimization of Industrial Fixed Bed Catalytic Reactors", G&B Science, 1993.
[15] S. Ergun, "Fluid Flow through Packed Columns", Chem. Engng. Prog., Vol 48, No 2, pp. 89, 1952.
[16] F. Zardi, D.Bonvin, "Modeling, Simulation and Validation for Axial- Radial Ammonia Synthesis" , Chem. Eng. Sci., Vol. 47, No. 9-11 , pp. 2523, 1992.
[17] "Feasibility Study on Technology Transfer and Localization of Ammonia Synthesis Process in Iran", Project report, Research Institute of Petroleum Industries, 2001.
[18] "GAs in Search, Optimization and Machine Learning", D.E. Goldberg, Addison-Wesley, Reading, MA, 1989.
[19] "Micro-Genetic Algorithms for Stationary and NON-Stationary Function Optimization", Kalmanje Krishnakumar, SPIE conference on Intelligent control and adaptive systems, Phil, PA, 1989