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OPTIMAL PARAMETERS OF THE α-METHYLSTYRENE OLIGOMERIZATION REACTION IN THE PRESENCE OF A ZEOLITE CATALYST

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ABSTRACT

Efficient methods and algorithms have been developed for the optimization of catalytic processes. In mathematical terms, these problems reduce to finding the extremum of a functional of a large number of variables whose domain of variation is subject to various constraints as sets of partial differential equations and algebraic inequalities. This implies solving problems in which the domain of extremals is closed. Applying Pontryagin's maximum principle to catalytic processes described by sets of differential equations with constrained phase and control variables allows the necessary set of optimal conditions to be found. A numerical algorithm has been developed for solving nonlinear boundary-value problems that arise when the maximum principle is employed. The efficiency of this algorithm is demonstrated by the example of the catalytic oligomerization of α-methylstyrene, a typical process requiring various kinds of optimization problems to be solved. The theoretical optimization of the process has served as the basis for the engineering optimization of an industrial reactor.

Key words: Modeling and simulation, Kinetic scheme, α-Methylstyrene oligomerization.

INTRODUCTION

The theoretical step of optimization will be considered for a kinetic model of α-methylstyrene oligomerization in the presence of a zeolite catalyst[1]. The products of this reaction (linear and cyclic dimers) have found application as plasticizers, polymer modifiers, rubber, reagents in the manufacture of synthetic oils, etc. Here, we introduce the following designations: x_1-α-methylstyrene; x_2-4-methyl-2,4-diphenylpentene-1 (α-dimer); x_3-4-methyl-2, 4-diphenylpentene-2 (β-dimer); x_4-1,1,3-trimethyl-3-phenylindan (cyclic dimer) and x_5-trimers. According to the law of mass action, the rate equations corresponding to the reaction network in α-methylstyrene oligomerization are written as –

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$$2x_1 \leftrightarrow x_2,\ 2x_1 \leftrightarrow x_3,\ 2x_1 \rightarrow x_4,\ x_2 \leftrightarrow x_3,\ x_2 \rightarrow x_4,\ x_3 \rightarrow x_4,\ x_1 + x_2 \rightarrow x_5,\ x_1 + x_3 \rightarrow x_5,\ x_1 + x_4 \rightarrow x_5$$

$$w_1 = k_1 x_1{}^2 - k_{10} x_2, w_2 = k_2 x_1{}^2 - k_{11} x_3, w_3 = k_3 x_1{}^2, w_4 = k_4 x_2 - k_{12} x_3, w_5 = k_5 x_2,$$
$$w_6 = k_6 x_3, w_7 = k_7 x_1 x_2, w_8 = k_8 x_1 x_3, w_9 = k_9 x_1 x_4$$

Here, w_j is the rate of the j-th step (m^3 (kg Cat)$^{-1}$ h^{-1}), j = 1–9; x_i is the mole fraction of the i-th component, i = 1–5; k_s is the rate constant of the s-th reaction (m^3 (kg Cat)$^{-1}$ h^{-1}), s = 1–12, which depends on temperature T according to the Arrhenius equation $k_s(T) = k_s^0 e^{-\frac{E_S}{RT}}$, in which $k^0{}_s$ is the preexponential factor and E_s is the activation energy of the s-th reaction (cal/mol); and R is the universal gas constant (cal mol^{-1} K^{-1}). When developing a mathematical model for a process, the variation of the number of moles N (reaction volume) during the reaction is taken into account. The material balance equations for α-methylstyrene oligomerization in the presence of zeolite are written as –

$$\frac{dx_i}{dt} = \frac{F_i - x_i F_n}{N},\ i = 1..5,\quad \frac{dN}{dt} = \frac{G_k}{V_p} \sum_{j=1}^{9} w_j \sum_{i=1}^{5} \nu_{ij},$$

where G_{Cat} is the catalyst weight, V_{r} is the reactor volume, and v_{ij} are stoichiometric coefficients. The initial (t = 0) conditions appear as $x_i = x_i^0,\ N = 1$.

The theoretical optimization of this catalytic process is viewed as the problem of finding the optimal reactor regime u minimizing (maximizing) the optimality criterion defined by the functional

$$I = \int_{t^{(0)}}^{t^{(k)}} \psi_0\,(\bar{x}, \bar{u})\,dt$$

Here, $\psi_0(\bar{x}, \bar{u})$ is the prescribed function of $\bar{x}$ (process state variables as functions of the independent variable t) and $\bar{u}$ (controls). Depending on the problem to be solved, the optimality criterion may take various forms, including the following: $t^{(k)} - t^{(0)} \rightarrow \min$ (for the operation speed problem); $x_2(t^{(k)}) + x_3(t^{(k)}) + x_4(t^{(k)}) \rightarrow \max$ (for the maximum product yield problem); $x_2(t^{(k)}) + x_3(t^{(k)}) - x_4(t^{(k)}) - x_5(t^{(k)}) \rightarrow \max$ (for maximizing the yield of desired products while minimizing the yield of by-products, which are cyclic dimmer and trimers); $\sum_{j=1}^{5} c_j x_j(\tau_k) \to \max$, where c_j is the estimated cost of the j-th reaction product (for the economic optimality problem). In the general case, it is possible that the initial ($t^{(0)}$) and final ($t^{(k)}$) values of t are not specified in the initial formulation of the optimization problem and their determination should be included in the solution procedure. The initial and final states of the process may be defined by an incomplete set of $x_i(t^{(0)})$ and $x_i(t^{(k)})$ values, or the final values of x_i may be subject to the constraint

$$\sum_{j=1}^{5} d_j x_j(\tau_k) = d_0$$

where d_j are positive or negative constant coefficients (some of them may be zero), τ_r stands for the reactor dimensions, and d_0 is the overall composition of the reaction mixture at the reactor outlet. This type of problem may arise when it is necessary to optimize a process at a fixed product yield or at a preset conversion of the starting reactant. The region of admissible controls may be defined as an aggregate of equalities or inequalities.

Let us consider the problem of optimizing the temperature regime $T(t)$ for α-methylstyrene oligomerization in order to maximize the product yield. Let the following constraint be imposed on the optimal temperature: $T_1 \le T \le T_2$. No initial assumptions are made as to reactor dimensions, and the specific features differentiating the cases of specified and unknown τ_r values will be discussed while presenting the solution.

EXPERIMENTAL

This problem will be solved using Pontryagin's maximum principle[2]. An advantage of this mathematical tool is that it allows solutions in the form of dis continuous functions. The set of constraints involved in the maximum principle is always closed; that is, the number of equations is always equal to the number of variables. It is clear from physical considerations that an optimal regime does exist; therefore, the single equation derived from the constraints of the maximum principle will be optimum. According to the maximum principle, the optimum temperature in each cross section of the reactor is derived from the maximum condition for the function

$$H(\bar{x}, T, \bar{\lambda}) = \sum_{i=1}^{5} \lambda_i \frac{F_i - x_i F_n}{x_6} + \lambda_6 \frac{G_{Cat}}{V_r} \sum_{j=1}^{9} w_j \sum_{i=1}^{5} \nu_{ij},$$

where $x_6 = N$ .Here, the $\lambda_i(t)$ functions satisfy the following set of conjugate equations: $\frac{d\lambda_i}{dt} = -\frac{\partial H}{\partial x_i}$, $i = 1..6$. The following boundary conditions at $t^{(k)}$ are derived from the transversality condition for the $\lambda_i(t)$ functions:

$$\lambda_1(t^{(k)}) = 0,\ \lambda_2(t^{(k)}) = 1,\ \lambda_3(t^{(k)}) = 1,\ \lambda_4(t^{(k)}) = -1,\ \lambda_5(t^{(k)}) = -1,\ \lambda_6(t^{(k)}) = 0$$

The algorithm for solving the problem is as follows. In the first step, all unknown functions are assigned some values. The missing values of variables are set in a somewhat random manner and are then refined based on the specified values of the $x_i(t)$ and $\lambda_i(t)$ functions at the end of the trajectory. In the second step, it is possible to determine the optimal control corresponding to the initial value of the independent variable t:

$$H(\lambda_i(t^{(0)}), x_i(t^{(0)}), T_{\text{опт}}(t^{(0)})) = \max_{T} H(\lambda_i(t^{(0)}), x_i(t^{(0)}), T)$$

If there are no constraints imposed on the control variable, the determination of optimal control can be carried out by any unconstrained minimization method. Once the optimal control at the initial time point $T_{\text{опт}}(t^{(0)})$, is determined, it is possible to make a step forward by setting $t = t^{(0)} + \Delta t$ and, using any numerical method for the integration of sets of differential equations, determining $x_i(t)$ and $\lambda_i(t)$. During numerical integration, it is necessary to see, how close the resulting trajectory is to the specified final point ? If the final point of intergration is preset, this can be done using the relationship $r = \sum_{i=1}^{5} \left[x_i(\tau_k) - x_i^{(k)}\right]^2 \to \min$, if $t^{(k)}$ is not preset, $r = \min_{t} \sum_{i=1}^{5} \left[x_i(t) - x_i^{(k)}\right]^2$. In both cases, the value of r shows, how good the initial approximations $\lambda_i(t^{(0)})$ are ? The quantity r is viewed as a function of $\lambda_i(t^{(0)})$ ($i = 1, ..., 6$). It should be minimized by choosing an appropriate set of $\lambda_i(t^{(0)})$. In other words, it is necessary to solve the minimization problem $\min_{\lambda(t^0)} r(\boldsymbol{\lambda}(t^{(0)})) = 0$.

RESULTS AND DISCUSSION

Based on available experimental data, the mathematical description of α-methylstyrene oligomerization, and the above algorithm, we developed software for solving the theoretical optimization problem in terms of criterion 3 with the initial data $x_1^0 = 1,\ x_2^0 = 0,\ x_3^0 = 0,\ x_4^0 = 0,\ x_5^0 = 0$. The constraint $30^oC \le T \le 130^oC$ was imposed on temperature. The zeolite content was 10%, and the duration of the reaction was 2 hr.

Consider the resulting time dependences of the optimal temperature and product concentrations corresponding to the optimal temperature regime. The optimal temperature is a sectionally continuous function consisting of three sections: in the first, the temperature grows from 86°C to the maximum; in the second and third, the temperature is constant and has the maximum and minimum values, respectively. For this temperature regime, the criterion chosen takes its maximum value and the dimer concentrations vary with time. The α isomer forms first. Its concentration reaches a maximum in a rather short time depending on the reaction temperature and then gradually decreases. The concentration of the β isomer increases much more slowly and reaches its maximum at the point at which the optimal control switches from one isothermal section to the other.

Thus, we have demonstrated the way of optimizing catalytic processes in terms of the generalized Pontryagin's maximum principle. A numerical algorithm has been developed for solving nonlinear boundary-value problems that arise when Pontryagin's principle is employed. The efficiency of this algorithm is demonstrated by the example of the catalytic oligomerization of α-methylstyrene, a typical process involving various kinds of optimization problems. The theoretical optimization of the process has served as the basis for the engineering optimization of an industrial reactor. Optimal controls were determined in both the theoretical and engineering optimization steps.

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