

Optimization of the fixed-bed reactor for ethylene epoxidation

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Received 15 April 2004; received in revised form 18 February 2005; accepted 9 March 2005

Available online 12 May 2005

Abstract

A number of variables are involved in the optimization of the fixed-bed reactor for ethylene epoxidation. In this article, optimal feed composition, feeding rate and operation pressure, which have only slight influences on the bed temperature, are determined by steady-state optimization, and the optimal performance are shown to be restricted by explosive limit, the capacity of down-stream decarbonater and the specification of circulation compressor. Conversely, the amount of EDC addition and coolant temperature, which are sensitive to the bed temperature for a constant productivity and thus have a large effect on catalyst sintering, are determined by dynamic optimization as functions of catalyst age. The optimal performance obtained by the dynamic optimization policy with time-dependent inlet EDC concentration is found to be very close to that of the constant EDC addition policy. Because of the opposite effects of EDC addition and coolant temperature increase, the optimal performance is not sensitive to the catalyst stability to temperature. In addition, the optimal EDC concentration level is found independent of the productivity rate.

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Keywords: Fixed-bed reactor; Ethylene epoxidation; Catalyst deactivation

1. Introduction

Ethylene epoxidation in fixed-bed reactors is currently the largest hydrocarbon partial oxidation process in industry and as a consequence has for a long time been the focus of fundamental and application-oriented research. Probing the mechanism of the reaction on silver catalysts was, and still is, the mainstream of research for the purposes of developing more efficient silver catalysts [1–3] and more reliable reaction kinetics [4–6]. As an exemplary process, ethylene epoxidation has also been served as the reaction system for modeling studies and non-linear behavior analysis [7,8]. Besides, it has been frequently the object of process intensification [9,10]. Due to its great importance in industry and large scale of production, process optimization of ethylene epoxidation is undoubtedly another important research topic. However, papers contributed to this topic are very scarce. Baratti et al. [11] proposed a strategy to maximize the reactor performance by

optimizing the catalyst distribution in the pellets or in the reactor, without consideration of the operating condition on the optimization performance. The only article [12] closely related to process optimization of ethylene epoxidation was only descriptive and more concerning the significance of optimization of this process, rather than a practicable optimization strategy.

Optimization of ethylene epoxidation is a non-trivial task because the performance of the reactor is related to a number of factors, including operation variables and catalyst performance, the physicochemical interactions among which are complicated and difficult to quantify. Apart from five main components, i.e., ethylene (ET), oxygen (O₂) ethylene oxide (EO), carbon dioxide (CO₂) and water (H₂O), an inert gas (currently methane) is also involved as the balance or ballast gas [13], which is mingled with other components, e.g., ethane, argon, etc., that have effects on the catalytic reaction by competitive adsorption or by changing the explosive limit of the gas mixtures. Chlorine is found, according to a mechanism not well understood, to selectively inhibit deep oxidation [14] and is used universally as an effective means

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to regulate the balance between productivity and feed consumption. The most complicating factor in optimizing this process is catalyst decay [15], which is a consequence of physical and chemical changes on catalyst surface and leads to a continuous decreasing reactor performance.

Because there are so many factors to be considered in optimization, a model which relates the performance of the reactor to the input variables is required, on the basis of which the input variables can be optimized to maximize an economic index. Currently, a widely accepted kinetics for ethylene epoxidation does not exist and one has to establish or find from the literature a reasonable kinetics for the catalyst of his own interests. Selecting a proper reactor model with sufficient accuracy and reasonable intricacy from the model library also requires deep investigation into the underlying reaction/transport processes.

In this article, problems involved in ethylene epoxidation optimization are discussed and analyzed. Steady-state and dynamic optimization approaches are presented and evaluated. In steady-state optimization, the optimal condition lies in the operation boundary (prescribed by the explosive envelope, the decarbonater capacity and the circulation compressor specification); while in dynamic optimization, the optimal ethylene dichloride (EDC) concentration level is determined mainly by the sensitivity of sintering to temperature, and is independent of productivity. Due to the opposite effects of EDC addition and coolant temperature increase, the optimal performance is not sensitive to the thermal stability of the catalyst.

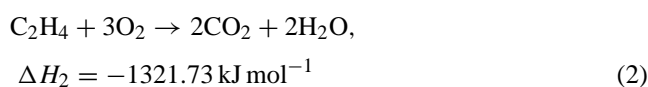
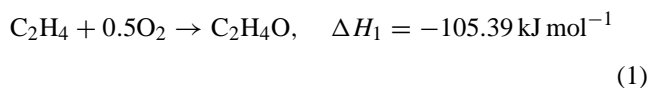
2. Reaction kinetics

Though a number of investigations have been devoted to the reaction kinetics and different kinetics have been reported in literature [4–6,16,17], there is not any reaction kinetics receiving general acceptance. Several reasons account for this. First, the catalysts used in kinetic study were different, some prepared in the laboratory by the researchers and others provided by different vendors. Second, some of the kinetic studies were based on fine catalysts particles (for the intrinsic kinetics free from pore diffusion), while others used directly industrial catalyst pellets with a specific form and size, and the kinetics reflected not only the surface reactions but also pore diffusion. Third, the reactors, e.g., Berty reactor and tubular reactor, for kinetic investigation were different, resulting in a different concentration level for the reaction [18]. Fourth, the range of experiment conditions was quite different. Most of the investigations were under normal pressure, while others covered the range of operating conditions for industrial use. However, the most important reason is that as for most other heterogeneous reactions, the real reaction mechanism is very complicated and has to be simplified to a large extent to make the kinetic parameter estimation feasible. In this sense, all the kinetics formulations (except those obtained from first principle calculations [19], i.e., microkinetics) that

have been reported in the literature were empirical and the final form and kinetic parameters were determined by data fitting.

Dependence of reaction rate on the kinetic parameters is highly non-linear, and there exists several local minima in the parametric space. In fitting of the kinetic data, the optimization algorithm may frequently stop at a local minimum; and different kinetic formulations may produce very similar fitting results. As a result, the finally emerged kinetic formulations are to a large extent related to the skills and patience used in parameter estimation and by the favor of the researcher.

Since experience plays an important role in formulating the kinetic equations, their specific mathematical form is not important, as long as it represents, the more the better, most of the important phenomena and trends observed in experiments. In this article, the reactions are considered in parallel,



and deep oxidation of EO is not considered in the reaction network. The corresponding kinetic equations are [17]:

$$r_{\text{EO}}^0 = \frac{k_1 \exp(-E_1/RT) P_{\text{ET}} P_{\text{O}_2}}{1 + K_1 \exp(\Delta H_1/RT) P_{\text{CO}_2} + K_2 \exp(\Delta H_2/RT) P_{\text{O}_2}^{0.5} P_{\text{H}_2\text{O}}}, \quad (3)$$

$$r_{\text{CO}_2}^0 = \frac{k_2 \exp(-E_2/RT) P_{\text{ET}} P_{\text{O}_2}^{0.75}}{1 + K_1 \exp(\Delta H_1/RT) P_{\text{CO}_2} + K_2 \exp(\Delta H_2/RT) P_{\text{O}_2}^{0.5} P_{\text{H}_2\text{O}}}, \quad (4)$$

These kinetic expressions are simple but reflect the facts of inhibition of CO_2 and H_2O on both epoxidation and combustion [16,20].

3. EDC inhibition

In industry, very small quantity of ethylene dichloride or monichlorethane is added to the feed to decrease the overall reaction rate but enhance the selectivity toward ethylene oxide formation. The presence of Cl decreases both the rate of oxygen adsorption and the total oxygen uptake [2]. However, it promotes silver surface roughening, leads to enhanced subsurface oxygen and thereby increases selectivity [14].

Since the mechanism of EDC inhibition is not quite clear, only empirical expressions [17,21] are available to account for the influence of EDC addition on the reaction rate. Here, in this article EDC inhibition is considered in the rate equations by dividing a term, which is linearly dependent on the EDC

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