

A novel approach to the design and operation scheduling of heterogeneous catalytic reactors

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Abstract—A number of studies have been conducted to reduce the overall level of catalyst deactivation in heterogeneous catalytic reactors, and improve the performance of reactors, such as yield, conversion or selectivity. The methodology generally includes optimization of the following: (1) operating conditions of the reaction system, such as feed temperature, normal operating temperature, pressure, and composition of feed streams; (2) reactor design parameters, such as dimension of the reactor, side stream distribution along the axis of the reactor beds, the mixing ratio of inert catalyst at each bed; and (3) catalyst design parameters, such as the pore size distribution across the pellet, active material distribution, size and shape of the catalyst, etc. Few studies have examined optimization of the overall catalyst reactor performance throughout the catalyst lifetime, considering catalyst deactivation. Furthermore, little attention has been given to the impact of various configurations of reactor networks and scheduling of the reactor operation (i.e., online and offline-regeneration) on the overall reactor performance throughout the catalyst lifetime. Therefore, we developed a range of feasible sequences of reactors and scheduling of reactors for operation and regeneration, and compared the overall reactor performance of multiple cases. Furthermore, a superstructure of reactor networks was developed and optimized to determine the optimum reactor network that shows the maximum overall reactor performance. The operating schedule of each reactor in the network was considered further. Lastly, the methodology was illustrated using a case study of the MTO (methanol to olefin) process.

Keywords: Modeling, Optimization, Kinetics, Reactor, Deactivation

INTRODUCTION

Catalytic reactors play a critical role in the process synthesis of chemical/petrochemical industries because they are involved directly in the production of chemical products and byproducts. Therefore, the design of reactors and catalysts is an important task for making efficient use of raw materials.

Considerable research in this area focuses on catalyst selection, evaluation of the reactor performance and trouble shooting of catalytic reactor operations. In particular, many studies have examined catalyst deactivation because most reactions in industry are involved in catalyst deactivation problems, which deteriorate the performance of the plant. For example, Gayubo et al. considered the mechanisms of a range of deactivations to quantify catalyst deactivation [1,2].

Meanwhile, few researchers considered multiple design variables simultaneously to increase the overall reactor performance throughout the catalyst lifetime. These variables include:

- Design parameters of the catalyst (e.g., pore size distribution across the pellet, active material distribution, size and shape of the catalyst)
- Reactor operating conditions (e.g., feed temperature, normal operating temperature, pressure, composition of feed streams)

- Selection of the reactor types and its design parameters (e.g., space velocity, dimension of reactor, side stream distribution along the reactor beds, mixing ratio of inert catalyst at each bed)

In particular, the above items have never been considered simultaneously with the synthesis of multiple reactor networks and operating schedule of the reactors. For example, in the case of using multiple fixed bed reactors, a number of reactor networks should be considered to enhance the overall reactor performance. Furthermore, a schedule of each reactor operation, such as the on-line and off-line, for regeneration should be considered together with the reactor temperature control strategy during the operation period. Therefore, this research considered multiple variables simultaneously, such as the feed inlet temperature, reactor operating cycle, and catalyst load. Furthermore, a range of catalytic reactor configurations and its operating schedule (i.e., online and offline for regeneration) are proposed to enhance the performance of the plant cycle. Finally, a superstructure of reactor networks was developed and both simulated annealing (SA) and successive quadratic programming (SQP) optimization algorithms were applied to determine the optimum reactor network, which shows the maximum performance of the reactor throughout the reactor operation cycle.

BACKGROUND

Over the past few decades, a number of methodologies have been studied to enhance heterogeneous catalytic reactions and mitigate

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catalyst deactivation in a reactor. This includes 1) the mitigation of catalyst deactivation using the side stream distribution of one of the feeds, 2) optimizing the active material distribution inside a pellet, and 3) adjusting the inlet temperature to the reactor to mitigate sintering.

Coke formation and its impact on the reactor performance have been modeled considering various aspects [3]. For example, catalyst deactivation was modeled at three different levels: the active sites, the particle and the reactor. A framework was also presented for a rigorous approach to derive the kinetic equations for coke formation and the resulting catalyst deactivation, based on a mechanistic approach of coke formation. The so-called deactivation function was introduced to quantify deactivation. Coke formation affects the main reactions, as well as the rate of coke formation itself. These have been defined as follows:

For main reaction(s):

$$\varphi_{Ai} = \frac{r_{ai}}{r_{ai}^0} \quad (1)$$

For coke formation:

$$\varphi_c = \frac{r_c}{r_c^0} \quad (2)$$

where

φ_{Ai} =Catalyst activity

φ_c =Deactivation function

r_{ai} =Rate of the reaction at any time

r_{ai}^0 =Rate of the reaction at the starting point

r_c =Rate of coking at any time

r_c^0 =Rate of coking at the starting point

The rate of catalyst deactivation was quantified using models with a particular function that is characterized by active sites in the proposed mechanisms [4]. These models were later extended to complex reactions by establishing a different activity for each individual reaction. The suggested kinetic model of deactivation was the Langmuir-Hinshelwood-Hougen-Watson (LHHW) type, and the kinetics can be given by the following expression:

$$r_d = \frac{(k_{dA}C_A + k_{dB}C_B + k_{dC}C_C + k_{dD}C_D)a}{(1 + k_{dA}C_A + k_{dB}C_B + k_{dC}C_C + k_{dD}C_D)^2} \quad (3)$$

Where, subscripts A, B, C and D are various components

C=concentration of component

r_d =rate of deactivation

k_{di} =deactivation rate constant for component i

a=catalyst activity

A kinetic model for catalyst deactivation in the transformation of MTO was studied further based on experiments in an isothermal fixed bed reactor [1]. The model allows the simulation of a reactor and examines the influence of the operating conditions on selectivity. The results were also proven experimentally; good agreement with the results of coke deposition through the reactor cycle was observed. An experimental kinetic study was carried out under certain conditions, in which deactivation was caused exclusively by coke deposition, along with the reaction-regeneration cycles for some cases.

The dynamic behavior of fixed bed or tubular reactors under catalyst poisoning was studied through experiment and modeling [5,6]. For example, the quasi-steady state behavior under poisoning con-

ditions was determined and compared at different levels of poison concentrations. The reactor behavior was simulated using a one-dimensional pseudo-homogeneous model, incorporating the effects of mass and heat dispersion [5]. Meanwhile, researchers in a Dow chemical laboratory recently developed a mathematical model to describe catalyst deactivation phenomena to manage the plant and optimize reactor throughput [6].

Benzene hydrogenation on a Ni catalyst that is poisoned by thiophenes in a fixed bed reactor was studied [7]. In this study, the cyclic policy for reactor operations was applied, where conversion was allowed to decrease under deactivating conditions up to a preset minimum and then readjusted to the initial conditions by increasing the reactor temperature. This cyclic policy was an initial approach to examine the constant conversion policy of operation often employed industrially. Meanwhile, Fortunatti and coworkers developed a mathematical model to predict physical properties of main products, and it was used to establish design and operating policies of the reactor [8].

Simulation work, considering the effects of reversible and irreversible catalytic deactivation on the reactor design, was carried out to determine how permanent deactivation occurs both during the reaction and during catalyst regeneration to predict the experimental observations in pilot plant studies [6,9]. In Mobil's methanol to gasoline (MTG) process, two types of catalyst deactivation occur. The first type is the reversible coking of zeolite, where the coke is burned off during regeneration, restoring its activity. The second type is permanent deactivation of zeolite. In this process, a dynamic simulation of the MTG process was developed to examine the interaction between these two types of deactivation. Permanent deactivation also occurred during both the reaction and catalyst regeneration.

Schipper and Krambeck's work was extended to the MTO process in the range of 300-500 °C, and the experimental results were obtained in a fixed bed reactor operating under reacting-regenerating cycles [2]. The total activity remaining in the catalyst was quantified as the product of a function for the recoverable activity due to coke deposition. The MTO process for the synthesis of light olefins arose from the development of the MTG process, as a supplementary route to the main objective of obtaining synthetic gasoline. The selectivity of olefins increased with increasing reaction temperature, as well as when water was fed with methanol. Water played a dual role (i.e., enhancing or mitigating catalyst deactivation) on the deactivation of the zeolite catalyst in the transformation of methanol, depending on the conditions under which the reaction was carried out.

The non-steady state process in a co-current tubular reactor with a single and multi-run catalyst was examined to formulate an optimization problem to obtain the optimum number of successive runs in the cycle time of reaction and regeneration [10]. For temperature dependent catalyst deactivation, the reaction system was considered to be an optimization problem to determine the optimal temperature profile, maximize the overall production rate of the desired product, and improve the catalyst life (low rate of catalyst deactivation).

Alternatively, considerable focus has been given to the use of side-streams and inert catalysts to control the temperature profiles, in addition to external cooling [11]. In this study, we suggested a

design procedure considering the combination of these two schemes simultaneously. The catalyst characteristics, such as the pellet diameter, shape and activity distribution inside a catalyst pellet, were considered to model and optimize a certain objective, such as the yield or selectivity. Considering the non-uniform catalyst pellet designs for decaying catalysts, including both non-selective and selective catalyst deactivation, the methodology was extended further to the design of an optimum heterogeneous catalytic reactor. The consideration of catalyst deactivation for a certain catalyst lifetime produced different reactor design results that were more reliable and practical than the results observed in the absence of deactivation.

Hwang and Smith simulated a fixed bed reactor under deactivating conditions using the kinetics under isothermal operating conditions [12]. They considered the optimum reactor design under shell-progressive poisoning using Langmuir-Hinshelwood kinetic equations. To consider the practical reactor designs, they used the reaction data of the benzene hydrogenation process in the vapor phase [12].

The above literature review suggests that the optimization of various catalytic reactor configurations, such as multi-bed operation, side streams, and inlet temperature strategy, can improve the catalytic cycle performance, and the operating conditions can be adjusted to compensate for the loss of catalyst activity to some extent.

SYNTHESIS OF THE REACTOR CONFIGURATIONS

The reactor design and synthesis of its networks determine the characteristics of the entire process flow sheet. The reactor design involves the types of reactor, size of the reactor, sequencing, scheduling and operating conditions of the reactors. On the other hand, there is no general procedure available for the production of reactor networks that can be integrated efficiently into an overall process scheme. The conventional approach is an intuitive method that attempts to distill the decisions of a good design concerning the flow-sheet. Very little has been published to explain the operation of multiple reactors at different times and continuous switching of the feed. Pota et al. examined the network of three catalytic reactors with periodical feed switching for methanol synthesis, and the influence of the switch time on the stability and performance was addressed [13]. The periodically forced network of three continuous stirred tank reactors (CSTR) was evaluated by cyclic switching of the feed and discharge positions [14]. Bifurcation analysis was performed to explore possible bifurcation scenarios. Sheintuch and Nekhamkina studied loop reactors to generate a rotating pulse solution, simulating two asymptotic cases where the ratio of the switching velocity to each reactor was examined. They compared the solutions of 4-8 reactors [15].

1. Synthesis Based on the Superstructure of a Reactor Network

Superstructure optimization was developed to utilize an optimi-

zation algorithm to evaluate a much larger set of possible flowsheets than would normally be explored by conventional process design. The method allows complex interactions between all the possible structures and to choose the combination of various operating and design parameters that optimize an objective function.

We addressed the problem of the optimal structure of a deactivating catalytic reactor network. These types of reactors always show decaying performance and need to be analyzed in a structured manner to obtain the optimal performance. We evaluated the operating time of each reactor for a given structure; e.g., if five reactors are considered in a network each must be regenerated periodically and be taken offline from the operating network. This means that it is necessary to determine the point when each regenerated reactor should be online and when the deactivated reactor should be offline. In addition, there could be also a case when two or more reactors are working at the same time in series or parallel. At the same time, the process flow scheme with the reactors online during each operating cycle should be determined. Therefore, this type of catalytic reactor structure leads to a cyclic performance (each reactor is made online and offline continuously), because of the continuous switching of the reactors. In this study, a few reactor superstructures were developed for illustration, where connections are allowed between the feed and reactors, between the reactors, and between the reactors and products. Fig. 1 gives an example of the superstructure.

The superstructure shown in Fig. 1 represents the total number of active reactors present in the network and the feasible connections among them. An active reactor matrix consists of integer values: 0, for an inactive reactor that is not in operation and 1 for an active reactor at a particular operating time. For example, multiple reactors can be active at a particular operating time (one time step), while one reactor can be active for longer time (more time steps) than the other. Table 1 shows an example of the active reactor matrix used in this study, showing that reactor R-1 is operated for time steps 1 to 6 and 14 to 18. The reactor is regenerated between 7 and 13 time

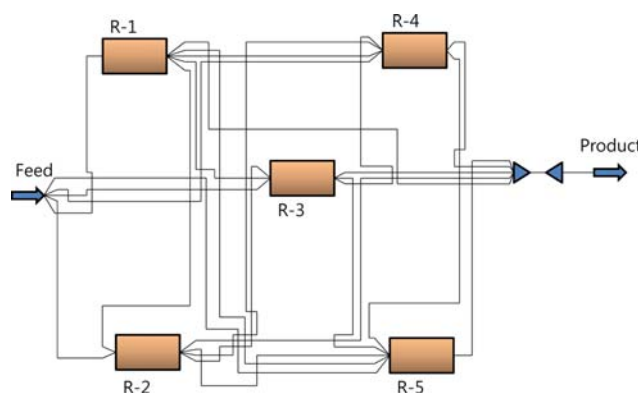


Fig. 1. Superstructure of the catalytic reactors network.

Table 1. Active reactor matrix

Reactor/Time step	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	...
R-1	1	1	1	1	1	1	0	0	0	0	0	0	0	1	1	1	1	1	0
R-2	0	0	0	1	1	1	1	1	1	1	0	0	0	0	0	0	1	1	1
R-3	0	0	0	0	0	0	1	1	1	1	1	1	1	0	0	0	0	0	0

steps. Reactor R-2 is operated with R-1 for time steps 4 to 6 and with R-3 for time steps 7 to 10. In this case, active time steps are optimized through the life cycle, taking into account the relative rates of reaction and deactivation. An operating strategy was also determined to operate the plant according to the active reactor matrix.

The algorithm to develop an active reactor matrix is as follows:
Steps:

1. Decide on the number of time steps: operating time/duration of a single time step.
2. Starting time step of each reactor: there can be multiple starting time steps.
3. Ending time step of each reactor: there can be multiple ending time steps, depending on the starting time steps.
4. Filling the matrix with 1 for each active reactor for all time steps, and zero with remaining, i.e., developing the active reactor matrix.

2. Various Reactor Networks

Conventional standby reactor networks have been in industrial use for a long time, in which one reactor is in operation at a time while the other is regenerated. This type of reactor network seldom maintains optimal performance due to a single reactor operation. Therefore, we evaluated a series of complex reactor network configurations to maintain the catalyst activity for the network, which follows the optimum performance of the network. Many reactor network configurations have been studied in this research to improve the mean value of conversion, yield or selectivity. A range of structural and operating parameters, such as the active time of each reactor in the network, catalyst load of each reactor, total cycle time, number of reactors in the network, connections between each reactor included in the network, and inlet temperature through the cycle time, were optimized to obtain the optimal configuration from

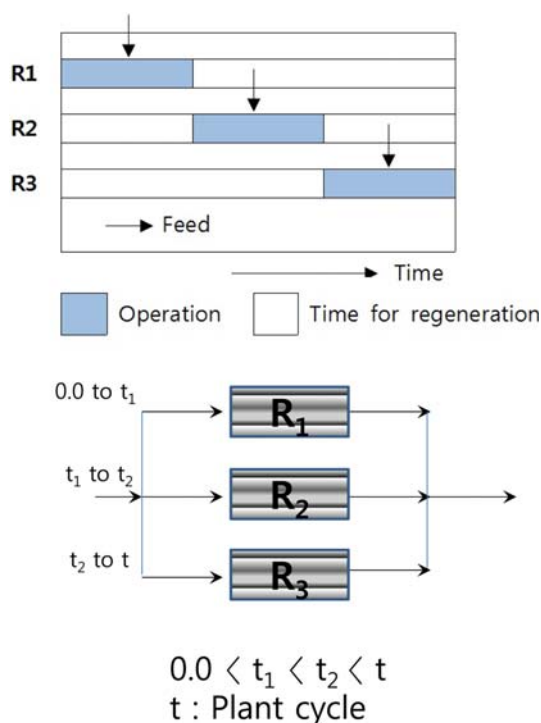


Fig. 2. Conventional standby reactors.

the superstructure described above. A number of complex configurations, including three reactors (or it can be more), were considered to obtain the optimum network, including simple conventional standby reactors as a base case. A series of examples are illustrated below.

2-1. One by One Reactor Networks (Base Case)

In this type of network, one reactor is operated at a time while others are regenerated and placed back online once the online reactor is deactivated. Fig. 2 presents this type of network with a Gantt chart, showing the scheduling of each bed. Each reactor is operated for a specific time, for t_1 hrs for R-1, $(t_2 - t_1)$ hrs for R-2 and $(t_2 - t_3)$ hrs for R-3.

2-2. Standby Series of Reactors

In this type of network, each reactor is operated either alone or with another reactor for a specific time step with the provision of sufficient regeneration time for each reactor. Each reactor is switched to regeneration when it is deactivated to a certain level of catalyst activity. Fig. 3 shows this type of network with a Gantt chart, showing the scheduling of each bed. Each reactor configuration was operated for a specific time, for t_1 hrs for R-1, $(t_2 - t_1)$ hrs for R-1 in series with R-2, $(t_3 - t_2)$ hrs for R-2, $(t_4 - t_3)$ hrs for R-2 in series with R-3 and $(t - t_4)$ hrs for R-3 alone.

2-3. Series-parallel of Reactors

In this type of network, multiple reactors are operated in parallel for some time up to a certain activity level. When both are deactivated partially, they are connected in series to maintain the performance and operated in series for some time, but leaving sufficient regeneration time for each bed. Another reactor is then operated

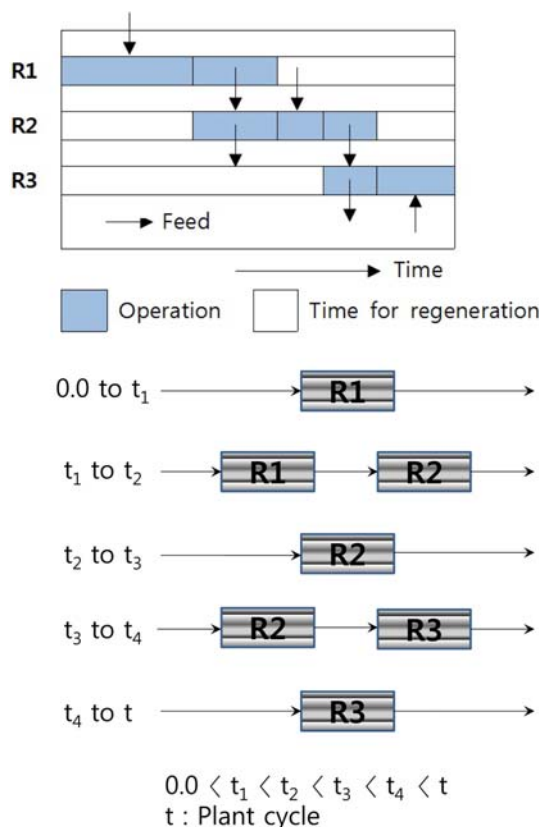


Fig. 3. Standby series of the reactors.

alone while the deactivated reactors are regenerated. Fig. 4 presents this type of network with a Gantt chart, showing the schedul-

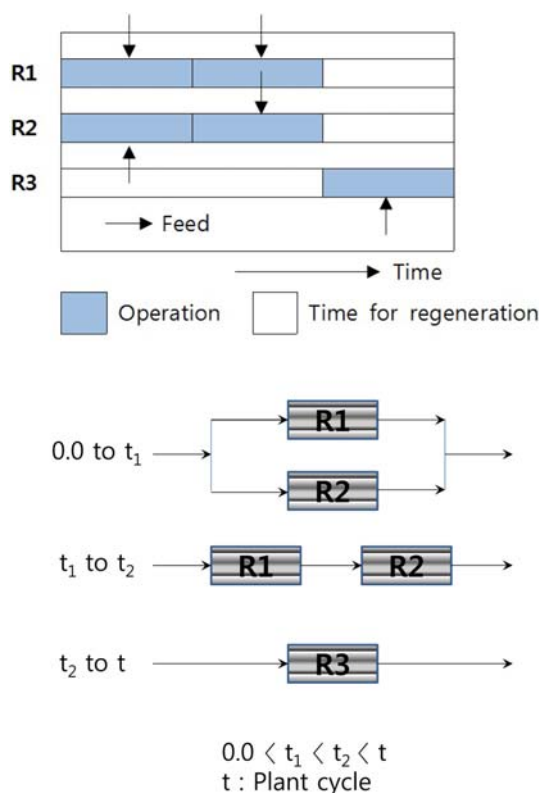


Fig. 4. Series-parallel of the reactors.

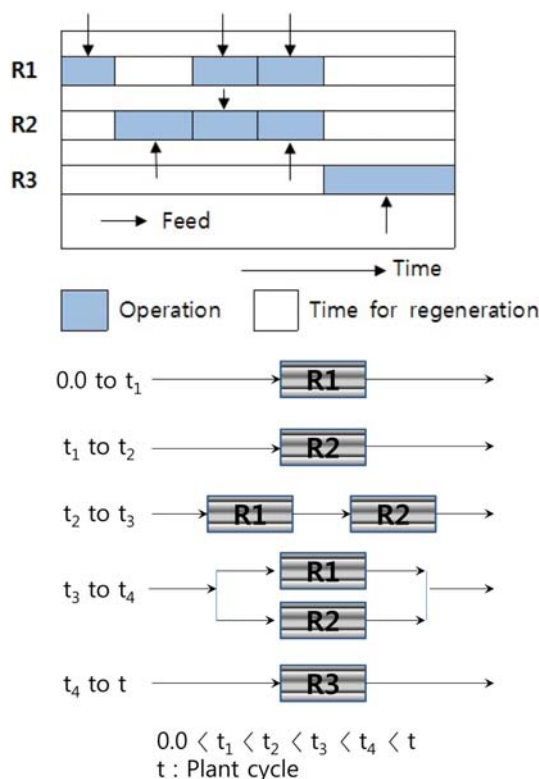


Fig. 5. Standby series-parallel of the reactors.

ing of each bed. Each reactor configuration is operated for a specific time, for t_1 hrs for R-1 and R-2 in parallel, (t_2-t_1) hrs for R-1 and R-2 in series and $(t-t_2)$ hrs for R-3 alone.

2-4. Standby Series-parallel of Reactors

In this type of network, multiple reactors are operated alone, as in conventional standby mode. They are then operated in series followed by parallel mode for some time. When both are deactivated, another reactor is operated alone, and both remaining reactors are being regenerated. Fig. 5 presents a Gantt chart of the scheduling of each bed. Each reactor configuration was operated for a specific time: for t_1 hrs for R-1, (t_2-t_1) hrs for R-2, (t_3-t_2) hrs for R-1 in series with R-2, (t_4-t_3) hrs for R-1 in parallel with R-2 and $(t-t_4)$ hrs for R-3 alone.

2-5. Standby Series-switch of Reactors

In this type of network, each reactor was operated alone or with other reactors in series for a specific time with the provision of sufficient regeneration time for each reactor. In a series configuration, the feed can be switched on and off to each reactor at intermediate times. Each reactor is switched to regeneration when it is deactivated to a certain level of catalyst activity. Fig. 6 presents a Gantt chart of the scheduling of each bed. Each reactor configuration is operated for a specific time: for t_1 hrs for R-1, (t_2-t_1) hrs for R-1 in series with R-2, (t_3-t_2) hrs for R-2 in series with R-1, (t_4-t_3) hrs for R-2 alone, (t_5-t_4) hrs for R-2 in series with R-3, (t_6-t_5) hrs for R-3 in series with R-2 and $(t-t_6)$ hrs for R-3 alone.

2-6. Standby Series of Reactors (i.e., the Feed is Fed to the Reactor with Higher Activity)

In this type of network, each reactor is operated alone or with

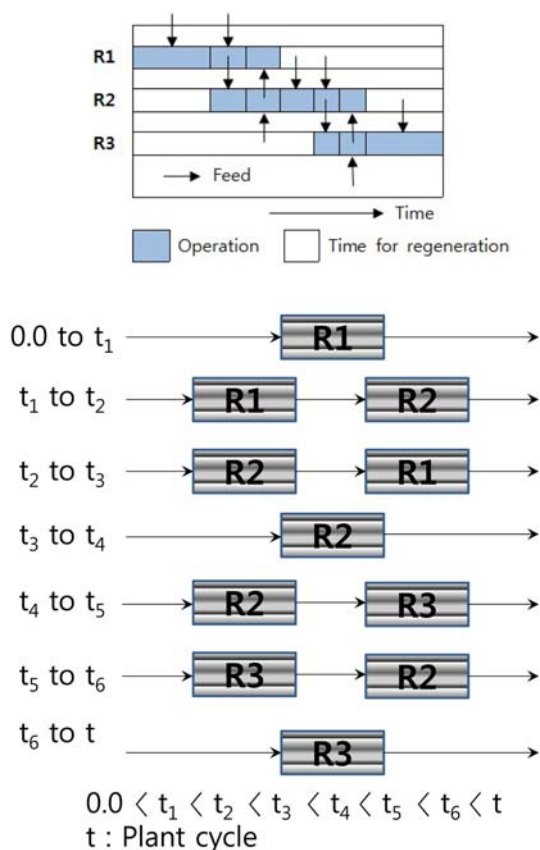


Fig. 6. Standby series-switch reactors.

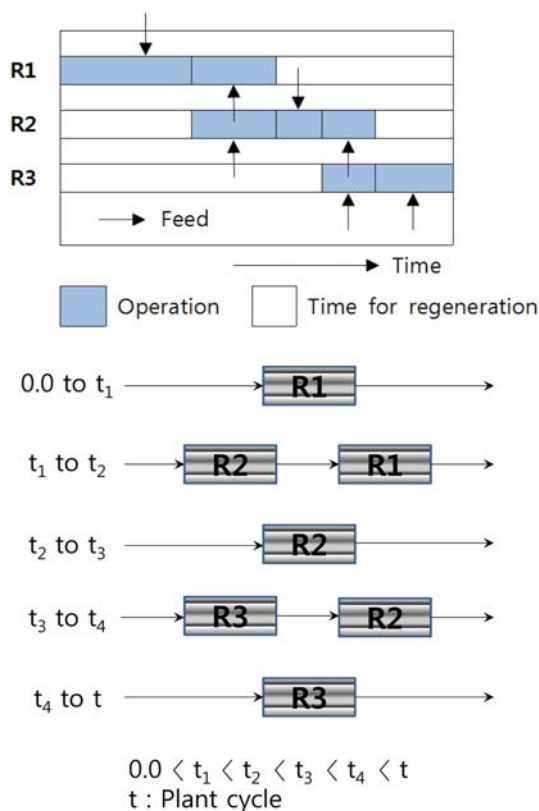


Fig. 7. Standby series reactors (i.e., Feed is fed to the reactor with higher activity).

other reactors for a specific time with the provision of sufficient regeneration time to each reactor. Reactors with higher activity (newly added) are fed with fresh feed. The feed for the reactors already in use is the effluent of the reactor, recently brought online. Each reactor is switched to regeneration when it is deactivated to certain level of catalyst activity. Fig. 7 presents this type of network with a Gantt chart, showing the scheduling of each bed. Each reactor configuration is operated for a specific time; for t_1 hrs for R-1, $(t_2 - t_1)$ hrs for R-2 in series with R₁, $(t_3 - t_2)$ hrs for R-2, $(t_4 - t_3)$ hrs for R-3 in series with R-2 and $(t - t_4)$ hrs for R-3 alone.

3. Simulation and Optimization

An optimization problem that can be considered for catalytic reactor designs was constructed based on the superstructure of catalytic reactor networks. This problem then becomes a scheduling problem for standby reactors so as to provide sufficient time for each reactor to regenerate the catalyst and regain its activity. Another optimization parameter in this type of reactor configuration is the inlet temperature through the lifetime of the catalyst. Maximizing the average conversion of the reactant is considered as an objective function for optimization.

3-1. Modeling of Fixed Bed Reactor

A fixed bed reactor consists of a number of sub-PFRs in series. The accuracy of the heterogeneous catalytic reactor model and the computational requirements for optimization can be controlled by manipulating the number of sub-PFRs. Eqs. (4) and (5) were applied to the mass and energy balances of each sub-PFR. A set of sub-PFRs represents a bed zone inside a reactor. This model was developed, assuming no radial temperature dispersions because the Biot

(Bi) number is much less than 1.

For the bulk/fluid phase:

The fluid phase mass and energy balance for heterogeneous, non-isothermal, non-adiabatic plug flow reactors are as follows:

- Mass balance

$$v \frac{dC_{f,i}}{dz} = -(1 - \varepsilon) \cdot \sum (v_{i,j} \cdot r_j) \quad (4)$$

- Energy balance

$$\rho C_p v \frac{dT_f}{dz} = (1 - \varepsilon) \sum (-\Delta H_j \cdot r_j) - U_o \alpha (T_f - T_c) \quad (5)$$

- Boundary condition,

$$z=0: T_f = T_f^o, C_{f,i} = C_{f,i}^o$$

where, v =velocity of the external fluid phase

$C_{f,i}$ =fluid concentration on species in the bulk phase i

Z =axial co-ordinate along the reactor

ε =bed void fraction

$v_{i,j}$ =stoichiometric coefficient of species i in reaction j

r_j =rate of reaction j

ρ =density of the fluid phase

C_p =heat capacity of the fluid phase

T_f =temperature of the fluid phase

ΔH_j =heat of reaction j

U_o =overall heat transfer coefficient between the reaction gases and cooling medium

$\alpha = 4/D_i$ (internal tube diameter)

3-2. Optimization of Reactor Networks

All of the design and operating variables were taken into account for the development of reactor network superstructure. This included a mathematical model to describe the behavior of the reactors throughout the reactor operating period. In the formulation of the optimization framework, both continuous and discrete variables were adopted, including a significant number of non-linear equations, in particular for the kinetics of reactions and catalyst deactivation.

To solve the MINLP (mixed-integer nonlinear programming) optimization problem, both stochastic algorithm and deterministic algorithms were used in this work, which have their own advantages and disadvantages. For example, stochastic optimization such as simulated annealing has the following features.

(1) Simulated annealing is relatively robust for highly nonlinear problems,

(2) Number of simulations is independent of total number of design variables,

(3) Suitable even when initial design is far from optimal design.

On the other hand, deterministic optimization algorithm such as successive quadratic programming has the following features.

(1) The algorithm is converging relatively fast enough,

(2) It requires small number of simulations (may be misled by local optimum) compared with stochastic optimization algorithms,

(3) It is suitable when initial design is close to optimal solution.

As shown in Fig. 8, stochastic optimization (simulated annealing) is initially used at early stage of optimization, followed by deterministic optimization (successive quadratic programming) to finalize the optimization process and obtain global optimum solution. This combination comparatively provides global optimum in less time

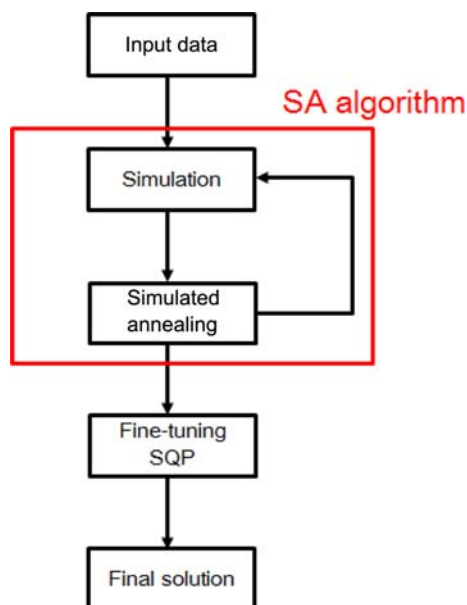


Fig. 8. Optimization framework.

for overall optimization [16-18].

In this work, it generally required about 5 to 6 seconds (for single reactor, without considering catalyst effectiveness factor) to 10 minutes (multi-reactors considering catalyst balances) to complete the simulation. It mainly depended on the type of reactor and configuration of the reactor network considered. On the other hand, required time for the optimization of such simulation varied from 12 hours to even a few days, respectively, based on the rigorous nature of the reactor system. Differential-algebraic equation (DAE) solver was used at early stage. However, because of its slowness and low capability to handle differential term effectively, DASSL solver was implemented to reduce the simulation and optimization time. As a result, the computational time was reduced approximately by 50% (typical simulation time was 10-12 seconds for DAE solver and 5-6 seconds for DASSL solver).

CASE STUDY : METHANOL TO OLEFINS (MTO)

1. Introduction

Mobil's novel synthetic gasoline process (the MTG process), which is based on the conversion of methanol to hydrocarbons over zeolite catalysts, was the first major new synthetic fuel development since the introduction of the Fischer-Tropsch Process. The MTO process for the synthesis of light olefins arose from the development of the MTG process, as a supplementary route to the main objective of obtaining synthetic gasoline. Recently, the interest in obtaining light olefins has increased [1]. HZSM-5 zeolite was chosen as the catalyst by Mobil for the MTO process. In this process, two types of catalyst deactivation occur. The first type is reversible coking of the zeolite, where coke is burned off during regeneration, restoring its activity. The second type is permanent deactivation of the zeolite because of high-pressure steam that is produced from the water product due to the high processing temperature. This type of deactivation is quite slow compared to the first and highly selective to excessive pressure and temperature.

The conversion of methanol to light olefins over HZSM-5 zeolite was examined and kinetic models of the reaction and deactivation are described below.

2. Kinetics of the Main Reactions

The kinetic scheme used in this work for the MTO process was adopted from the open literature [1,19,20]. This kinetic scheme uses groups of components with a similar hydrocarbon structure in the MTG process. Methanol and dimethyl ether were considered separately because of their different reactivity.



Where, MeOH: Methanol

DME: Dimethyl ether

A: Oxygen

C: Olefins

G: Gasoline

The following show the net rate equations at zero time for three of the four components (methanol, dimethyl ether and light olefins) of the kinetic scheme, where the concentrations of components are expressed as mass fractions:

$$-r_{A0} = k_1 X_A + k_3 X_A X_C \quad (11)$$

$$-r_{C0} = k_1 X_A + k_2 X_C^2 - k_3 X_A X_C - k_4 X_G X_C$$

$$-r_{G0} = k_2 X_C^2 + k_3 X_A X_C \quad (13)$$

The kinetic parameters for this model, as advised by Gayubo et al., are as follows [20]:

$$k_1 = 0.315 \times 10^7 \exp\left[-\frac{15720}{RT}\right] \quad (14)$$

$$k_2 = 0.155 \times 10^3 \exp\left[-\frac{6055}{RT}\right] \quad (15)$$

$$k_3 = 0.154 \times 10^7 \exp\left[-\frac{13500}{RT}\right] \quad (16)$$

$$k_4 = 0.141 \times 10^3 \exp\left[-\frac{5000}{RT}\right] \quad (17)$$

$$K_A = 0.375 \times 10^{-7} \exp\left[-\frac{22129}{RT}\right] \quad (18)$$

where, k_i =rate constant of the i_{th} reaction= $k_{i0} \exp [(-E_i/RT)]$, h^{-1}

K_A =equilibrium constant

X_i =mass fraction of the i_{th} component

r_{i0} =reaction rate of the i_{th} component at zero time

3. Kinetic Model for Catalyst Deactivation in the MTO Process

The kinetic modeling of catalyst deactivation in the MTO process includes reversible deactivation by coking at a lower temperature. The deactivation model is partially selective because it considers the same catalyst activity for all the steps of the kinetic scheme. The activity loss by coke deposition is a function of the remaining

activity, composition of the components and temperature of the reacting medium:

$$r_d = -\frac{da}{dt} = (k_{dA}X_A + k_{dC}X_C + k_{dG}X_G)a \quad (19)$$

This equation is based on a previous one for coke deactivation in the MTG process, in which coke deactivation depends on the concentration of all species present. The kinetic parameters of the deactivation are as follows [2,19]:

$$k_{dA} = 0.165 \times 10^9 \exp\left[-\frac{25870}{RT}\right] \quad (20)$$

$$k_{dC} = 0.121 \times 10^6 \exp\left[-\frac{18930}{RT}\right] \quad (21)$$

$$k_{dG} = 0.603 \times 10^8 \exp\left[-\frac{26280}{RT}\right] \quad (22)$$

Where, X_i =mass fraction of the i^{th} component

r_d =rate of deactivation

k_{di} =rate constant for deactivation, h^{-1}

Simulation of the transformation of methanol into olefins and light gasoline was carried out in an isothermal fixed bed reactor using the reaction and deactivation kinetics. The kinetic models for the main reaction and for deactivation are adequate in the range between 575 K and 650 K [2].

4. Results

The MTO process was simulated under a range of reactor configurations shown below, and the conversions of methanol to olefins at each configuration were compared. Meanwhile, the inlet temperature profile through the operating cycle was optimized simultaneously with the reactor network structure optimization. Furthermore, fractions of the flow rate from the feed to different reactors were optimized together. Lastly, a novel configuration of reactor networks is developed in case 5.

- Case 1: Conventional standby reactors with and without inlet temperature profile optimization (base case)
- Case 2: Standby series (option-1) reactors for the same catalyst loading as the base case
- Case 3: Standby parallel reactors for the same catalyst loading as the base case
- Case 4: Standby series (option-2) reactors for the same catalyst loading as the base case
- Case 5: Novel reactor network configurations with flow rate optimization.

4-1. Conventional Standby Reactors (Base Case)

Conventional standby reactors in Fig. 9 were simulated with a fixed amount of catalyst, where the total catalyst was divided between three parallel beds. Each bed was operated alone one at a time while the others were being regenerated. The following data was used to operate the reactor configuration.

Reactors data:

No. of reactors=3

Volume=0.9725 m^3

Porosity=0.6

Catalyst bulk density=1,650 kg/m^3

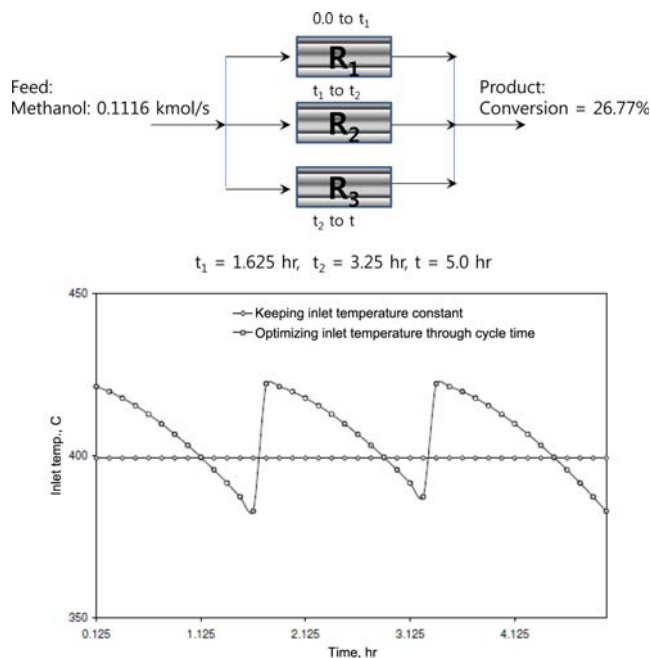


Fig. 9. Conventional standby reactors with and without the optimized inlet temperature profile.

The performance decreases with time in a monotonic manner due to the decaying catalyst in the fixed bed. When the feed is switched to another standby reactor with a fresh catalyst bed, the performance improves and again begins decreasing due to the further catalyst deactivation. The average performance in terms of methanol conversion was 26.77% for the full operating cycle in the case of an optimized constant inlet temperature profile through the cycle time, whereas methanol conversion achieved 27.55% in the case of an optimized inlet temperature profile through the cycle time of the reactor network. The performance of the network does not appear to be sensitive to the inlet temperature, which really depends on the type of process and the relative effects of temperature on the reaction and deactivation rates.

4-2. Standby Series (Option-1) Reactors for the Same Catalyst Loading as the Base Case

In this configuration, the total catalyst was divided into three beds operating one at a time or in series. The same amount of catalyst as the base case was used and operated for the same cycle time. Conversion was increased from 27.55% to 27.91% using a series connection with the optimized operating time for each bed, compared to conventional standby reactors. In both cases, the inlet temperature was optimized for the full operating cycle.

The operating time of each reactor in the network was optimized simultaneously with the profile-based optimization of the inlet temperature in Fig. 10. The inlet temperature was varied to enhance the reaction rate and mitigate the rate of deactivation. From t_1 to t_2 , the feed was fed into the first reactor that was active, and the effluent of this reactor was fed to the second reactor.

4-3. Standby Parallel Reactors for the Same Amount of Catalyst Loading as the Base Case

In this type of network, simultaneously operated beds were connected with a parallel arrangement to increase the residence time of the fluid in the bed, as shown in Fig. 11. The active time of each

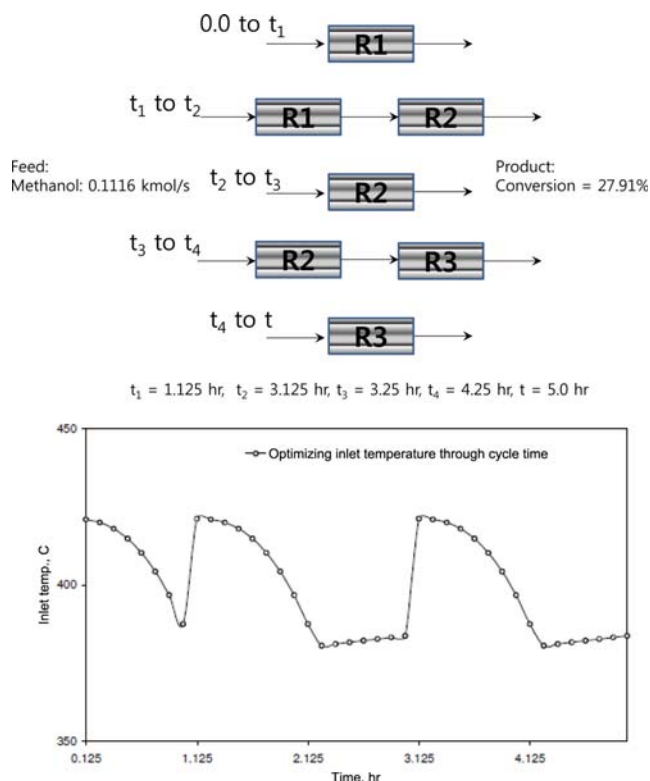


Fig. 10. Standby series reactors with the optimized inlet temperature profile through the cycle time.

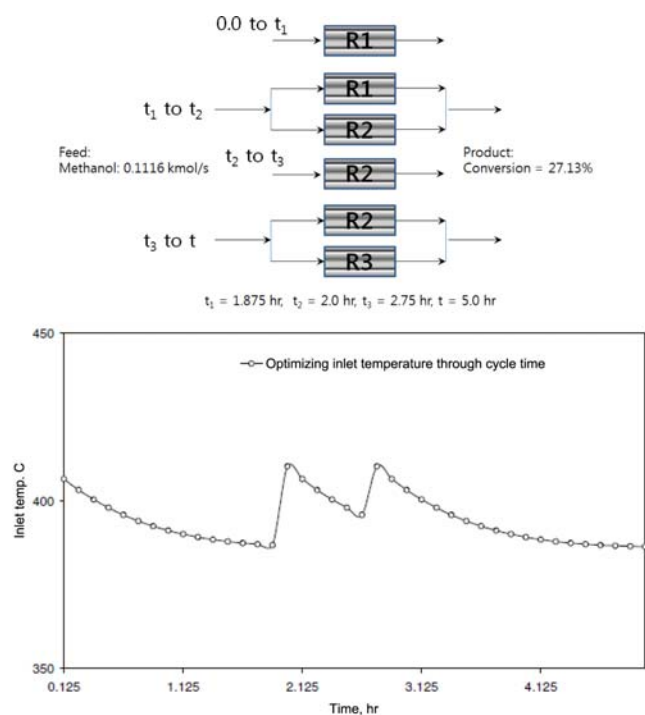


Fig. 11. Standby parallel reactors with the optimized inlet temperature profile through the cycle time.

bed was optimized in this case. Methanol conversion was 27.13% in this case due to the different catalyst activity of the beds operating in parallel.

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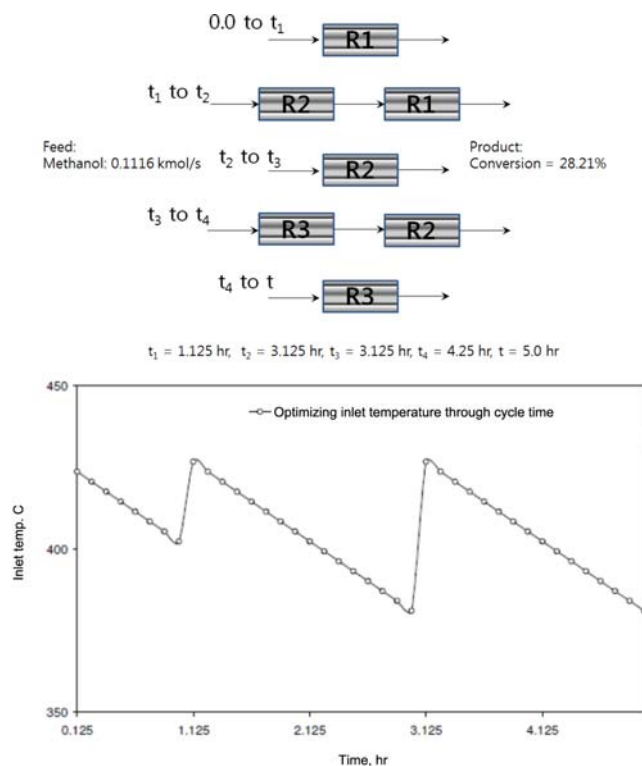


Fig. 12. Standby switch series reactors with the optimized inlet temperature profile cycle time.

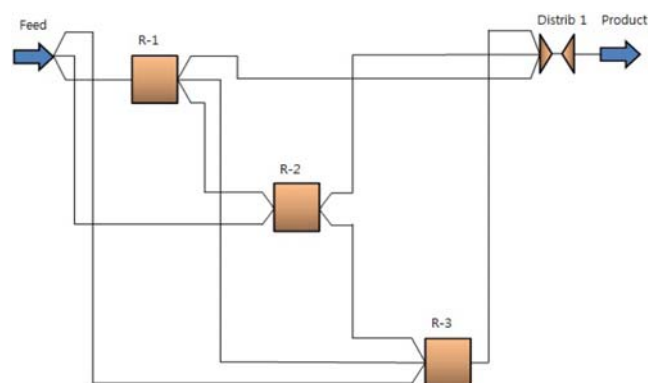


Fig. 13. Novel configurations for reactor network (Feed: 0.1116 kmol/s of methanol, conversion: 29.07%).

4-4. Standby Series (Option-2) Reactors for the Same Catalyst Loading as the Base Case

In this case, each bed was operated alone and in series with other operating beds at different times. The only difference from option-1 was the supply of the feed to the higher catalyst activity bed. The feed was fed to the reactor that was more active at a particular time, and if any other reactor was online with that reactor at a particular time, the effluent from this reactor was fed to the next reactor. This configuration is shown in Fig. 12. The methanol conversion was improved (28.21%) compared to option-1 (27.91%).

4-5. Novel Reactor Network Configurations with Flow Rate Optimization

Based on the superstructure, a novel reactor configuration was developed in Fig. 13, which provides connections in both series and

parallel. The feed can be supplied to any reactor; the effluent of each reactor can be fed to the next reactor and to the product stream. This type of configuration was optimized simultaneously with the variables of the active time of each reactor and the inlet temperature profile through the cycle time. Table 2 lists the active times for the different reactors, which form the active reactor matrix. An operat-

Table 2. Active reactor matrix (total time steps=40, total time=5.0 hrs)

Reactors/Operating time	Start time step*	End time step
Reactor 1	1	24
Reactor 2	14	36
Reactor 3	26	40

*One time step equals 0.125 hr

ing strategy at Table 3 was also developed to operate the plant cycle as per the active reactors. After this optimization, different fractions of the flow from the feed to the reactors, reactors to reactors and reactors to product were also optimized for methanol conversion. Hence, the relative amounts of the feed could be supplied to different reactors based on the catalyst activity of the active reactor. The highest performance in terms of methanol conversion (29.07%) was obtained from this configuration. Table 4 lists the reactor network simulated at particular times based on the active range of each reactor and the operating strategy of the structure.

SUMMARY

Scheduling and optimization of standby reactors is quite useful for faster deactivation by coking (cannot be too significant for some

Table 3. Operating strategy

Operating time steps connections	F to R-1	F to R-2	F to R-3	R-1 to R-2	R-2 to R-3	R-1 to P	R-2 to P	R-3 to P
1 : 13	√	X	X	X	X	√	X	X
14 : 24	√	√	X	√	X	√	√	X
25 : 25	X	√	X	X	X	X	√	X
26 : 36	X	√	√	X	√	X	√	√
37 : 40	X	X	√	X	X	X	X	√

※ F: feed, P: product, R: reactor, √: active connection, X: no connection

Table 4. Active network at each time interval (total operating time steps=40)

Operating time step	Active reactor No.	Active reactor network
1 : 13	1	
14 : 24	1,2	
25 : 25	2	

Table 4. Continued

Operating time step	Active reactor No.	Active reactor network
26 : 36	2,3	
37 : 40	3	

One time step equals 0.125 hr

processes). This study found that the performance of the reactor network is also sensitive to the inlet temperature, which can be improved by optimization of the inlet temperature profile through a cycle time. The active time of each reactor in the given structure is a key parameter to enhance the performance through a cycle. A network of fixed bed reactors was configured to provide an optimal operation. The results showed that the standby reactor network is one of the best options where deactivation is relatively fast and the catalyst is being regenerated in the other bed simultaneously. The case study results showed that it improves methanol conversion from 26.77% for the standby case to 29.07% for the novel configuration case. The performance improvement originates from optimization of the inlet temperature profile and scheduling of the catalytic reactors in the network. Scheduling can be more effective in the case study of a longer operating time of the network, where a larger number of reactors can be used.

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NOTATION

C_i : concentration of component i [kmol/m³]

C_p : heat capacity of the fluid phase
 E_{act} : activation energy [KJ/mol]
 h : external heat transfer coefficient
 ΔH_j : heat of reaction j
 $k_{g,i}$: external mass transfer coefficient of component i
 k_i : rate constant of i^{th} reaction = $k_{i0} \exp [-E_d/RT]$ [hr⁻¹]
 K_A : equilibrium constant
 k_{di} : rate constant for deactivation [h⁻¹]
 p : number of data points
 r : reaction rate [1/s]
 r_a : rate of reaction at anytime [1/s]
 r_d : rate of deactivation [1/s]
 r_c : rate of coking [1/s]
 r_{i0} : reaction rate of the i^{th} component at zero time
 T : temperature [K, °C]
 T_0 : initial temperature [K, °C]
 T_c : temperature of catalyst surface [K, °C]
 T_f : temperature of the fluid phase [K, °C]
 U_o : overall heat transfer coefficient between the reaction gases and cooling medium
 V_p : volume of the pellet
 X_i : mass fraction of the i^{th} component
 y_i : gas concentration of the gas component i [kmol i/kmol B]
 Z : axial co-ordinate along the reactor

Subscripts

i, j, k : states of the system

Superscripts

c : coolant

f	: fluid phase
i	: component
j	: reaction
p	: pellet
o	: initial condition
s	: catalyst surface

Greek Letters

γ	: cooling parameter
ε	: bed void fraction
η	: effectiveness factor
v	: velocity of the external fluid phase
$\nu_{i,j}$: stoichiometric coefficient of species, i in reaction j
ρ	: density of the fluid phase [kg/m ³]
φ_{Ai}	: catalyst activity
φ_c	: catalyst deactivation function

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