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Optimization of methanol synthesis reactor using genetic algorithms

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Abstract

This paper presents a study on optimization of methanol synthesis reactor to enhance overall production. A mathematical heterogeneous model of the reactor was used for optimization of reactor performance, both at steady state and dynamic conditions. Here, genetic algorithms were used as powerful methods for optimization of complex problems. Initially, optimal temperature profile along the reactor was studied. Then, a stepwise approach was followed to get an optimal two-stage cooling shell to maximize production rate. These optimization problems were performed through steady-state optimizations with regard to dynamic properties of the process. The optimal reactor with two-stage cooling shell presented higher performances. This optimization approach enhanced a 2.9% additional yield throughout 4 years, as catalyst lifetime. Therefore, we can deduce to redesign methanol synthesis reactor with a two-stage cooling shell reactor based on this study.

Keywords: Methanol synthesis; Methanol reactor; Optimization; Genetic algorithms

1. Introduction

Methanol is one of the most important petrochemical products. It is used as a fuel, solvent and as a building block to produce chemical intermediates. The main step of methanol process is methanol synthesis. Methanol synthesis reactors are designed based on two technologies, high-pressure synthesis operating at 300 bar and low-pressure synthesis operating between 50 and 100 bar [1].

The methanol synthesis reactor studied here was a Lurgi-type, which is operated in the low-pressure regime [2]. The synthesis gas—CO_2, CO, H_2—is produced from natural gas in reformer plant and enters to the reactor. Methanol synthesis reactions occur in a set of vertical tubes packed with CuO-based catalyst. Heat of exothermic reactions is removed from tubes using boiling water, which is circulating as a coolant in the shell of reactor. The methanol synthesis reactor exhibits a dynamic behavior, mainly due to catalyst deactivation. The operating period of the reactor starts with fresh catalyst and ends in a certain low activity (about 0.4) so that operation of the reactor at that time is not economic. The operating period of the reactor is about 4 years as its catalyst lifetime. After this catalyst cycle time, the deactivated catalyst must be replaced with a fresh one.

There are several researches on methanol process in the literature. Lange presented a review of methanol synthesis technologies [1]. Moreover, several studies were reported on kinetic models of methanol synthesis [3,4] and deactivation models regarding effects of temperature and gas composition [5,6]. Because of severe temperature effects, both on methanol synthesis kinetics and catalyst deactivation, optimal temperature policies is a key to optimal operation of methanol synthesis reactor. Løvik studied dynamic modeling and optimization of methanol synthesis reactor and estimation of a catalyst deactivation model [7]. She presented an optimal temperature trajectory along the methanol reactor and optimal recycling ratio in her work.

There are several aspects in optimization of tubular reactors. Velasco et al. presented optimal inlet temperature trajectories for adiabatic packed reactors in the face of catalyst deactivation [8]. Dixit and Grant studied optimal coolant temperature in a non-isothermal reactor [9]. Optimization of tubular reactors had focused on reversible and exothermic

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Nomenclature

A_c	cross-sectional area of each tube (m^2)
a_v	specific surface area of catalyst (m^2/m^3)
a	activity of catalyst
c_{pg}	specific heat of the gas at constant pressure (J/mol)
c_{ps}	specific heat of the solid at constant pressure (J/mol)
c_t	total concentration (mol/m^3)
D_i	tube inside diameter (m)
E_d	activation energy used in the deactivation model (J/mol)
F_{MeOH}	production rate (t/day)
F_t	total molar flow rate per tube (mol/s)
h_f	gas–solid heat transfer coefficient (W/m^2 K)
K_d	deactivation constant (1/h)
k	node number
k_{gi}	mass transfer coefficient for component i (m/s)
I	objective function
P	penalty function
r_i	reaction rate of component i (mol/kg s)
T	bulk gas phase temperature (K)
R	universal gas constant (J/mol K)
T_s	catalyst temperature (K)
T_{shell}	temperature of boiling water in the shell side (K)
T_R	reference temperature used in deactivation rate (K)
t	time (s)
t_{gen}	generation number
U_{shell}	boiling water-gas overall heat transfer coefficient (W/m^2 K)
x	state variable
y_i	bulk gas phase mol fraction for component i in gas phase
y_{is}	mol fraction component i on the solid phase
z	axial reactor coordinate (m)

Greek letters

$\Delta H_{f,i}$	enthalpy of formation of component i (J/mol)
ε_B	void fraction of catalytic bed (m^3/m^3)

Superscripts and subscripts

0	inlet conditions
ss	initial conditions

reactions so far [10]. Mansson et al. applied optimal control theory to find an optimal temperature profile along an ammonia synthesis reactor, which maximized the concentration of ammonia in effluent stream of the reactor [11].

The objective of the current study was to optimize methanol synthesis reactor and consisted two different approaches. The first approach was to find the optimal temperature profile along the methanol synthesis reactor to maximize methanol production rate, while the second one was an investigation to develop a two-stage reactor with different coolant temperatures in cooling shells as a realistic approach. The idea of redesigning of methanol synthesis reactor with a two-stage cooling shell was used to increase the overall methanol production throughout in 4 years of operation. Both approaches were performed by steady-state optimization for some certain catalyst activity levels. These different catalyst activities were selected to stand for reactor dynamics in the catalyst lifetime. Genetic algorithms (GAs) were used for optimization of the reactor. GAs enable us to solve this constrained non-linear problem with numerous variables. It is believed that GAs could be used as powerful techniques to solve complex and real-world problems.

Almost since last two decades, GAs have been used in a large-scale application of engineering problems. Some applications of GAs have been reported in chemical engineering problems such as optimal design, operation and control [12–14].

2. Genetic algorithms

Genetic algorithms (GAs) are a class of non-traditional stochastic methods solving complex optimization problems of the real world [15,16]. They are optimization techniques that artificially simulate the gradual adaptation of natural chromosomes in the quest of producing better and more suitable individuals. A typical structure of genetic algorithms is shown in Fig. 1, in which $p(t)$ is a population of solutions in generation of t.

Genetic algorithms begin with a population of starting points initialized randomly ($t = 0$). Each point is evaluated based on objective function value. Then, a new population (iteration $t + 1$) is formed according to fitness value of individuals (selection). Some of these points randomly generate offspring through a number of predefined rules or operators. After some number of generations, the program converges. It

Genetic algorithms

Begin
  $t \leftarrow 0$;
  Initialize $p(t)$;
  Evaluate $p(t)$;
  While t_{gen} ***do***
  Begin
    $t \leftarrow t+1$;
    Select $p(t)$ from $p(t-1)$;
    Alter $p(t)$;
    Evaluate $p(t)$;
  End;
End;

Fig. 1. Structure of a typical genetic algorithm.

is hoped that the best individuals represents a "near-optimum or reasonable solution".

3. Kinetic, model and simulation

3.1. Kinetic

In the methanol synthesis, three overall reactions are possible: hydrogenation of carbon monoxide, hydrogenation of carbon dioxide that is strongly exothermic and reverse water-gas shift reaction:

$$2CO + 4H_2 \leftrightarrow 2CH_3OH + H_2O$$

$$2CO_2 + 5H_2 \leftrightarrow 2CH_3OH + H_2O$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

Kinetic model and the equilibrium rate constants are selected from Graaf's studies [4,17].

The catalyst of low-pressure methanol synthesis is $CuO/ZnO/Al_2O_3$ and during the course of process, it is deactivated mainly due to thermal sintering. Among several studies, the deactivation model suggested by Hanken was found appropriate to use [6]:

$$\frac{da}{dt} = -K_d \exp\left(\frac{-E_d}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right) a^5 \quad (1)$$

3.2. Model

Here, optimizations are investigated with heterogeneous model. In the heterogeneous model development, the gradient between solid and fluid phases is considered. In the modeling, axial dispersion is neglected, and it is assumed that there is no viscous flow on the catalyst pellets and also isotherm catalyst pellet is considered. The equations of heterogeneous model are as below. Solid-phase equations:

$$\varepsilon_s c_t \frac{dy_{is}}{dt} = kg_i(y_i - y_{is}) + r_i \rho_B a \quad i = 1, 2, \ldots, N-1 \quad (2)$$

$$\rho_B c_{ps} \frac{dT_s}{dt} = a_v h_f (T - T_s) + \rho_B a \sum_{i=1}^{N} r_i(-\Delta H_{f,i}) \quad (3)$$

where y_{is} and T_s are the solid-phase mole fraction and temperature, respectively. Fluid-phase equations:

$$\varepsilon_B c_t \frac{\partial y_i}{\partial t} = -\frac{F_t}{A_c}\frac{\partial y_i}{\partial z} - a_v c_t k g_i (y_i - y_{is}) \quad i = 1, 2, \ldots, N-1 \quad (4)$$

$$\varepsilon_B c_t c_{pg} \frac{\partial T}{\partial t} = -\frac{F_t}{A_c}\frac{\partial T}{\partial z} + a_v h_f (T_s - T) + \frac{\pi D_i}{A_c} U_{shell}(T_{shell} - T) \quad (5)$$

Table 1
Design specifications of industrial methanol reactor

Specifications	Value
Number of tubes	2962
Length of reactor (m)	7.022
Bulk density of bed (kg/m^3)	1132
Void fraction of bed (m^3/m^3)	0.39
Internal radius of tubes (mm)	38
Catalyst diameter (mm)	5.4

where y_i and T are the fluid-phase variables. The boundary conditions are:

$$y_i = y_{i0}, \qquad T = T_0 \quad \text{at } z = 0 \quad (6)$$

The initial conditions are:

$$y_i = y_i^{ss}, y_{is} = y_{is}^{ss}, T = T^{ss}, T_s = T_s^{ss}, a = 1 \quad \text{at } t = 0 \quad (7)$$

where y_i^{ss} and y_{is}^{ss} are profiles of mole fractions and T^{ss} and T_s^{ss} profiles of temperature along the reactor in fluid-phase and solid-phase, respectively. The industrial reactor specifications are demonstrated in Table 1.

3.3. Simulation

The mathematical heterogeneous model involves of a system of partial differential equations solved in steady state and dynamic modes. These equations are discretized with respect to axial coordinate to 30 nodes along the reactor. This provides a set of ordinary differential equations in each node.

Solution of the steady-state model was implemented on steady-state optimizations, as well as to determine the concentrations and temperature profile along the reactor at zero time (initial conditions). Steady-state 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 "Gauss–Newton" method. Results of simulation are shown in Fig. 2a and b for profiles of temperature and methanol concentration along the reactor. To solve the system of partial differential algebraic equations, different methods were tested and it was observed that Rosenbrock method of order 2 was more efficient for such set of stiff equations.

In Fig. 3, the predicted production rate of the reactor is compared with plant data of Shiraz Petrochemical Complex over a period of about 1200 operating days. The error of simulation was found to be less than 5% in most cases. In addition, dynamic simulation showed a decline in catalyst activity (of middle point of the reactor for sample) as it is shown in Fig. 4.

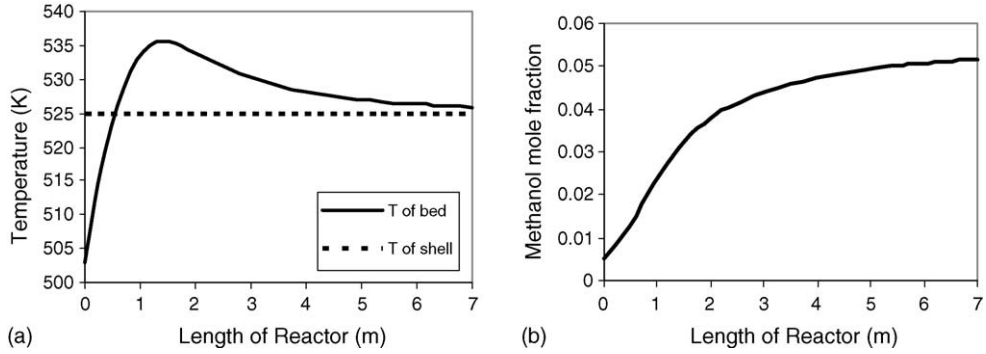

Fig. 2. Steady-state simulation result for methanol synthesis reactor: (a) temperature; (b) methanol concentration.

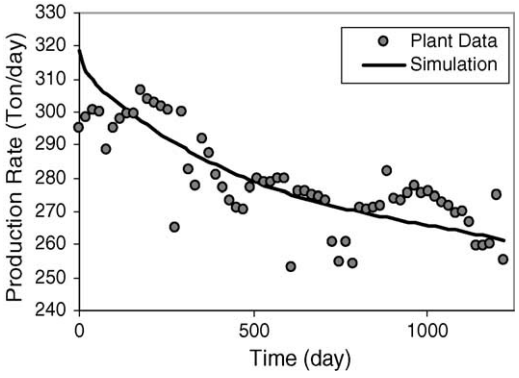

Fig. 3. Comparison of dynamic simulation result and plant data for methanol synthesis reactor.

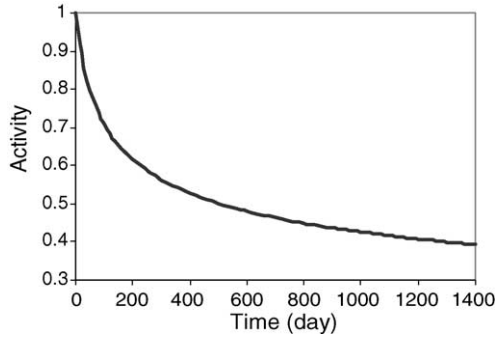

Fig. 4. Average catalyst activity in reactor for 1400 days of operation.

4. Optimization and results

Methanol synthesis reactor of Shiraz Petrochemical Complex was chosen as a case study. The coolant temperature was about 525 K. Therefore, all of the results were compared with operation conditions in 525 K as reference. In this study, the optimization of reactor was investigated in two approaches, optimal temperature profile approach and optimal two-stage cooling shell approach. Steady-state model was used to evaluate objective function, while dynamic simulation was used to evaluate overall methanol production throughout in 4 years.

4.1. Optimal temperature profile approach

From a theoretical point of view, there is an optimal temperature profile along the methanol synthesis reactor, which maximizes methanol production rate as reported in literature for tubular and exothermic reactors [10]. Because of catalyst deactivation, this optimal profile changes during operation so that there is not a unique optimal temperature profile in different times. Therefore, according to deactivation rate shown in Fig. 4, three activity levels equal to $a = 0.9$, 0.7 and 0.5 were chosen to study optimal temperature profile. These values stand for dynamic properties of reactor operation and give some information about variation of optimal profile through catalyst lifetime.

As mentioned in modeling and simulation, the reactor was discretized with respect to axial coordinate in 30 nodes. The most accurate optimal temperature profile was achieved with optimization of 30 parameters standing for coolant temperature in 30 nodes. These temperatures were bounded between 510 K and 535 K. The objective function was to maximize the methanol production rate. The equations of steady-state model are the equality constraints. Here, there is just one path constraint that states temperature of catalyst beds—as a state variable—which must be less than 543 K along the reactor [7]. It was attempted to avoid dramatically catalyst deactivation. Because optimization problem was implemented with heterogeneous model, temperature of the solid phase was considered as constraint rather than temperature of the fluid phase. This constraint was implemented with penalty method. Penalty function was taken zero provided that the solution satisfies constraint and equals to "10 ($T_s - 543$)" in order to discard the violator solution. Then, optimization problem was formulated as below:

$$\text{Max } I = F_{\text{MeOH}} - P \quad \text{that } P = 10(T_s - 543)$$

subjected to

$$x(k+1) = f(x(k), T_{\text{shell}}), \quad x(0) = x_0;$$

$$510(\text{K}) < T_{\text{shell}} < 535(\text{K}); \qquad T_s < 543(\text{K});$$

where P is the penalty function. Through optimization, optimal temperature profiles of coolant in the shell were obtained

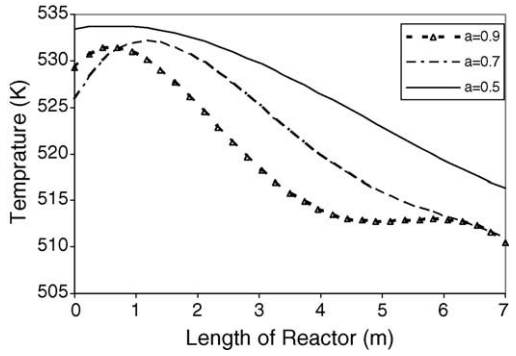

Fig. 5. Optimal coolant temperature profile along the cooling shell of reactor.

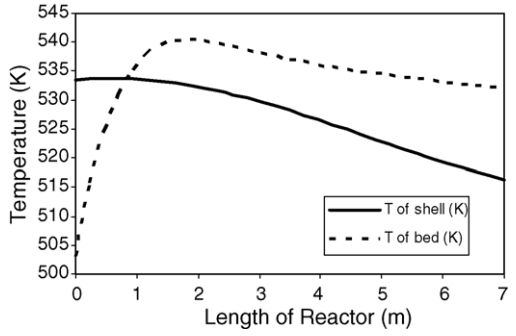

Fig. 6. Optimal temperature profile in cooling shell and in catalyst beds at $a = 0.5$.

for three different activities. These profiles are presented in Fig. 5. All of them have a peak near the entrance, and then, decline toward the end of reactor. Furthermore, there are some differences among them. The lower the activity the optimal temperature profile is obtained in higher temperature and the temperature declines more gradually.

Optimal temperature profile of coolant causes an optimal temperature profile in the tubes of the reactor. Fig. 6 shows optimal temperature profile along the cooling shell and in the tube for $a = 0.5$. As temperature of coolant declines, the reactions shift to the equilibrium slowly and consequently, that temperature of the catalyst bed declines gradually. This effect of optimal coolant temperature could be observed on mole fraction profiles along the reactor. Fig. 7 shows that

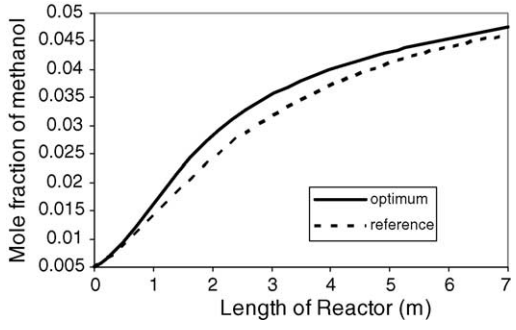

Fig. 7. Methanol mole fraction along the reactor.

Table 2
Additional yield achieved with optimal temperature profiles

Activity	Reference (t/day)	Optimum (t/day)	Additional yield (%)
$a = 0.9$	304	321	5.6
$a = 0.7$	296	307	3.7
$a = 0.5$	278	286	2.8

methanol mole fraction along the reactor for reference and optimal temperature at $a = 0.5$. Higher methanol mole fractions were observed in the reactor. The differences between methanol mole fractions in optimal and reference status increase in the earlier lengths of reactor and start to decrease toward the end of reactor. There are similar results for other two activity levels of $a = 0.9$ and 0.7.

To show the effect of optimal temperature profile of coolant on the reactor performance, methanol production rates were evaluated. The results are given in Table 2, and as it is seen, the lower the activity, the lower additional yield.

4.2. Optimal two-stage reactor approach

Optimal temperature profiles give us some useful information about reactor operating condition. The results show that it is possible to achieve more production rate with a suitable temperature strategy in the reactor. An instantaneous suggestion is to design a multi-stage cooling shell for methanol synthesis reactor so that optimal temperature profile can be achieved by using different temperature profiles along the shell. These optimal temperatures do dynamically change.

To provide optimal multi-stage cooling shell, the best number of cooling stages, the best length of stages, and the best temperature in each stage must be available. This approach, as former, was implemented for three different activity values to get qualified solutions for dynamic operation of the reactor. Here, the objective function, equality constraints, temperatures bound and path constraint are the same as the first approach. Length of cooling stages is searched within the node number—as an optimization variable—and is bounded between 1 and 29.

As first step, the best number of stages should be found. Therefore, optimal temperatures and length of stages for a three-stage cooling shell is needed. Several runs shows optimizations converge on a solution that length of the second stage becomes almost zero for all three activity. Optimization investigation for a four-stage reactor shows similar results. Therefore, it means a reactor with a two-stage cooling shell is the best choice and in the second approach optimal length and temperatures of each stage should be searched.

Optimization result of two-stage reactor is shown in Table 3. Optimal temperatures, length of first stage and additional yield are given in Table 3 for $a = 0.9$, 0.7 and 0.5. As seen, for all activities, temperatures of the first stage are higher than temperatures of second stage. Moreover, in each stage, coolant temperatures of different activity levels are close to each other and significant differences are observed

Table 3
Optimization results of two-stage cooling shell reactor

Activity	*T* of first stage (K)	*T* of second stage (K)	Length of first stage (m)	Additional yield (%)
$a = 0.9$	532	515	2.1	4.8
$a = 0.7$	532	516	3.26	3.1
$a = 0.5$	534	518	4.7	2.6

among the optimal lengths of stages regarding different activity levels. In addition, the results show that the higher the activity, the shorter the length of the first stage and more the additional yield. The temperature and the length of stages are the fittest solution to optimal temperature profile.

In spite of significant additional yield, the result shown in Table 3 is not useable from engineering point of view because of different lengths of cooling stages. Surely, dynamic optimization is the best performance to find optimal length of stages and optimal temperature of stages; but dynamic optimization has high computing cost.

As Fig. 4 shows, in the most catalyst lifetime, activity level is less than 0.6; so, we base our decision mainly on the optimal solution of $a = 0.5$. According to the length obtained from optimization at different activity levels (Table 3), and the corresponding operating time duration of the process between distinct activity levels, the optimal length was modified using operating time-based weight factors (obtained from Fig. 4). After this modification, the optimal lengths of first and second steps changed to 4.45 and 2.56 m, respectively.

In this last step of second approach, optimization was investigated to find the optimal temperature of each stage for three activity levels. Optimal temperatures of each stage and additional yield achieved for optimal two-stage reactor are given in Table 4. As seen, optimization converges on significant lower temperature in both stages, especially for $a = 0.9$. The considerable low temperature in period that catalyst activity is $a = 0.9$, avoids dramatic catalyst deactivation in the earlier times that deactivation rate is very fast and affects the conversion in later operating period. These acceptable and realistic solutions are obtained with a small difference in yield improvement rather results in Table 3. A typical configuration of the two-stage reactor is represented in Fig. 8. As seen, the output of the first reactor is the input of the second stage. In this two-stage reactor, the coolant temperature of each stage is controlled with different steam pressures.

In order to evaluate the effect of these optimal steady-state solutions on total methanol production during catalyst lifetime, 1400 days, dynamic simulation was used. Based on

Table 4
Optimization results of two-stage reactor

Activity	*T* of first stage (K)	*T* of second stage (K)	Additional yield (%)
$a = 0.9$	526	511	4.6
$a = 0.7$	531	515	2.9
$a = 0.5$	533	519	2.5

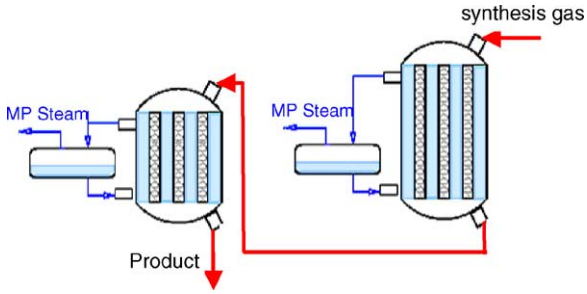

Fig. 8. Typical design of the two-stage methanol synthesis reactor.

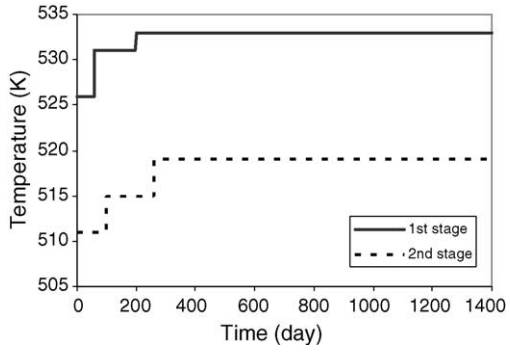

Fig. 9. Optimal coolant temperature trajectory in each stage of cooling shell during operating time.

the results shown in Table 4, the temperature trajectory used in dynamic simulation is shown in Fig. 9. These trajectories are presented according to activity value during operation. Simulation results show this presented new design of methanol synthesis reactor with two-stage cooling shell and temperature trajectory according to Fig. 9 provides 2.9% additional production throughout 4 years. As seen in Fig. 9, reactor is constructed of a high-temperature stage and a low-temperature stage that each stage tracks an independent stepwise temperature trajectory. Moreover, optimal temperature of methanol synthesis reactor in earlier operating time is more important than the later time.

Fig. 10 shows optimal temperature surface in catalyst beds. This surface describes effects of coolant temperature

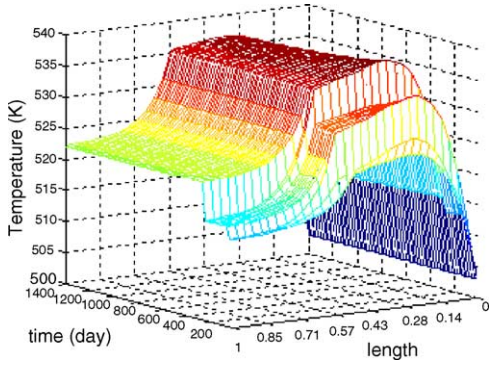

Fig. 10. Optimal temperature surface in reactor.

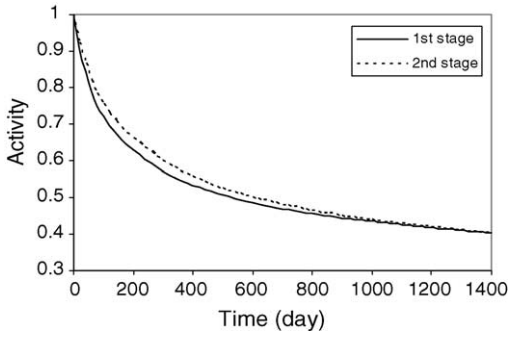

Fig. 11. Average activity in first and second stages of reactor during operating period.

Table 5
Typical GAs used in this optimization problem

	v	P_{size}	C	P_c (%)	P_m (%)	t_g
First approach	30	250	6	80	0.03	80
Second approach I	3	25	2	70	0.01	25
Second approach II	2	20	2	70	0.01	15

v, the number of optimization variables; P_{size}, the population size; C, the number of crossover points; P_c and P_m, the crossover and Mutation probability; and t_g, the generation number.

switching between first and second stages, also temperature varying along time on catalyst beds.

Fig. 11 shows average catalyst activity in the first and second stages. As seen, in about first 600 days average activity in the second stage is more than the first one; but, in following days of 4 years they converge to each other so that at the end of operating period, average activity level in both stages enclose to each other in about $a = 0.4$. It is shown that different operating temperatures do not affect on final activity level.

A quite simple GA was used in this study. The program of optimization ran for several times and based on different sets of GAs parameters generally, real encoding (real genes), classic multi-point crossover, classic mutation and roulette wheel method of selection were used in this study. Although, a suitable set of GA parameters were used in each step of optimization according to the optimization variables and the other properties of the optimization problem. Typical sets of GA parameters are available in Table 5.

5. Conclusion

In this study, methanol synthesis reactor has been optimized to maximize methanol production yield. Optimization problem includes two approaches. In the first approach, optimal temperature profile along the reactor is studied for different activity level. In the second approach, a reactor with optimal two-stage cooling shell and optimal temperature trajectory during this time is obtained. This new design yields 2.9% additional methanol production during operating period. Mathematical heterogeneous model is used in optimization investigation.

In this study, GAs are used as powerful optimization techniques which give good solutions for this constrained nonlinear problem. Although dynamic optimization is the best investigation for this problem, this study possesses important results. This paper allows us to perform on a similar design for methanol synthesis reactor and the solutions prepare a good starting point to implement dynamic optimization with reduced computing cost.

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