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Catalytic propane dehydrogenation: Advanced strategies for the analysis and design of moving bed reactors

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Abstract–A moving bed reactor (MBR) is one of the most innovative reactors that are commonly used in industry nowadays. However, the modeling and optimization of the reactor have been rarely performed at conceptual design stage due to its complexity of design, and it has resulted in increased capital and operating costs of the overall chemical processes. In this work, advanced strategies were introduced to model an MBR and its regenerator mathematically, incorporating catalyst deactivation, such as coke formation. Various reactor designs and operating parameters of the MBR were optimized to increase the overall reactor performance, such as conversion or selectivity of the main products across the reactor operating period. These optimization parameters include: (1) reactant flow inside a reactor, (2) various networks of MBRs, (3) temperature of the feed stream, (4) intermediate heating or cooling duties, (5) residence time of the catalyst or velocity of catalyst flow, and (6) flow rate of the fresh make-up catalyst. The propane dehydrogenation process was used as a case study, and the results showed the possibility of significant increase of reactor performance through optimization of the above parameters. For optimization, the simulated annealing (SA) algorithm was incorporated into the reactor modeling. This approach can be easily applied to other reaction processes in industry.

Keywords: Modeling, Optimization, Kinetics, Moving Bed Reactor

INTRODUCTION

The fixed bed reactor has been a major working force in chemical processes for many decades. On the other hand, a number of difficulties are encountered when catalyst deactivation occurs rapidly, resulting in significant operating and capital cost due to the need for frequent catalyst replacement and regeneration. In such a case, moving bed reactors (MBRs) are generally suitable for catalytic reactions because the deactivated catalyst can be removed continuously for regeneration and returned to the reactor. An MBR allows relative ease of withdrawal of the deactivated catalyst and simultaneous introduction of a portion of fresh or regenerated catalyst. The residence time of the catalyst bed can be controlled by regulating the circulation rate of the catalyst to maintain a certain level of catalyst activity in the MBR. For this reason, MBRs have been used widely in a number of gas-solid handling industries in the petrochemical, environmental and biochemical industries nowadays.

An MBR is characterized by the movement of both the solid and fluid phase during chemical reactions, and a number of gas-solids reactions in a MBR have been studied so far. However, literature review reveals that there has been considerable shortage with regard to the conceptual design of an MBR and simultaneous optimization of operating and design parameters including catalyst deactivation. As a result, both operating capital costs of the overall chemical processes tend to increase. For example, the reactor performance, such as conversion, selectivity and yield, is not maximized because the operating condition such as reaction temperature inside a reactor is not optimized, and it leads to additional cost for byproduct treatment and recycle of unconverted raw materials, for example. Furthermore, ineffective reactor design ends up with additional capital and operating costs. Therefore, despite the major advantage for the optimum design of an MBR at early stage of process development, the main aspects of conceptual design and optimization of MBR have received less attention in comparison with the fixed bed reactors. Lack of studies in this area is felt due to the complexity of MBR design and its computational burden for optimization of multiple design and operating variables in addition to the absence of numerical techniques in modeling and optimization of a MBR.

For a few decades, different aspects of MBR modeling have been studied. For example, many researchers considered various types of main process streams and catalyst flow types in an MBR.

Schaefer et al. developed a mathematical model of a vertical descending MBR, considering various factors, such as the catalyst characteristics, enthalpies of both streams and feed compositions of the gas stream, etc. [1]. At that time, relatively simple models of the MBRs were analytically and numerically presented through the solutions of the steady state problem.

Marb and Vortmeyer examined an adiabatic moving bed reactor with cross flow in a sensitive range of multiple steady states [2].

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Experiments for the exothermic catalytic oxidation of ethane were completed, and measured ignition temperatures were compared with the estimates from two-dimensional heterogeneous reactor models.

Haynes and Caram developed a novel method for maintaining a transient cyclic steady state in a fixed bed tubular reactor, which was called a simulated moving bed reactor (SMBR) [3]. The study results showed that the system was primarily applicable to mild exothermic reactions, and could be considered as an alternative to the reverse flow reactor.

Wolff evaluated a circulating cross-flow moving bed reactor to assess the feasibility of obtaining stable catalyst flow in a circulating MBR [4]. Experiments were carried out to determine the range of superficial gas velocities in the reactor. The results showed that the residence time must be selected in seconds or minutes when it is a highly selective regenerative solid catalytic process.

Fricke and Schmidt-Traub developed a mathematical model considering the counter-current movement of the fluid and solid phase to increase the yield, and enhance the selectivity compared to a conventional process [5]. The model included continuous separation of the products from the reactor to achieve higher performance of a MBR.

Mu et al. examined the hydrodynamics of MBRs through a model with radial flow of the reactants across the moving catalysts to maintain the optimal design and operation [6]. A two-dimensional model was adopted to calculate velocity and pressure of fluid in the catalyst bed, flow related parameters in the main flow channels, and the pressure drop across the bed.

Sahebdelfar et al. studied adiabatic radial-flow moving bed reactors for dehydrogenation of isobutane to isobutene [7]. For the main reaction, first-order rate expressions were considered, while deactivation kinetics were incorporated into the model.

Szwast and Sieniutycz developed a dynamic model of a co-current tubular reactor under single and multi-run catalysts [8]. Because catalyst deactivation depends on the temperature inside a reactor, they optimized the temperature profile to achieve a higher overall production rate of the desired product and lower rate of catalyst deactivation. Alternatively, Fogler and Gurmen considered a model of the MBR using an irreversible reaction [9]. Analytical solutions of various rate models in MBRs were discussed.

For the impact of catalyst deactivation on reactor performance, Larsson evaluated a range of commercial processes that are prone to rapid deactivation by coking. He considered various types of transport bed reactors to enable regeneration of the catalyst [10].

Beyond propane or isobutane dehydrogenation process, an MBR has been studied for many different types of processes, including methanol to propylene, methane steam reforming, coal gasification, thermal cracking, esterification, and glucose and fructose production [11-19].

In this study, advanced strategies for mathematical design and optimization of the MBR and its regenerator are introduced. As described earlier, only a few design and operating parameters of the MBR have been individually considered by many researchers so far, and they were not considered at the same time for the design of MBR. Therefore, multi-variables were optimized in this work to enhance the overall reactor performance and reduce the capital and operating costs.

First, the flow types of the catalyst and the feed and product streams were considered as follows.

1. Axial flow moving bed reactor, where the reactants flow parallel to the catalyst flow.
2. Radial flow moving bed reactor, where reactants flow across the moving catalyst.

The use of radial flow MBRs has a number of advantages, including low pressure drop across the reactor bed length and better temperature control in the case of highly non-isothermal reactions.

Secondly, MBRs were examined under catalyst deactivation, such as coking in a heterogeneous catalyst. For this, the catalyst deactivation kinetics was applied to an MBR model. The reactor performance across the entire catalyst lifetime was evaluated computationally, considering the loss of activity through each reaction-regeneration cycle. Lastly, an optimization algorithm of simulated annealing (SA) was integrated with an MBR model to optimize design and operating parameters simultaneously. These parameters include: (1) reactant flow inside the reactor, (2) various reactor configurations of MBRs, (3) temperature of the feed stream, (4) intermediate heating or cooling duties, (5) residence time of the catalyst or velocity of catalyst flow, and (6) flow rate of the fresh make-up catalyst. As a result, the MBR was optimally designed to maximize its performance.

For a case study, we considered propane dehydrogenation process. Gascon et al. investigated the kinetics of propane dehydrogenation and catalyst deactivation in a wide range of temperatures [20]. The model predicted coke formation under the experimental conditions. Different models were then tested to obtain the best fit for the effective reaction rate for the dehydrogenation of propane, such as power law, Langmuir-Hinshelwood (LHHW) mechanisms, etc. A model of the LHHW kinetics with the strong adsorption of propane showed good agreement with the experimental data. The same kinetics of propane dehydrogenation and catalyst deactivation by coking were adopted in the present study.

MATHEMATICAL MODELING AND OPTIMIZATION OF MBRs

For the modeling of an MBR a number of parameters should be considered, such as the kinetics of the reactions involved, kinetics of the related deactivations, hydrodynamics of the multiple phases, rating parameters of the reactor, and operating condition.

In particular, movement of both the solid and fluid phase should be considered during chemical reactions to achieve high accuracy for the modeling of an MBR. The possible flow regime inside a reactor includes countercurrent, co-current or cross-flow depending on the relative directions of the fluid and solid.

In this study, the following aspects were mainly considered for the modeling of an MBR.

1. Movement of the Catalyst

Movement of the catalyst is the main advantage to an MBR compared to fixed bed reactors, which provide stable performance in a reactor. In an MBR, a portion of deactivated catalyst is removed continuously from the reactor and is regenerated in a different unit, as shown in Fig. 1. For this reason, the main bed does not need to

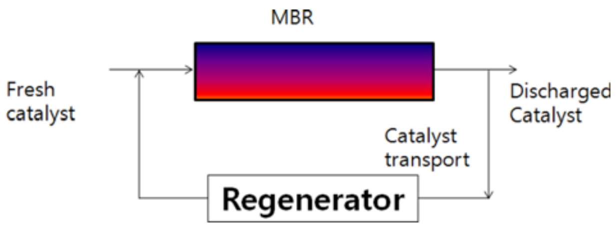


Fig. 1. Movement and recycle of the catalyst in an MBR.

be in standby mode during the catalyst regeneration period. Different residence times for different particle sizes or a piston model (plug flow behavior) is applied to the modeling of an MBR. The residence time or catalyst velocity in the bed is controlled based on the activity loss over the reactor length. In addition, parameters, such as the reactant velocity, total catalyst loading, sensitivity of the deactivation rate to various concentrations, and temperature need to be included for the modeling of moving catalysts.

2. Modeling of Catalyst Deactivation

The kinetics of different types of deactivation, such as coking, poisoning or sintering, must be incorporated into the modeling of an MBR.

The activity of a catalyst throughout the reactor operation period is defined as follows:

$$a_d = \frac{\text{Actual reaction rate of A at each time interval}}{\text{Reaction rate with a fresh pellet}} = \frac{-r'_A}{-r'_{A,o}} \quad (1)$$

In general, the main reaction has an activity term, rate constant and kinetic terms, as shown in Eq. (2). The deactivation rate is expressed in the same mathematical form as the main reaction rate as described in Eq. (3).

Main reaction

$$r'_a = a(t) \cdot k(T) \cdot f(C_A, C_B, \ldots C_P) \quad (2)$$

Deactivation rate

$$r_d = -\frac{da}{dt} = k_d \cdot C_i^m \cdot a^d = k_{d0} \cdot e^{-E_d/RT} \cdot C_i^m \cdot a^d \quad (3)$$

3. Types of Flow within a Catalyst Bed

In most configurations of MBRs, the catalyst bed moves downward under gravity, and the reactant mixture (in gas or liquid phase) flows radially across the catalyst bed, either inwards or outwards, co-currently or counter-currently, as shown in Fig. 2. Modeling of the hydrodynamics provides a theoretical basis and a better understanding of the optimum design and operation of the MBR. In this study, process stream is considered either across or in parallel to the catalyst bed.

4. Modeling of a Cross-flow Reactor

Fig. 3 describes the schematic diagram for the modeling of a cross-flow reactor. Feed was distributed evenly along the moving bed of the catalyst, where the catalyst bed was divided into a series of compartments. Each compartment was simulated by using plug flow behavior. The concentrations and conditions of the feed stream to each compartment were identical to each other, but the product stream concentrations and conditions were different for all compartments because the bulk of the catalyst at each compartment had different catalyst activity. Finally, the concentrations and conditions of the final products were estimated based on the information from individual product streams of all compartments.

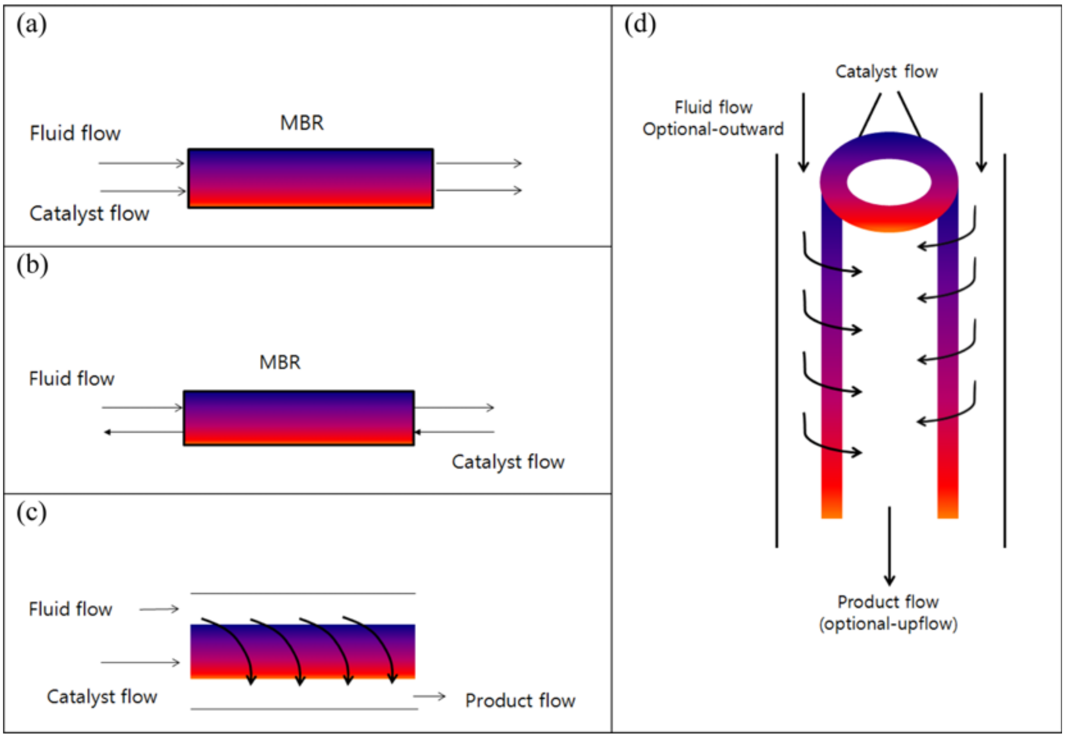


Fig. 2. Different flow patterns in the MBR.

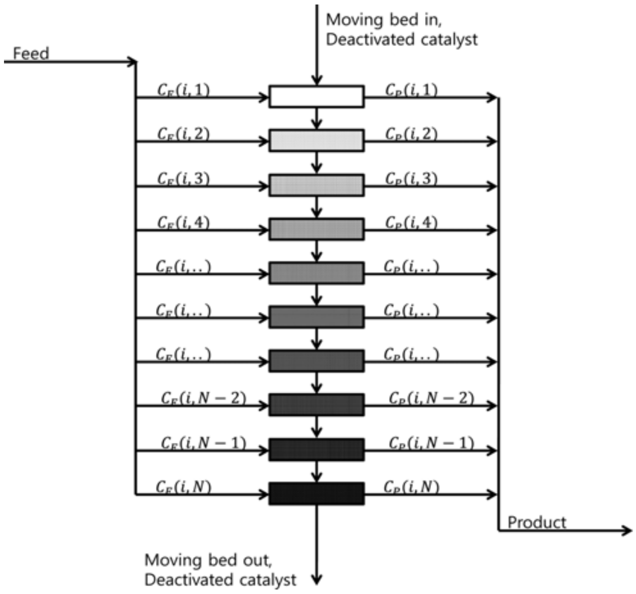


Fig. 3. Modeling of cross-flow reactors.

5. Algorithm and Numerical Scheme

Fig. 4 describes the numerical scheme used in this study for various types of reactors. The algorithm was developed using the DASSL numerical method to solve a range of differential equations of the concentration, temperature and catalyst activity for single and multicycle operations of the reactors.

6. Multistage Modeling

A wide range of operating or design parameters should be considered to promote the selectivity of the reaction or enhance the overall reaction conversion. Sometimes, it is important to change the velocity of both phases along the length of the reactor to mitigate catalyst deactivation. Highly non-isothermal reactions in the MBR require inter-stage cooling or heating to prevent decomposition of the reactants and sintering of the catalyst pellets. This also helps maintain high effective reaction conversion or selectivity. In a radial flow MBR, the flow direction of the reactants across the moving catalyst should be considered to decrease the rate of deactivation. An intermediate feed of secondary streams can reduce the rate of side reactions and provide intermediate cooling. Fig. 5 presents various configurations of these types.

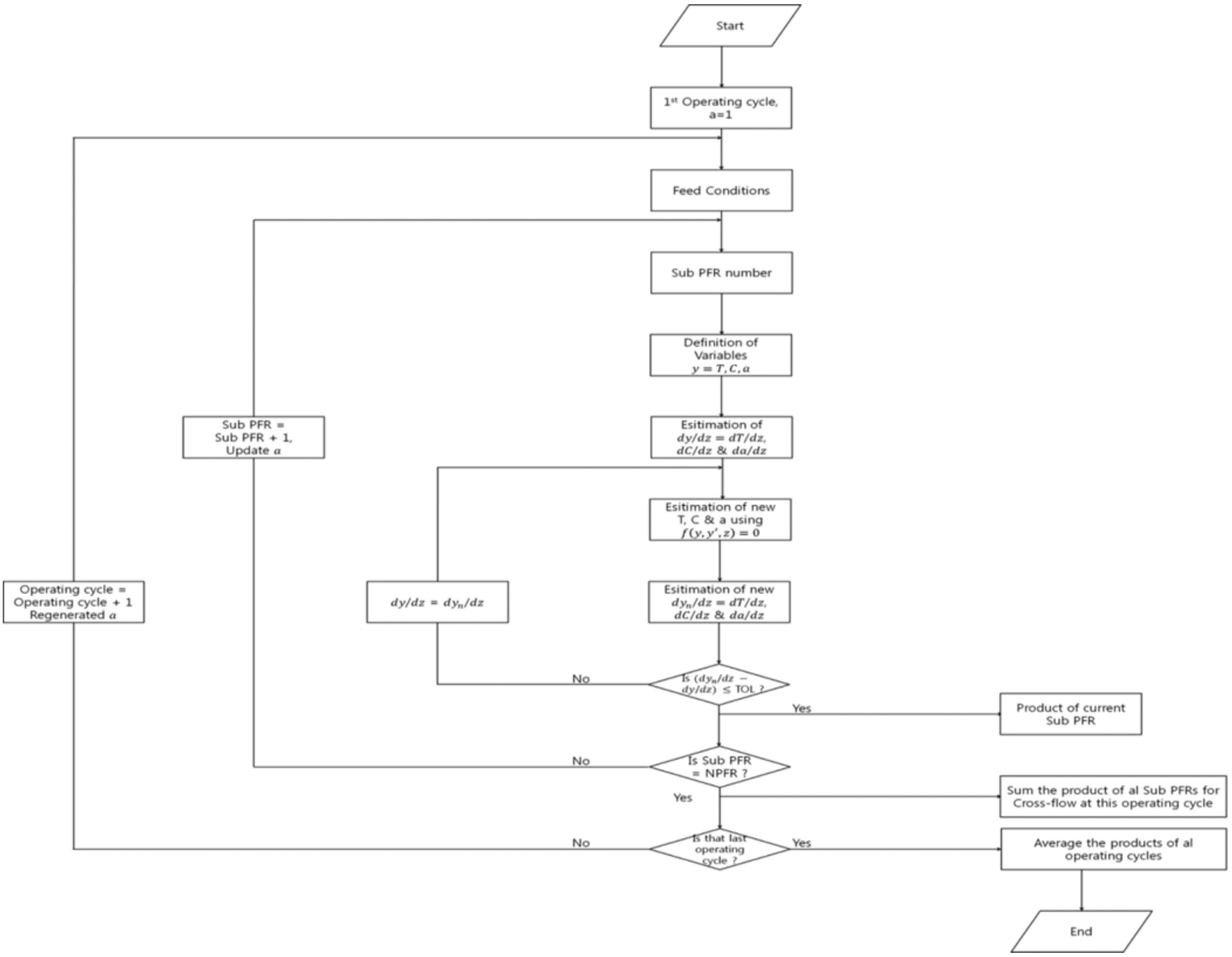


Fig. 4. Algorithm for a numerical solution of the reactors for single and multi-cycle operation.

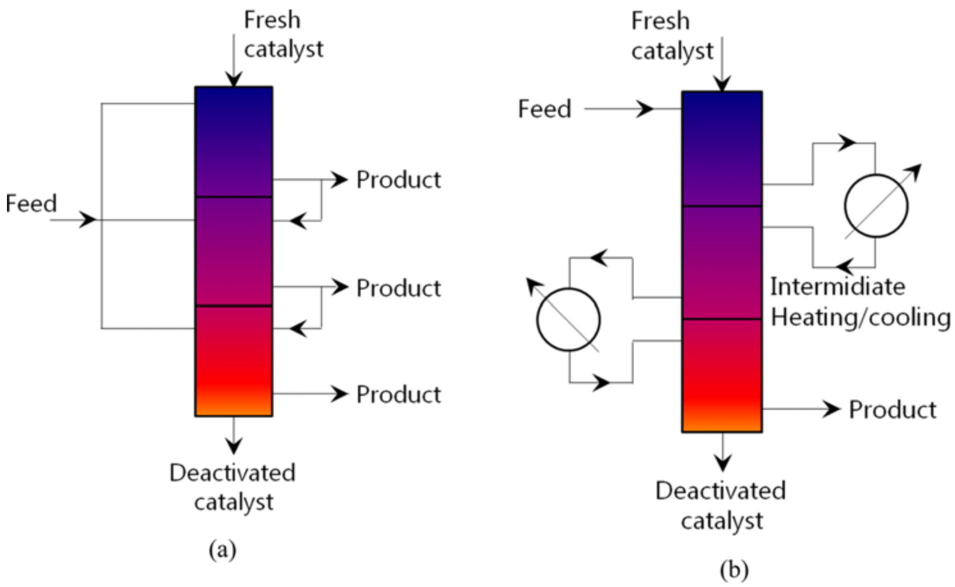


Fig. 5. Examples of various multistage MBR modeling.

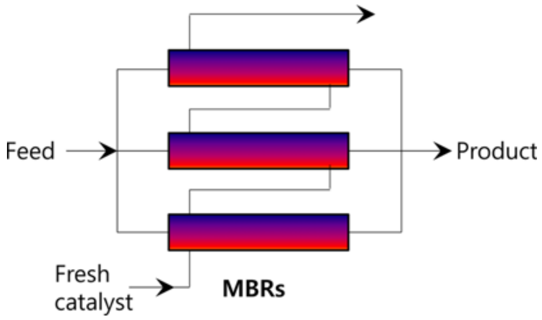


Fig. 6. Example of reactor networks.

7. Networks of MBR

Various reactor configurations for series and (or) parallel flows of reactants and catalysts were considered to maximize the overall reactor performance. Fig. 6 presents one of the reactor configuration examples, of which feed is introduced to three reactors in parallel while catalyst in series. For the operation of various MBR networks, a strategy to control of stream flow rate and temperature of the reactors within the network should be developed at conceptual design stage.

8. Modeling Background of a MBR

As an initial step for the modeling of an MBR, the mass and energy balances of (1) bulk/fluid phase, (2) fluid/particle interface, and (3) catalyst particle are used as shown below.

8-1. For the Bulk/Fluid Phase

The fluid phase mass and energy balance for heterogeneous, non-isothermal, non-adiabatic plug flow at each compartment of the MBR are expressed. Eqs. (4) and (5) describe concentration and temperature changes of the bulk / fluid phase along the reactor axis.

- Mass balance

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

- Energy balance

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

- Boundary condition,

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

8-2. For the Fluid/Particle Interface

The mass and energy balances in the catalyst phase with the external transfer resistances are expressed in this term. The gradients of each component concentration and temperature between catalyst surface and fluid/bulk phase are described by using Eqs. (6) and (7).

- Mass balance

$$k_{g,i}(C_{s,i} - C_{f,i}) = -D_{e,i}\frac{dC_i}{dx} = \eta\sum(\upsilon_{i,j}\cdot r_{s,j})\rho_p S' \tag{6}$$

- Energy balance

$$h(T_s - T_f) = -\lambda\frac{dT}{dx} = \eta\sum(\Delta H_j\cdot r_{s,j})\rho_p S' \tag{7}$$

where, $S' = V_p/S_p$

8-3. For the Catalyst Particle

Eqs. (8) and (9) model the mass and energy balance in the catalyst phase with internal diffusional resistances. The temperature and each component concentration profiles inside a catalyst pellet were considered by using Eqs. (8) and (9). The effective diffusivity coefficients of each component were included in Eq. (8) to take into account diffusion of each component inside a pellet.

- Mass balance

$$D_{e,i}\left[\frac{1}{x^n}\frac{d}{dx}\left(x^n\frac{dC_i}{dx}\right)\right] = \sum(\upsilon_{i,j}\cdot r_j)\cdot a(x) \tag{8}$$

- Energy balance

$$\lambda\left[\frac{1}{x^n}\frac{d}{dx}\left(x^n\frac{dT}{dx}\right)\right] = -\sum[(-\Delta H_j)\cdot r_j]\cdot a(x) \tag{9}$$

- Boundary condition

$$x=0;\ \frac{dC_i}{dx}=\frac{dT}{dx}=0$$

$$x=1;\ C_i=C_{s,\,i},\ T=T_s$$

The catalyst activity along the reactor length is expressed as Eq. (10).

$$v\frac{da(x)}{dz}=-\varepsilon * r_d * \frac{F}{F_{cat}} \tag{10}$$

Eqs. (4)-(10) need to be solved simultaneously. For this, they were encoded into the FORTRAN and the program utilized a subroutine called 'C05NCF' from numerical algorithms group (NAG) library. DASSL solver was used to increase simulation speed.

The assumptions for the modeling in this work are as follows:

1. The model assumes the same residence time of each catalyst particle in a moving bed of the reactor (piston flow of a moving catalyst). This results in the same activity at each point across the cross-section at a particular point along the reactor.
2. Pressure drop, drag effects and wall effects are not considered along the reactor, and the velocity of the reactants is assumed to be constant across the cross-section of the reactor.
3. Distribution of the fluid concentration over the catalytic surface is assumed to be uniform.
4. Hydrodynamic and physical properties are assumed to be constant during the process.
5. Intermediate feed or product removal gives a step change to the corresponding section of the reactor.
6. No loss or constant nominal loss of catalyst activity per reaction-regeneration cycle is assumed based on the data of the catalyst life.

We considered the simulation of the axial and radial flow MBRs with catalyst deactivation by coking. A wide range of design and operating parameters of the MBRs in various configurations were studied to improve the product quality and make efficient use of the raw materials. In addition, we considered the optimization of the temperature at the inlet and intermediate position of cross-flow to enhance the performance of the reactor via the mitigation of fouling. Simultaneous optimization of the make-up catalyst amount across the lifetime was also carried out to maintain the catalyst activity in a reactor.

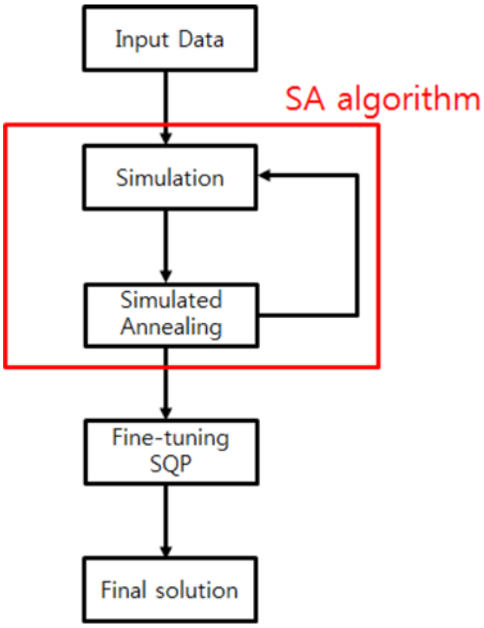


Fig. 7. Optimization framework.

9. Optimization Algorithm

As shown in Fig. 7, the optimization framework in this work used a combination of stochastic optimization (i.e., simulated annealing) and deterministic optimization (i.e., successive quadratic programming). This combination comparatively provided global optimum solution for overall optimization more quickly than if each algorithm was individually used [22]. It combined the advantages of both techniques. Simulated annealing is relatively robust for highly nonlinear problems; number of simulations is independent of total number of design variables, and is suitable when initial design is far from optimal design. Meanwhile, successive quadratic programming converges relatively fast, requires rather fewer simulations, and is suitable when the initial design is close to an optimal solution. Since SQP is commonly used in engineering problems, details of the algorithm are not discussed here. Furthermore, the basics and application of SA to reactor design can be found from the works of Hwang and Smith [23].

CASE STUDY

1. Propane Dehydrogenation

Many industries use catalytic dehydrogenation technology for the production of light olefins from their corresponding paraffin. One of the specific applications of this technology is the production of propene from propane. Propene is one of the world's largest petrochemical commodities and is used in the production of polypropylene, acrylonitrile, propylene oxide, glycols, cumene, acetones and others. The process uses a Cr_2O_3/Al_2O_3 catalyst to promote the dehydrogenation reaction, avoiding the competing combustion of propane, to enhance the selectivity of propene.

Propane dehydrogenation is an equilibrium-limited and highly endothermic reaction that is generally carried out at 530-630 °C under atmospheric pressure using a chromium-based catalyst. We examined the kinetics of propane dehydrogenation at 525-575 °C under atmospheric pressure, and proposed a reaction rate model using the Langmuir-Hinshelwood mechanism [20]. A layer mechanism was proposed for the modeling of deactivation, and its experimental results showed good agreement [20].

As described earlier, coke formation and cracking are some of the main concerns in the dehydrogenation of alkanes. Gascon et al. proposed the kinetics of the main reactions and catalyst coke formation [20]. In this study, the kinetics used for modeling are expressed as Eqs. (11) to (19), and the parameters summarized in Table 1 [20].

Dehydrogenation reaction:

$$C_3H_8 \leftrightarrow C_3H_6 + H_2 - r_1 = \frac{k_1 g\left(p_{C_3H_8} - \frac{P_{C_3H_8}P_{H_2}}{K_{eq}}\right)}{1+P_{C_3H_8}K_2} \tag{11}$$

Table 1. Summary of the kinetic parameters [20]

Parameter	Value	Units
k_{01}	0.0516	mmol/g·s
K_{02}	3,450	mmol/l
E_{a1}	35.5	kJ/mol
ΔH	−595	kJ/mol
α_1	813	g catalyst/g coke
α_2	289	g catalyst/g coke
k_{02}	0.00242	s^{-1}
k_{03}	0.000357	s^{-1}
E_{a2}	221	kJ/mol
E_{a3}	325.8	kJ/mol
C_{max}	0.000682	mg coke/mg catalyst
k_{04}	10E-5	mmol/g·s
E_{a4}	308	kJ/mol

$$k_i = k_{0i} \cdot \exp\left[-\frac{E_{ai}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \tag{12}$$

$$g = \exp(-\alpha_1 \cdot C_m) \cdot \exp(-\alpha_2 \cdot C_M) \tag{13}$$

$$K_2 = K_{02} \cdot \exp\left[-\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \tag{14}$$

Cracking reaction:

$$C_3H_8 \rightarrow CH_4 + C_2H_4 \quad -r_3 = k_4 P_{C_3H_8} \tag{15}$$

Coke formation:

$$C = C_m + C_M \tag{16}$$

$$C_m = C_{max} \cdot [1 - \exp(-k_2 t)] \tag{17}$$

$$C_M = C_{max} \cdot k_3 \cdot t - C_{max} \cdot \frac{k_3}{k_2} \cdot [1 - \exp(-k_3 t)] \tag{18}$$

Where,

$E_{ai}, k_{0i}, K_{02}, K_{eq}, H, R, \alpha_1, \alpha_2$: Constants

2. Various Options of Moving Bed Reactors

Various configurations of an MBR were modeled and simulated. In this work, the MBR is categorized into different types as follows based on structure and flow dynamics of the solid and gas:

a. A moving bed reactor
b. MBRs with complex networks
c. Multistage cross-flow MBRs

To compare various designs, all the configurations of the moving bed reactor used the same residence time of the catalyst and the same amount of reactants. The total amount of catalyst was also kept same for each design of the moving bed reactor.

3. Moving Bed Reactor

Generally, the most common configuration of an MBR is a single bed with continuously moving catalyst, as shown in Fig. 8. The catalyst bed moves downward under gravity in a vertical channel and the gas phase of the reactant mixture flows in parallel through the catalyst bed. For the design of a reactor, 6 m^3 of reactor volume was applied to all various types of reactors, while 1,650 kg/m^3 of catalyst bulk density was used for the modeling. For the overall heat transfer and mass transfer coefficients, 0.176 kW/m^2K and 5×10^{-4} m/s were used, respectively. The inlet temperature of the feed stream was optimized to increase the average conversion of propane, while the minimum selectivity of propene was maintained above 80% as a constraint.

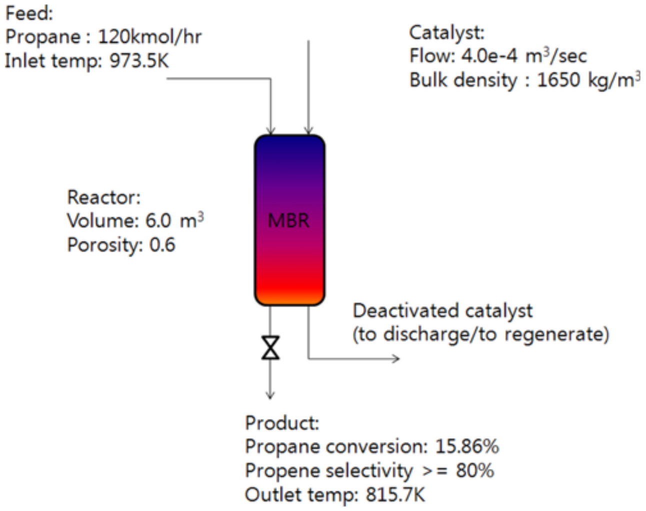


Fig. 8. Single cycle operation of a MBR.

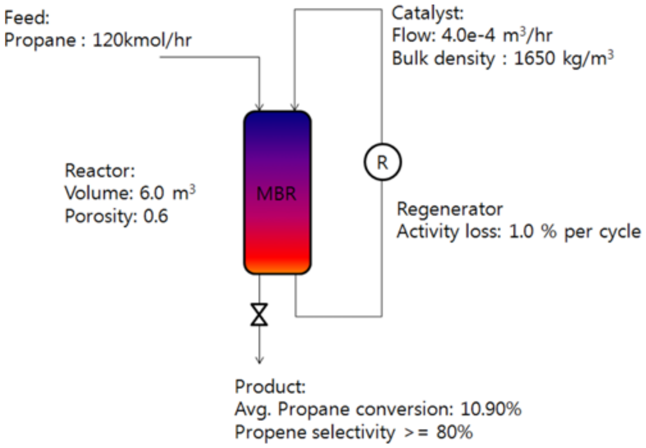


Fig. 9. Multi-cycle operation of an MBR with a nominal loss of activity per regeneration cycle.

The results of this case showed a conversion of 15.86% for a single cycle of reaction-regeneration. The process was then expanded to multiple cycles with total or partial regeneration, as shown in Fig. 9. In that case, loss of catalyst activity was neglected during regeneration. A nominal loss of activity was assumed per cycle, based on the total life of the catalyst. The steady state operation was assumed for each cycle. When it reached to the next cycle, a time step was applied to modeling, whereas steady state operation was considered for the cycle with an updated time. A large number of operating cycles for the entire operating period makes it virtually continuous in terms of operation.

Fig. 10(a) shows the optimized inlet temperature of each cycle to maintain a high level of propane conversion. Fig. 10(b) shows the performance in terms of propane conversion, which decreases

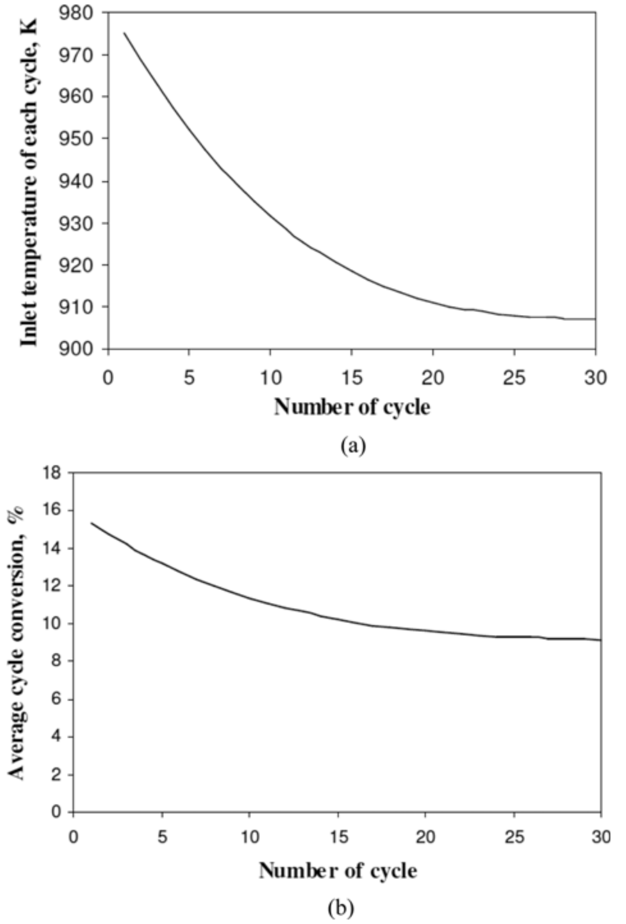


Fig. 10. (a) Inlet temperature profile through the operating cycle and (b) average conversion at each cycle.

across the operation time due to the loss of catalyst activity. In general, reactor temperature is maintained at a higher temperature to compensate loss of the catalyst activity as reactor operating time increases. However, this case was found to be more complicated, since the main reaction is an equilibrium reaction that is mainly affected by temperature, and the activity, byproduct reaction and coke formation are a function of operating time and reactor temperature. Furthermore, a constraint of minimum selectivity as 80% was included into the mathematical optimization formulation. For this reason, it was interesting to find that the optimization results suggested constant decrease of feed inlet temperature to maximize the overall conversation rate across the entire reactor operating periods, satisfying the minimum required selectivity.

Multi-beds of moving catalysts can also be operated in parallel or series to the reactants. In this case, catalyst flow is considered to be in series, while the reacting mixture is considered to be in parallel with the moving beds. The configuration is shown in Fig. 11, where the total volume of a single moving bed from the previous case is divided into three identical beds. The feed and catalyst data are also kept same as for the single bed reactor, except for the feed temperature, which is optimized to enhance the conversion and mitigate deactivation. The simulation results showed an increase in the average propane conversion from 10.9% in a previous case up to 12.9%.

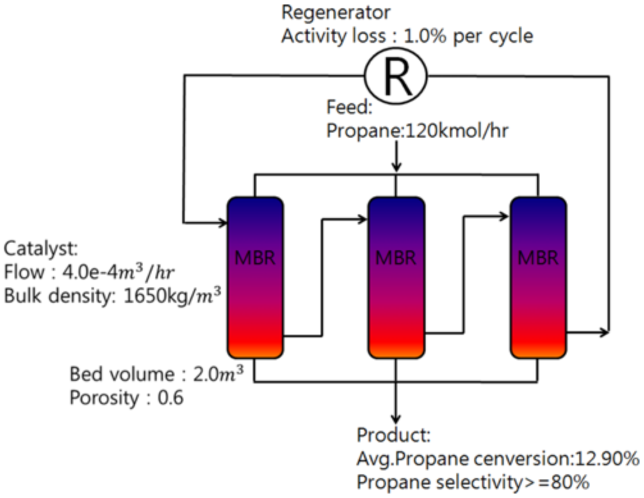


Fig. 11. MBRs parallel to the feed and series to a moving catalyst.

Each bed inside a reactor retains catalyst that shows different activity, and it leads to a variation in performance along the reactor length. Therefore, it is advisable to adjust the residence time of the catalyst at each bed to utilize the bed more effectively and to reduce the rate of deactivation. The catalyst velocity (pellet residence time) is optimized at each bed to maximize the level of propane conversion. The mean propane conversion was found to be 13.7% in this case, compared to 12.9% in the previous case, where the residence time of the catalyst was kept constant at each bed. The beds in a parallel feed network improved the performance (propane conversion) from 10.9% to 13.7% with an optimum inlet temperature range of 885-975 K.

4. Multi-stage Cross Flow Moving Bed Reactor

An MBR model was developed to account for the cross flow of reactants to the moving catalyst bed with multiple stages utilizing intermediate heating and cooling. This generally works well with a

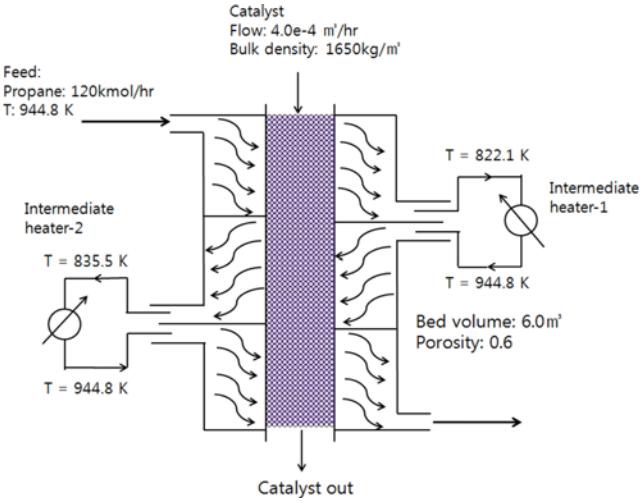


Fig. 12. Multi-stage MBR with a cross flow of reactants to the moving bed (same inlet temperature profile to each stage).

fast non-isothermal catalytic reaction to enhance the selectivity of products or conversion of the reactants. The optimal operation of this type of MBR was achieved by controlling the residence time of the catalysts and the inlet temperature to each stage.

The advantages of the cross flow moving bed reactor are summarized as follows [24-28]

a. Good contact of the gas-solid to improve the selectivity and yield

b. Adjustment of the solid and gas residence time

c. Low gas pressure drop

d. Control of the highly non-isothermal behavior of reactants

e. Inlet temperature optimization through intermediate cooling or heating to mitigate catalyst deactivation by coking

f. Easy separation of the gas and solid

In this work, the following three cases of a cross flow MBR were proposed to examine the effect of various designs and operating parameters on the product quality.

a. Single cross flow MBR

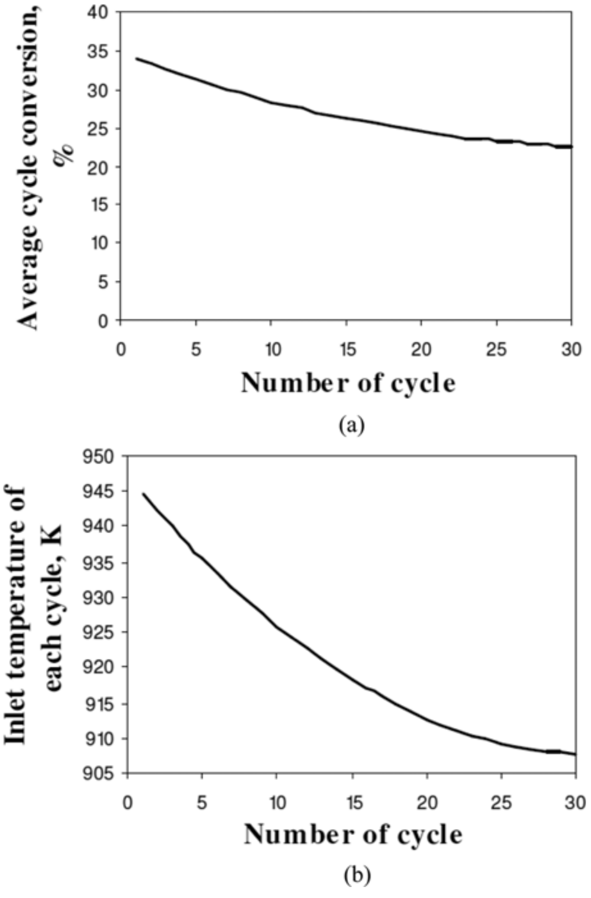
b. Three stage cross flow MBR with intermediate heating

c. Removal of the deactivated catalysts and the addition of fresh catalysts (i.e., optimization of a make-up catalyst addition profile)

Lastly, a cross-flow MBR was examined with the optimization of different catalyst velocities, intermediate heating duties, and make-up catalyst profiles. Each configuration was studied and optimized for propane conversion to propene satisfying a constraint of a minimum propene selectivity above 80%.

5. Single Cross Flow MBR

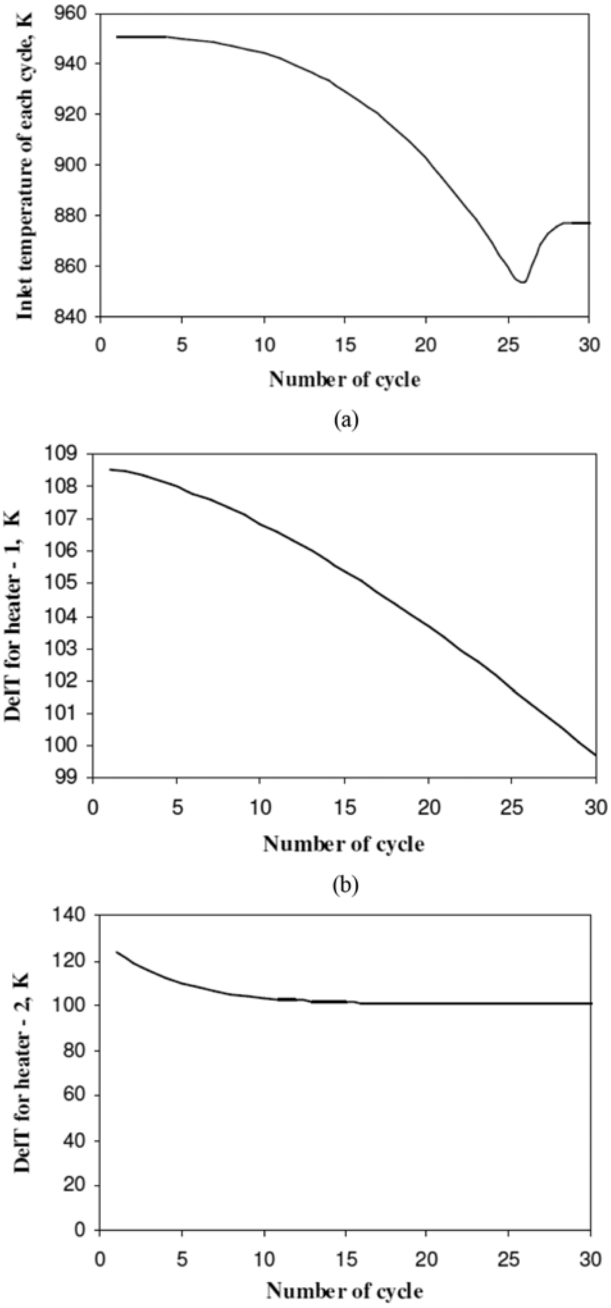
This option differs from the conventional single bed MBR in terms of the flow pattern of the reactants (i.e., cross flow through moving catalysts). The reactor section of this configuration consists of three cross flow stages with inter-stage heaters, as shown in Fig. 12. This is considered to be a base case for various types of



(a)

(b)

Fig. 13. Performance of a single cross flow MBR with an optimized inlet temperature profile.



(a)

(b)

(c)

Fig. 14. Multi-stage MBR with a cross flow of reactants to the moving bed (optimized inlet temperature profile to each stage). (a) Inlet temperature of each cycle, (b) ΔT for heater 1 of each cycle, (c) ΔT for heater 2 of each cycle

cross flow options.

The reactor model assumes a uniform distribution of feed to the surface of the catalyst bed. Degree of catalytic reaction varies across the moving beds due to the change in catalyst activity. In this configuration, using the same reactor and feed data as for the moving bed reactor, the level of propane conversion was found to be 33.84% for a single cycle. Note that one cycle was equivalent to 100minutes in this case study.

The moving catalyst bed was regenerated continuously and fed back to the reactor with little or no loss of activity in the regenerator, depending on the type of deactivation. To make a reactor model close to industrial case, a nominal loss of activity per reaction-regeneration cycle was assumed based on the life of the catalyst to make it more realistic. Then this configuration was operated as a multicycle for the life of the catalyst to maintain a high level of average conversion of propane (23.6%), optimizing the inlet temperature profile through the life time of catalyst, as shown in Fig. 13(a). Fig. 13(b) shows the optimized inlet temperature profile through number of cycles. In this case, the optimum inlet temperature profile decreased through the cycle to maximize the average propane conversion maintaining a minimum selectivity of 80%.

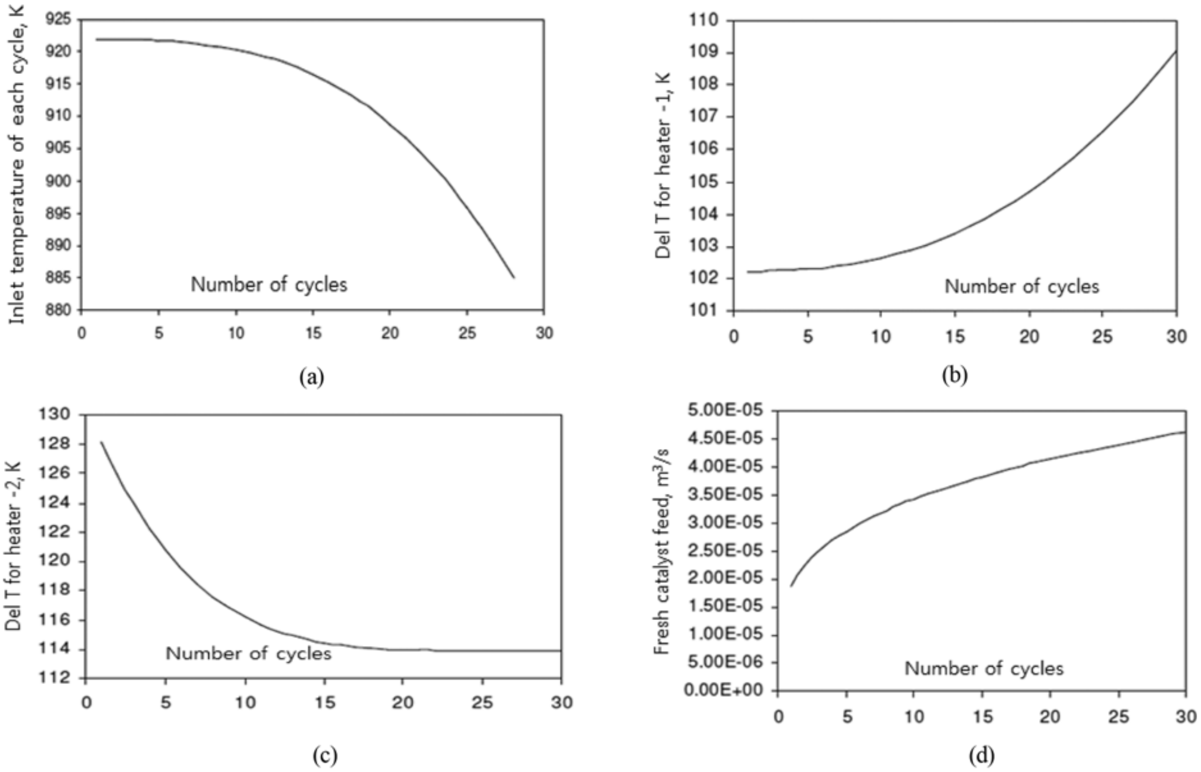
6. Three Stage Cross Flow MBR with Multiple Intermediate Heatings

In this case, the duty of each heater was optimized independently to reduce the impact of a variation in the catalyst activity at different stages. The duties were also optimized for multiple cycles through the life time of the catalyst, considering the nominal loss of activity, as discussed in the previous case. Fig. 14 shows the optimized inlet temperature profiles at each stage and the average propane conversion under this configuration. The inlet temperature profile to the 1st stage was found to keep decreasing for 25 cycles. At this point, the catalyst activity was comparatively low, and the catalyst activity could not be retained any further by decreasing the inlet temperature after this stage. Instead, the reaction rate could be increased by increasing the inlet temperature, and the rate of catalyst deactivation was relatively small.

Therefore, after 25 cycles, the effective reaction rate (catalyst activity×reaction rate) was increased by increasing the inlet and intermediate temperatures. Propane conversion was improved from 23.6% to 28.72% on average, compared to the previous case, when individual heat duties were not optimized.

7. Catalyst Feed Addition Profile Optimization (Make-up Catalyst)

A continuous nominal loss of catalyst activity during the catalyst life requires the deactivated catalyst to be replaced with fresh catalyst. In this model, the deactivated catalyst is removed continuously at the exit of the MBR and replaced with the same amount of fresh catalyst at the inlet of the MBR. The amount of fresh catalyst to be added (or removal of deactivated catalysts) at each time was optimized through time to maintain a specific level of catalyst activity in the bed, as shown in Fig. 15. The simultaneous optimization of the heating duties of inter-stage heaters was also performed to enhance propane conversion. The continuous addition of fresh catalyst established a virtual steady state operation in the MBR, which



(a) (b)

(c) (d)

Fig. 15. Multi-stage MBR with a cross flow of reactants to the moving bed (make-up catalyst profile optimization).
(a) Inlet feed temperature of each cycle, (b) ΔT for heater 1 of each cycle, (c) ΔT for heater 2 of each cycle, (d) Fresh makeup catlayst rate of each cycle

Table 2. Summary of the case study results

	Base case	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Conversion	10.90%	12.90%	12.90%	13.70%	23.60%	28.70%	29.15%

Case 1: MBRs in parallel to feed and series to moving catalyst, Case 2: MBRs with side stream addition and removal of products along the reactor, Case 3: Case 2 plus optimum temperature profile of feed stream, Case 4: Multi-stage MBR with cross flow of reactants to the moving bed and optimum inlet temperature profile of feed stream, Case 5: Multi-stage MBR with cross flow of reactants to the moving bed and optimum inlet and intermediate heatings, Case 6: Case 5 plus optimum make-up catalyst flowrate and catalyst circulation rate

led to approximately constant performance. As a result, the propane conversion performance was improved from 28.72% to 29.15%, while maintaining a minimum propene selectivity of more than 80%.

SUMMARY

As mentioned earlier, only a few design or operating parameters of MBRs have been considered individually by a number of researchers so far. Therefore, it has led to ineffective design and operation of the MBRs, causing additional cost increase in terms of both design and operation of the whole processes.

In this work, various design and operating parameters of moving bed reactors (MBRs) were considered at the same time, and the performance of the reactor was found to improve through optimization of the multiple design and operating parameters. These optimization parameters included the following: (1) reactant flows inside a reactor, (2) various networks of MBRs, (3) temperature of feed stream, (4) intermediate heating or cooling duty, (5) residence time of the catalyst or velocity of catalyst flow, and (6) flow rate of the fresh make-up catalyst.

The propane dehydrogenation process was considered as a case study, and the above parameters were simultaneously optimized to maximize the overall propane conversion during the operating periods, maintaining the minimum selectivity of the propene product above 80%. We incorporated the catalyst deactivation kinetics into the model, and divided the entire catalyst lifetime into multiple cycles of reaction and regeneration.

A moving bed with a parallel flow of gas and solid was considered initially as the base case. Then, six different designs of MBRs were developed through the optimization of the design and operating parameters. Table 2 summarizes the conversions of these cases.

The results showed that the conversion of the reaction increased significantly from 10.90% in the base case to up to 29.15% in case 6, maintaining a minimum selectivity of more than 80% through the optimization, while the total amounts of the catalyst and reactor volume were kept same for all cases. Note that maximization of conversion was adopted as a target for optimization in this case. Meanwhile, the other objective function such as economic profit can be also used on the basis of capital and operating costs, and sales price of products, etc.

This methodology can be easily applied to various types of reaction processes that are discussed in section 1.

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NOTATION

a^d : catalyst activity
C : coke concentration [kmol/m^3]
$C_{f,i}$: fluid concentration of the species in bulk phase i [kmol/m^3]
C_S, C_F : heat capacities of the solid and gas [kJ/kg·K]
C_i : concentration of the component i [kmol/m^3]
C_m, C_M : coke concentration in the mono and multi-layer [kmol/m^3]
C_{max} : maximum coke concentration in the monolayer [kmol/m^3]
C_p : heat capacity of the fluid phase [kJ/kg·K]
$C_{s,i}$: fluid concentration of the species on the surface of the catalyst, i
d : order of deactivation
$D_{e,i}$: effective diffusivity coefficient of component, i
F : fluid volumetric flow rate [m^3/s]
$\mathrm{F}B$: porosity of bed
F_{cat} : catalyst volumetric flow rate [m^3/s]
h : external heat transfer coefficient [KJ/(m^2·K·s)]
ΔH_j : heat of reaction j [kJ/kmol]
k_0 : rate constant at zero time
k_d : deactivation rate constant
$k_{g,i}$: external mass transfer coefficient of component i [m/s]
L : length of reactor [m]
M : molecular weight of the reactants [kg/kmol]
m : order of reaction or order of concentration dependency
n : integer characteristic of the pellet geometry (n=0 for infinite slab; n=1 for infinite cylinder; n=2 for sphere)
Q : heat liberated by reaction [kJ/hr]
r_a' : rate of reaction [kmol/m^3s]
r_d : rate of catalyst deactivation [s^{-1}]
r_j : rate of reaction j [kmol/m^3s]
$r_{s,j}$: rate of reaction, j on the catalyst surface [kmol/m^3s]
S′ : characteristic pellet length (=V_p/S_p) or catalyst activity
S_F : space velocity of reactants [s^{-1}]
S_p : surface of pellet [m^2]
t : reactor operating time
T_m : reference temperature [K]
T_f : temperature of the fluid phase [K]
T_s : temperature of the catalyst surface [K]
U_o : overall heat transfer coefficient between the reaction gases

and cooling medium $[KJ/(m^2\cdot K\cdot s)]$
v : fluid velocity [m/s]
V_p : volume of the pellet $[m^3]$
x : distance from the pellet centre to the surface [m]
y_A : mole fraction of the reactants
Z : axial co-ordinate along the reactor

Subscripts
B : bed
d : deactivation
i : component
j : reaction type
m, M : mono, multi-layer
F : fluid
P : pellet
S : surface

Greek Letters
α : $4/D_t$ (internal tube diameter)
ε : bed void fraction
η : effectiveness factor of the catalyst
λ : effective thermal conductivity [kJ/s·m·K]
ν : velocity of the external fluid phase [m/s]
$\nu_{i,j}$: stoichiometric coefficient of species, i in reaction j
ρ : density of fluid phase $[kg/m^3]$
ρ_F : density of reactants $[kg/m^3]$
ρ_p : density of pellet $[kg/m^3]$

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