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# Dynamic Optimization Strategies of a Heterogeneous Reactor for CO<sub>2</sub> Conversion to Methanol

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The inherent sustainability and low carbon dioxide (CO<sub>2</sub>) emissions of renewable energy technologies provide the necessary features of future energy policy goals. To secure the contribution of renewables in the future energy supply, practical dynamic optimization strategies for CO<sub>2</sub> conversion into methanol in a heterogeneous reactor are proposed. The conversion provides a solution to the problem of carbon dioxide emissions reduction and at the same time produces a readily storable and transportable fuel. The dynamic optimization is carried out on an industrial scale methanol reactor and considers shell temperature and inlet hydrogen mole fraction, separately and simultaneously, as optimization variables. The optimizations have been carried out in both steady- and unsteady-state modes. A heterogeneous model of the reactor has been used to obtain accurate optimization results. In the dynamic mode, a stagewise optimization for 4 years of reactor operation has been considered. The methanol production rate (MPR) has been selected as the objective function to find optimal profiles. In the steady-state case, the optimal input mole fractions of CO, CO<sub>2</sub>, and H<sub>2</sub> have been investigated. The calculated concentration profiles are realistic and appropriate for the application of an industrial methanol reactor. The staged optimization suggests a new guideline for operating the reactor. For the optimization of input mole fractions, it was indirectly concluded that CO<sub>2</sub> concentration adversely affects the overall process as compared to catalyst poisoning due to the presence of CO.

## 1. Introduction

The global warming caused by increasing concentrations of greenhouse gases in the atmosphere is a serious problem concerning the fundamental conditions of life on Earth. CO<sub>2</sub> is considered to be the major cause of global warming. The net increase of 13 000 million tones of carbon dioxide estimated to be added to the atmosphere annually is alerting.<sup>1</sup> The rising level of CO<sub>2</sub> is already affecting the atmosphere, sea level, and ecological systems. The global sea level rose 10–20 cm over the past century, and in this century, it may rise by as much as 88 cm. The current atmospheric concentration of carbon dioxide at 380 ppm is 30% higher than the pre-industrial level and is expected to increase to somewhere between 800 and 1000 ppm by the year 2010. The third session of the conferences of parties to the United Nations framework convention on climate change held in Kyoto in December 1997 produced an agreement known as the Kyoto Protocol. The Kyoto Protocol calls for the majority of industrialized countries to limit their emissions of greenhouse gases over the period from 2008 to 2012.<sup>2</sup> As a CO<sub>2</sub> reduction measure, the current study considers the conversion of CO<sub>2</sub> to methanol. The latter is considered to be a valuable product because of its use as a feed stock to produce chemical intermediates. Methanol is also easily transported and is

considered to be a future renewable energy.<sup>3</sup> The current paper attempts to suggest practical methods to enhance methanol production from current industrial methanol reactors.

Methanol is one of the worldwide consumed chemicals which is usually used as fuel, as solvent, and as a building block to produce chemical intermediates.<sup>4</sup> The following reactions can be assumed to occur in methanol synthesis:



Equation 2 is dependent on the other two equations and can be obtained by the addition of eqs 1 and 2.<sup>5</sup> In this study, eqs 1 and 3 have been used to represent the reaction system. Independent reactions 1 and 3 are exothermic, and thus, the formation of methanol is preferred with low temperature and high pressure. Synthesis gas consists of H<sub>2</sub>, CO<sub>2</sub>, CO, and some inert components like methane and nitrogen. Figure 1 illustrates a typical methanol plant.<sup>6</sup> Table 1<sup>7</sup> represents specifications of the plant.

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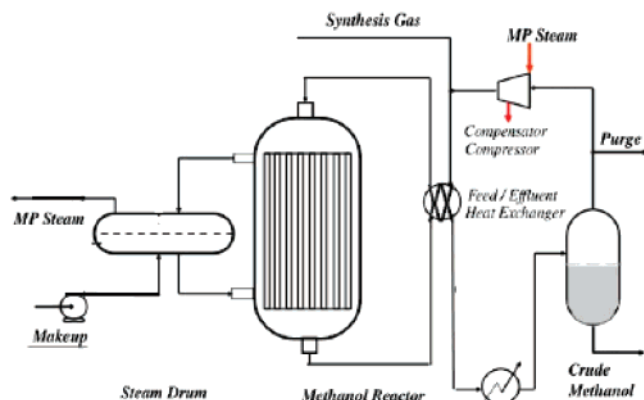


Figure 1. Schematic of methanol production plant.

Table 1. Specifications of SPC Methanol Reactor<sup>7</sup>

feed component	mole fraction
hydrogen	0.659
carbon monoxide	0.046
carbon dioxide	0.094
methane	0.1026
water	0.0004
nitrogen	0.093
methanol	0.005

Because of catalyst deactivation, the usual practice is to continuously increase the working temperature or decrease the feed rate of the reactants. A temperature increase has a secondary side effect that accelerates the deactivation rate, while a decrease in the feed rate decreases the reactor production rate. So considering these facts, an optimum operating temperature and feed rate should be found in order to have sustainable methanol production.

The optimization of a methanol reactor has been the subject of few studies. Larsson et al.<sup>8</sup> considered the unconstrained optimization of an isothermal methanol reactor at steady state. The reactor was modeled as a series of isothermal continuously stirred tank reactors (CSTRs), with a kinetic model from Vanden Bussche, and Froment.<sup>9</sup> Lovik et al.<sup>10</sup> studied dynamic optimization of a methanol reactor. They reported the optimal shell temperature as time goes on. Jahanmiri and Eslamloueyan<sup>11</sup> investigated the optimal temperature profile in a steady-state methanol reactor. Their model finds the optimal temperature profile inside the reactor, which is impractical to implement in industrial units. Recently, Kordabadi and Jahanmiri<sup>12</sup> attempted to find the optimal temperature of a methanol reactor using a genetic algorithm. They also investigated the optimal division of a bed into two sections as two reactors. Their work focused on combining steady state and multi-objective optimization techniques to estimate optimal conditions.

Only Lovik et al.<sup>10</sup> and Kordabadi and Jahanmiri<sup>12</sup> used dynamic industrial heterogeneous models to optimize the

methanol reactor performance. The simultaneous effect of inlet hydrogen and coolant temperature as optimization variables has not, however, yet been studied in the literature. Furthermore, the “stagewise” optimization for methanol reactors with a narrow time increment (i.e., for each 100-day increment of operation) has not been considered previously.

The present paper, therefore, deals with the simultaneous optimization of inlet hydrogen and shell temperature regarding reversible reactions with an industrial methanol reactor model. In addition, inlet hydrogen and temperature are optimized individually. Both effects of equilibrium and catalyst deactivation on reactor behavior are analyzed. Furthermore, dynamic optimization and steady-state optimization are presented in this research in order to provide a complete picture of the optimization of the reactor.

## 2. Process Modeling

To get a mathematical model for the methanol reactor, it is essential to write mass and energy balances. A heterogeneous model is considered in this paper.<sup>13</sup> The application of the conservative principles to the bulk gas stream and film of gas on the surface of the catalyst leads to the following equations for the reactor:

Continuity equations

$$\epsilon_B c_t \frac{\partial y_i}{\partial t} = -\frac{F_t}{A_c} \frac{\partial y_i}{\partial z} + a_v c_t k g_i (y_i - y_i^s) \quad i = 1, 2, \dots, N-1 \quad (4)$$

$$\epsilon_s c_t \frac{\partial y_i^s}{\partial t} = k g_i (y_i - y_i^s) + r_i \rho_B a \quad i = 1, 2, \dots, N-1 \quad (5)$$

Energy equations

$$\epsilon_B c_t c_{pg} \frac{\partial T}{\partial t} = -\frac{F_t}{A_c} \frac{\partial T}{\partial z} + a_v h_f (T^s - T) + \frac{\pi D_i}{A_c} U_{\text{shell}} (T_{\text{shell}} - T) \quad (6)$$

$$\rho_B c_{ps} \frac{dT^s}{dt} = a_v h_f (T - T^s) + \rho_B a \sum_{i=1}^N r_i (-\Delta H_{f,i}) \quad (7)$$

Deactivation rate<sup>14</sup>

$$\frac{da}{dt} = -K_{\text{act}} \exp\left(\frac{-E_{\text{act}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) a^5 \quad (8)$$

Boundary and initial conditions

$$y_i(0, t) = y_i^0$$

$$T(0, t) = T^0 \quad (9)$$

$$y_i(z, 0) = y_{i0}$$

$$y_i^s(z, 0) = y_{i0}^s$$

$$T(z, 0) = T_0$$

$$T_s(z, 0) = T^{s0}$$

$$a(z, 0) = a_0 \quad (10)$$

where  $y_i^{\text{ss}}$  is the steady-state profiles of the component  $i$  mole fraction and  $T^{\text{ss}}$  is the steady-state temperature profile along the reactor. The values of  $T^{\text{ss}}$  and  $y_i^{\text{ss}}$  are determined from a steady-

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(8) Larsson, T.; Skogestad, S.; Cheng-Ching, Yu. Presented at the AIChE annual meeting, Dallas, TX, 1999.

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(11) Jahanmiri, A.; Eslamloueyan, A. Optimal Temperature Profile in Methanol Synthesis Reactor. *Chem. Eng. Commun.* **2002**, *189*, 713–741.

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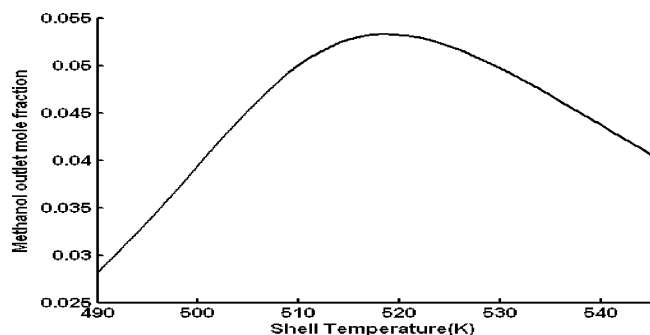


Figure 2. Steady-state optimum shell temperature.

state simulation. In the steady-state simulation, the left-hand sides of eqs 4–7 are set to zero.

### 3. Process Optimization

As was mentioned earlier, both dynamic and steady-state optimization are carried out. The objective function,  $J$ , for dynamic optimization is the methanol production rate (MPR), which was described in our earlier work<sup>15</sup> and is presented in eq 11 below. In steady-state optimization, the effluent methanol mole fraction is considered as the objective function,  $J$ . Different optimization strategies for both the steady and the dynamic modes were implemented and will be described in detail in the following sections.

The dynamic optimization problem is formulated as follows:

$$\max (J = \text{MPR} = \text{FM}_{\text{w, methanol}} \int_0^t x_{\text{methanol}}|_{z=1} dt) \quad (11)$$

which is subject to the process model (eqs 4–10) and the following additional constraints

$$490 \leq T_{\text{shell}} \leq 540 \quad (12)$$

$$0 \leq T \leq 543 \quad (13)$$

$$0 \leq y_{\text{H}_2} \leq 114 \quad (14)$$

For steady-state optimization, the deactivation is assumed to be unity, and  $J = y_{\text{methanol}}|_{z=1}$ . Taking into account the length of the reactor and time simultaneously in optimization is another challenge considered in the current study. Matlab 7 was used to implement all optimization strategies.

### 4. Steady-State Optimization

**4.1. Optimization of Shell Temperature ( $T_{\text{shell}}$ ).** The optimization variable shell temperature is often controlled by a proportional and integral (PI) controller in a real plant.<sup>7</sup> Therefore, manipulating  $T_{\text{shell}}$  is of practical importance. The Levenberg–Marquart technique was employed to find the optimum  $T_{\text{shell}}$ . Figure 2 shows the variation of  $y_{\text{methanol}}$  with  $T_{\text{shell}}$ . For steady state, a  $T_{\text{shell}}$  value of 518 K was found as an optimum temperature.

(13) Rezaie, N.; Jahanmiri, A.; Moghtaderi, B.; Rahimpour, M. R. A comparison between homogeneous and heterogeneous modeling in Lurgi-type methanol reactor. *Chem. Eng. Process.* **2005**, *44*, 911–921.

(14) Hanken, L. Optimization of methanol reactor. Master's Thesis, The Norwegian University of Science and Technology, Norway, 1995.

(15) Zahedi, G.; Elkamel, A.; Lohi, A.; Jahanmiri, A.; Rahimpour, M. R. Hybrid model formulation for the unsteady state simulation of a packed bed reactor for CO<sub>2</sub> hydrogenation to methanol. *Chem. Eng. J.* **2005**, *115* (1–2), 113–120.

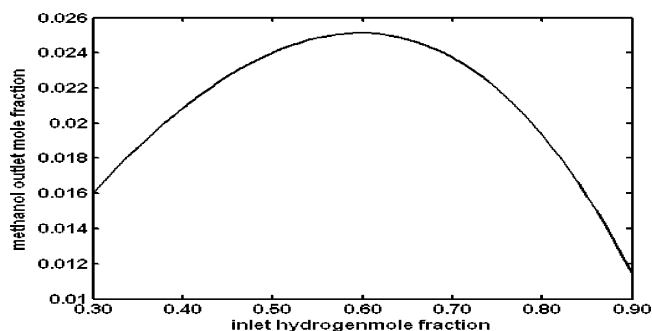


Figure 3. Steady-state optimum inlet hydrogen mole fraction.

**4.2. Optimization of Inlet Hydrogen Mole Fraction.** In contrast to the CO<sup>16</sup> and CO<sub>2</sub><sup>17</sup> roles in catalyst deactivation, H<sub>2</sub> does not deactivate the catalyst directly. Noting eqs 1–3, an increase in H<sub>2</sub> can cause more methanol production but at the same time leads to an increase in CO and CO<sub>2</sub> production. This fact motivates us to find an optimum mole fraction for inlet hydrogen. In order to implement such a policy, the inlet hydrogen mole fraction and consequently other components' inlet mole fractions should vary. These are changed in this research in a way that the following equations are satisfied:

$$x_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}}^0 (1 - x_{\text{H}_2}) \quad (15)$$

$$x_{\text{N}_2} = x_{\text{N}_2}^0 (1 - x_{\text{H}_2}) \quad (16)$$

$$x_{\text{CO}} = x_{\text{CO}}^0 (1 - x_{\text{H}_2}) \quad (17)$$

$$x_{\text{CO}_2} = x_{\text{CO}_2}^0 (1 - x_{\text{H}_2}) \quad (18)$$

$$x_{\text{MeOH}} = x_{\text{MeOH}}^0 (1 - x_{\text{H}_2}) \quad (19)$$

$$x_{\text{CH}_4} = 1 - (x_{\text{H}_2} + x_{\text{H}_2\text{O}} + x_{\text{N}_2} + x_{\text{CO}} + x_{\text{CO}_2} + x_{\text{MeOH}}) \quad (20)$$

$$x_{\text{H}_2} = x_{\text{H}_2} \quad (21)$$

The mole fractions indicated with the superscript 0 are Shiraz Petrochemical Complex (SPC) plant data that are listed in Table 1. The philosophy behind this is to change other components' mole fractions in a way consistent with their initial mole fractions. Methane and nitrogen are inert components, and changing the methane proportion in the feed is easily achieved in the SPC methanol reactor because of the available natural gas resources. The optimal hydrogen mole fraction was found to be 0.6. Figure 3 illustrates the variation of the methanol outlet mole fraction with inlet hydrogen.

**4.3. Simultaneous Optimization of  $x_{\text{H}_2}$  and  $T_{\text{shell}}$ .** Figure 4 shows the variation of produced methanol mole fraction as a function of inlet hydrogen fraction ( $x_{\text{H}_2}$ ) and shell temperature

(16) Rahimpour, M. R.; Fathikalajahi, J.; Jahanmiri, A. Selective kinetic deactivation model for methanol synthesis from simultaneous reaction of CO<sub>2</sub> and CO with H<sub>2</sub> on a commercial copper/zinc oxide catalyst. *Can. J. Chem. Eng.* **1998**, *76*, 1–9.

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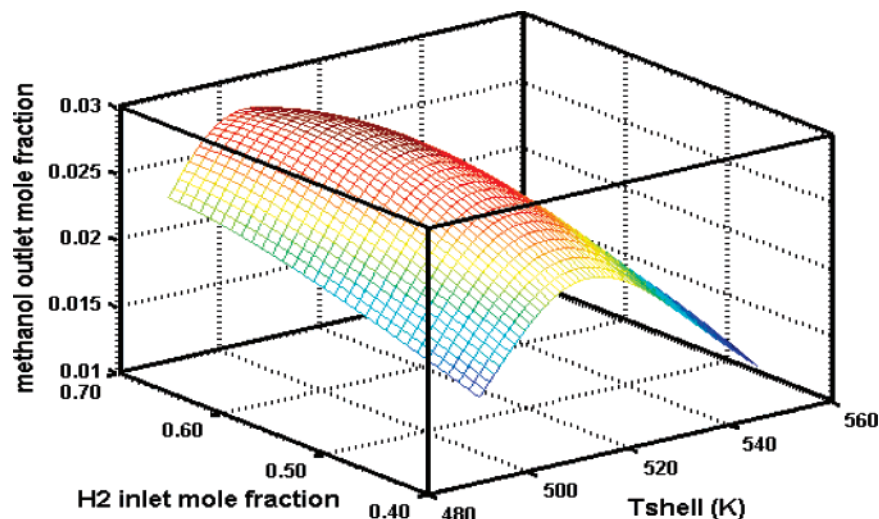


Figure 4. Simultaneous steady-state optimization of  $x_{H_2}$  and  $T_{shell}$ .

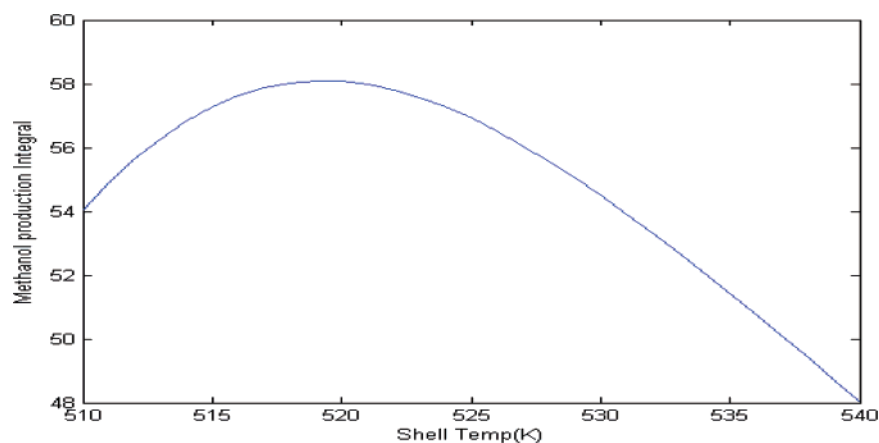


Figure 5. Unsteady-state optimization of  $T_{shell}$  during 4 years of operation.

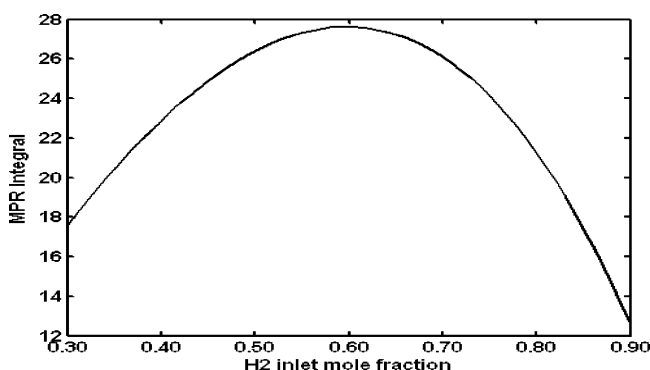


Figure 6. Unsteady-state optimization of  $x_{H_2}$  during 4 years of operation.

( $T_{shell}$ ). The optimal values were found to be  $x_{H_2} = 0.62$  and  $T_{shell} = 508$  K.

## 5. Dynamic Optimization

**5.1. Dynamic Optimization of  $x_{H_2}$  and  $T_{shell}$  during 4-year Operation.**  $T_{shell}$  was found to be 519 K during 4 years of plant operation. The optimization code for  $x_{H_2}$  as a single variable provided a value of 0.6. Choosing  $x_{H_2}$  and  $T_{shell}$  simultaneously as optimization variables led to  $x_{H_2} = 0.61$  and  $T_{shell} = 512$  K. Figures 5–7 show the variations of

the MPR integral (eq 22) as a function of shell temperature and hydrogen inlet mole fraction.

$$\max (\text{MPR integral} = \int_0^t x_{\text{methanol}}|_{z=1} dt) \quad (22)$$

**5.2. Dynamic Staged Optimization.** **5.2.1.  $T_{shell}$  Dynamic Staged Optimization.** The time interval for this section has been set as 100 days which is the narrowest increment in methanol optimization. At each 100 days of operation, the optimum values of  $T_{shell}$  are shown in Table 2. As time goes on, the optimal  $T_{shell}$  increases. This seems reasonable as the raised temperature is for compensating the deactivation effect on MPR.

**5.2.2. Simultaneous  $x_{H_2}$  and  $T_{shell}$  Dynamic Staged Optimization.** This section is the most computationally intensive part of the optimization. The optimization is a kind of an optimal control problem. Broadly speaking, the necessary conditions that will determine an optimal policy  $u(t)$  that causes a system to follow a path  $x(t)$  such that a performance functional  $J = \int_{t_0}^{t_f} F(x, u, t) dt$  is maximized will be obtained. In order to apply these circumstances, the Hamiltonian or adjoint eq 19 is often introduced as follows:

$$H = F(x, u, t) + \lambda^T f(x, u, t) \quad (23)$$

where  $\lambda$  is a vector containing dynamic Lagrange multipliers.



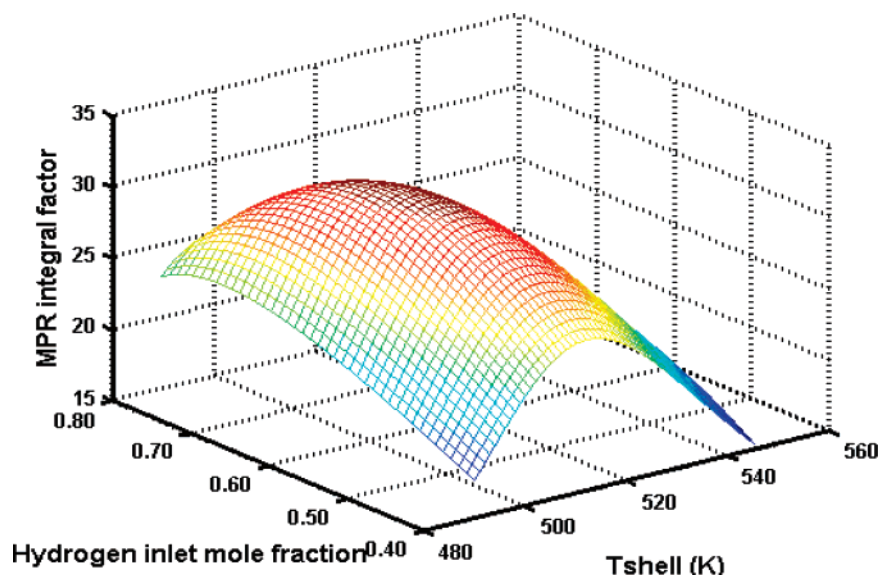


Figure 7. Unsteady-state optimization of  $x_{H_2}$  and  $T_{shell}$  during 4 years of operation.

Table 2. Optimal Values of  $T_{shell}$  Every 100 days of Reactor Operation

day	$T_{shell}$ (K)
0–100	498
100–200	504
200–300	511
300–400	513
400–500	514
500–600	515
600–700	518
700–800	520
800–900	522
900–1000	526
1000–1100	529
1100–1200	534

The necessary conditions according to the fundamental theorem of the calculus of variation are the following:<sup>20</sup>

Euler–Lagrange equation

$$\dot{\lambda} = -\frac{\partial H}{\partial x} \quad (24)$$

Process model

$$\dot{x} = -\frac{\partial H}{\partial \lambda} \quad (25)$$

Optimal control

$$\frac{\partial H}{\partial u} = 0 \quad (26)$$

Transversality

$$-\lambda^T(t_f)\delta x_f + H(t_f)\delta t_f = 0 \quad (27)$$

$u$ ,  $\lambda$ ,  $x$ , and  $H$  all are vectors of dimension  $N - 1$ . As the operating time is constant (4 years), eq 27 reduces to the following:

$$\lambda^T(t_f) = 0 \quad (28)$$

(20) Pinch, E. R. *Optimal Control and the Calculus of Variations*; Oxford University Press: Oxford, 1993.

The inlet hydrogen mole fraction and the shell cooling temperature have been set out as the optimization variables. Implementing and changing their values in the real plant is practical. Equations 12–14 are used as inequality constraints, and the process model (eqs 4–10) serves as equality constraints.

The solution techniques for optimal control problems can be categorized into two groups: indirect and direct methods. The indirect methods solve eqs 23–26 and 28 and thus indirectly solve the optimal control problem. The most well-known methods in this category are boundary condition iteration (BCI) and control vector iteration (CVI).<sup>21</sup> However, these methods can exhibit numerical instabilities or slow convergence rates for many problems.

There are two possible strategies for the direct methods: sequential and simultaneous. The sequential strategy is often called control vector parametrization (CVP).<sup>21</sup> Here, piecewise-constant control profiles are used. Hence, an infinite-dimensional optimization problem in continuous control variables is transformed into a finite-dimensional nonlinear programming (NLP) problem that can be solved by any gradient-based method (e.g., sequential quadratic programming (SQP)). The performance index evaluation is carried out by solving an initial value problem (IVP) of the original ordinary differential equation (ODE) system and gradients of the performance index as well as the constraints. Moreover, this method is a feasible-type method, i.e., the solution is improved in every iteration. In the simultaneous strategy, both the control and state variables are discretized using polynomials (e.g., Lagrange polynomials) whose coefficients become the decision variables in a much larger NLP problem.<sup>23,24</sup> Unlike the CVP method, the simultaneous method does not require the solution of IVPs at every iteration of the NLP. The method is, however, of the infeasible-type (i.e., the solution is available only once the iterative process has converged).

(21) Ray, W. H.; Szekeley, J. *Process Optimization with Applications in Metallurgy and Chemical Engineering*; John Wiley and Sons: New York, 1973.

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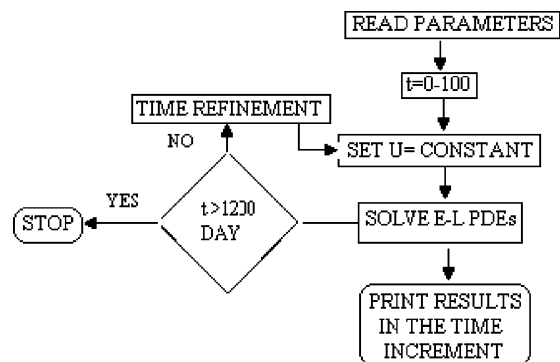


Figure 8. Schematic of simultaneous  $x_{H_2}$  and  $T_{shell}$  dynamic staged optimization.

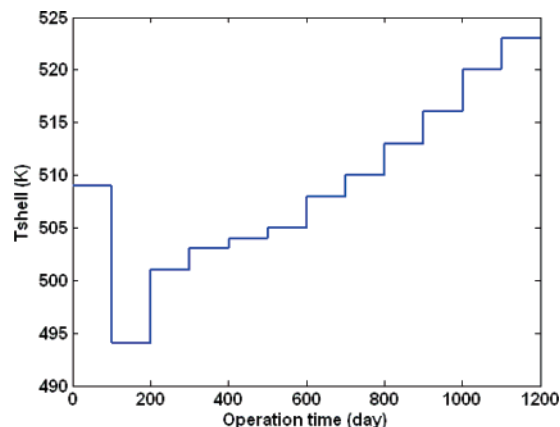


Figure 9. Time varying reactor shell temperature for simultaneous optimal control of  $T_{shell}$  and  $y_{H_2}$ .

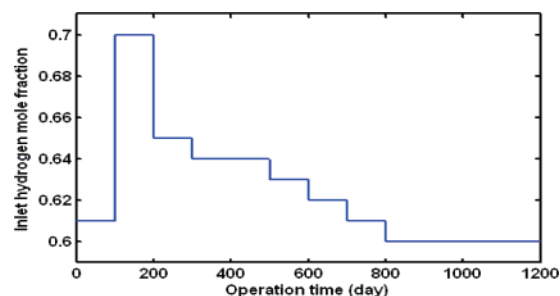


Figure 10. Trajectory of inlet hydrogen mole fraction for simultaneous control of  $T_{shell}$  and  $y_{H_2}$ .

In order to solve the optimal control problem for the methanol reactor, the control variables,  $T_{shell}(t)$  and  $x_{H_2}(t)$ , were discretized as piecewise-constant profiles (Figure 8) and the control vector

Table 3. Comparison of Optimal MPR with Reference Case

time (day)	ref MPR (heterogeneous model (ton/day))	optimal MPR (ton/day)
0–100	305.66	311.2
100–200	293.28	296.2
200–300	285.30	288
300–400	279.36	282.5
400–500	274.57	277.7
500–600	270.53	273.15
600–700	267.03	268.6
700–800	263.94	265.1
800–900	261.16	262.2
900–1000	258.64	260.2
1000–1100	256.32	257.2
1100–1200	254.19	255.3

$u(t)$  was approximated with 12 constant-piecewise profiles over 1200 days of operation. The profiles were taken to be of the same length, but this restriction can be easily waived in our numerical implementation scheme. The optimization problem is therefore constrained by a set of partial differential equations (PDEs).

Assuming that a constant control vector at each time increment (100 days) accelerates the solution of Euler–Lagrange equations. Compared to other indirect methods, the convergence of the current method (which is similar to CVI) is fast. A schematic representation of this algorithm is shown in Figure 8. The integration of the model differential equations and because of their stiff nature was performed by the modified Rosenbrock<sup>25</sup> formula of order 2. The integrals in the model and optimization algorithm were numerically evaluated using a recursive adaptive Simpson quadrature. Matlab 7 has been used too in this part of the study to implement all of the routines and optimization procedures.

Figure 9 shows the cumulative effect of deactivation kinetics and chemical equilibrium on the optimal evaluation of shell temperature. The first characteristic noticed is the continuous increase of the shell temperature after day 200. This is to compensate for the effect of catalyst deactivation on the MPR. The second characteristic effect is the temperature drop after day 100. According to ref 13, it is obvious that there is a great amount of  $H_2O$  formation at the beginning of the operation and then its production trend becomes slow. Noting this fact and noting that eqs 1 and 3 are the governing equations of the reactor, one can conclude that, at the beginning, endothermic eq 3 is the rate-controlling step and, in order to increase the MPR at the beginning, temperature should increase. By the passage of time, the exothermic reaction (eq 1) becomes the rate-controlling step so the temperature should decrease. The

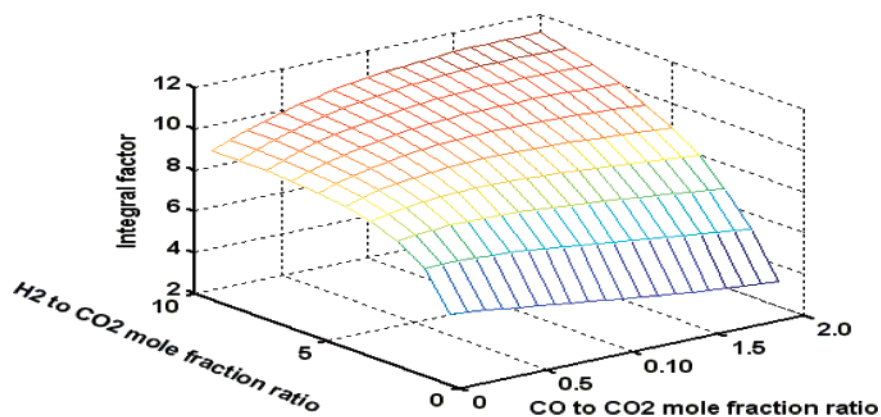


Figure 11. Unsteady optimization based on the presence of only CO, CO<sub>2</sub>, and H<sub>2</sub> in the feed.

latter is required in order to move the reaction mixture away from the equilibrium state and therefore to increase reactant conversion.

Figure 10 illustrates the hydrogen mole fraction variation with time. On the basis of the above arguments for days 0–100, eq 3 is the controlling step. After day 100, eq 1 is controlling, so hydrogen demand increases according to the stoichiometric coefficient of hydrogen in eq 1. After day 200, by the passage of time, the deactivation mechanism will be the dominant controlling mechanism and hydrogen demand decreases to compensate for this effect. Table 3 provides a comparison of MPR based on the proposed optimal method and a reference case. This reference case is MPR based on SPC operating conditions tabulated in Table 1. It is obvious from Table 3 that the simultaneous strategy provides better MPR. Comparing with the reference case, MPR increases by 1.4045% over 4 years and this is equivalent to a profit of about \$1 400 000 USD.

For more details on variations of other component mole fractions affected by our optimal control policy and singularity of control, see ref 27.

**5.3. Optimization of Inlet Components.** For this section, an ideal case was considered. Inlet syngas was assumed to contain only CO, CO<sub>2</sub>, and H<sub>2</sub>. The  $x_{\text{CO}}/x_{\text{CO}_2}$  and  $x_{\text{H}_2}/x_{\text{CO}_2}$  ratios were chosen as optimization variables. Figure 11 represents the results for this optimization. It was found that  $x_{\text{CO}} = 0.147\,29$ ,  $x_{\text{CO}_2} = 0.077\,52$ , and  $x_{\text{H}_2} = 0.775\,19$  to be the optimum inlet mole fractions during 4 years of reactor operation. It is interesting to note that the mole fraction of CO<sub>2</sub> has decreased compared to CO. This can be another proof for our previous result that the role of CO<sub>2</sub> in deactivation is important.<sup>17</sup> This case is an ideal case which can be implemented in a laboratory-scale setting. In an industrial-scale reactor, however, syngas has other components like methane, nitrogen, and water and their removal is not economical.

## 6. Conclusion

The optimization of an industrial methanol reactor in order to enhance its economical performance in both steady- and unsteady-state modes was considered in this paper. In the steady-state mode, the optimum values of  $T_{\text{shell}}$  and  $x_{\text{H}_2}$  as separate and simultaneous optimization variables have been found. In the dynamic mode, the optimum values of  $T_{\text{shell}}$  and  $x_{\text{H}_2}$  as separate and simultaneous optimization variables during 1200 days of operation have also been investigated. Furthermore, the optimization has also considered  $T_{\text{shell}}$  and also  $T_{\text{shell}}$  combined

with  $x_{\text{H}_2}$  at each 100 days of operation. As a final effort and in the dynamic mode of operation, the optimal feed mole fractions when the feed contains only CO, CO<sub>2</sub>, and H<sub>2</sub> have also been obtained. This optimization emphasized our previous finding that the CO<sub>2</sub> effect on catalyst deactivation is more important than that of CO.

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## Nomenclature

$A_c$  = cross area of each tube (m<sup>2</sup>)  
 $a_v$  = external particle surface area per unit of reactor volume (m<sup>2</sup>·m<sup>-3</sup>)  
 $a$  = activity of catalyst (–)  
 $a_0$  = initial activity of catalyst (–)  
 $c_{pg}$  = specific heat of the gas at constant pressure (J·mol<sup>-1</sup>)  
 $c_{ps}$  = specific heat of the solid at constant pressure (J·mol<sup>-1</sup>)  
 $c_t$  = total concentration (mol·m<sup>-3</sup>)  
 $D_i$  = tube inside diameter (m)  
 $E_{\text{act}}$  = activation energy used in the deactivation model (J·mol<sup>-1</sup>)  
 $F_t$  = total molar flow per tube (mol·s<sup>-1</sup>)  
 $f$  = function denotes process model  
 $H$  = Hamiltonian  
 $J$  = objective function (kg)  
 $K_{\text{act}}$  = deactivation model parameter constant (s<sup>-1</sup>)  
 $kg_i$  = mass transfer coefficient for component  $i$  (m·s<sup>-1</sup>)  
 $M_w$  = molecular weight (kg·kg·mol<sup>-1</sup>)  
 $R$  = universal gas constant (J·mol<sup>-1</sup>·K<sup>-1</sup>)  
 $r_i$  = reaction rate of component  $i$  (mol·kg<sup>-1</sup>·s<sup>-1</sup>)  
 $T$  = bulk gas-phase temperature (K)  
 $T^s$  = temperature of gas on the solid surface (K)  
 $T_{\text{shell}}$  = temperature of boiling water in the shell side (K)  
 $T_{\text{ref}}$  = reference temperature (K)  
 $t$  = time (s)  
 $t_f$  = final operating time (s)  
 $u(t)$  = vector of optimization variables  
 $U_{\text{shell}}$  = boiling water–gas overall heat transfer coefficient (W·m<sup>-2</sup>·K<sup>-1</sup>)  
 $x$  = states of the system  
 $y_i$  = bulk gas-phase mole fraction for component  $i$  (–)  
 $y_i^s$  = mole fraction of the  $i$ th component in the solid phase (–)  
 $z$  = axial reactor coordinate (m)

## Greek Letters

$\Delta H_{f,i}$  = formation enthalpy of component  $i$  (J·mol<sup>-1</sup>)  
 $\epsilon_B$  = void fraction of catalytic bed (m<sup>3</sup>·m<sup>-3</sup>)  
 $\epsilon_s$  = solid particle void fraction (m<sup>3</sup>·m<sup>-3</sup>)  
 $\rho_B$  = bed density (kg·m<sup>-3</sup>)  
 $\lambda$  = Lagrange multiplier

## Superscripts and Subscripts

0 = inlet or initial conditions

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