

Catalysis, Kinetics and Reaction Engineering

Evaluation of an improved epichlorohydrin synthesis from dichloropropanol using a microchemical system[☆]

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ABSTRACT

Synthesizing epichlorohydrin (ECH) from dichloropropanol (DCP) is a complicated reaction due to the partial decomposition of ECH under harsh conditions. A microchemical system can provide a feasible platform for improving this process by conducting a separation once full conversion has been achieved. In this work, referring to a common DCP feed used in industry, the reaction performance of mixed DCP isomers with NaOH in the microchemical system on various time scales was investigated. The operating window for achieving high conversion and selectivity was on a time scale of seconds, while the side reactions normally occurred on a time scale of minutes. Plenty of Cl⁻ ions together with a high temperature were proved to be critical factors for ECH hydrolysis. A kinetic study of alkaline mediated ECH hydrolysis was performed and the requirements for an improved ECH synthesis were proposed by combining quantitative analysis using a simplified reaction model with experimental results on the time scale of minutes. Compared with the conventional distillation process, this new strategy for ECH synthesis exploited microchemical system and decoupled the reaction and separation with potentials of higher productivity and better reliability in scaling up.

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1. Introduction

Epichlorohydrin (ECH) is an important intermediate in the production of epoxide resins, chlorohydrin rubbers and other organic products [1–3]. There have been several industrial manufacturing processes to produce ECH such as propylene chlorination and glycerol chlorination [4–7]. One of the most common routes for the synthesis of ECH is through the elimination of hydrogen chloride from dichloropropanol (DCP). Fig. 1 illustrates this process, in which the desired ring closure is generally followed with hydrolysis as the major side reaction [8]. The immediate removal of ECH is necessary for limiting further hydrolysis.

Dichloropropanol has two isomers: 1,3-dichloro-2-propanol (1,3-DCP) and 2,3-dichloro-1-propanol (2,3-DCP). A 1:2 ratio is normally obtained from the chlorohydrination of allyl chloride. Due to inductive effects and steric hindrance, the reaction rate of the elimination of hydrogen chloride from 1,3-DCP was reported to be 20 times faster than that from 2,3-DCP [8,9]. Industrial ECH synthesis aims to convert 2,3-DCP sufficiently while avoiding subsequent hydrolysis. In this regard, the reactive distillation column is conventionally used for ECH synthesis, in which ECH can be stripped with steam once being produced. Carrá *et al.* [8,9] determined the reaction kinetics for a complete description of ECH production process using lime milk as alkaline and provided

a model for simulating a multistage unit coupling reaction with distillation. Ma *et al.* [10] investigated the apparent kinetics of ring closure and hydrolysis using sodium hydroxide solution as alkaline. They indicated that raising the temperature favored the desired reaction pathway if the residence time of ECH was sufficiently short. All of the analyses or simulations in these studies were based on the assumptions of ideal feed mixing and flow as well as instantaneous ECH separation. However, actual reaction output in production was frequently different from the expected results for several reasons. First, the apparent kinetic parameters determined in a conventional reactor are usually case-dependent (Ma *et al.* [9] even obtained two different kinetic equations according to different temperature ranges). Second, in a cascade reactive distillation column, it is impossible to realize exact idealities in mixing, two-phase counter-flow or instantaneous phase equilibrium [11–13]. Thus, it is still a challenge to control and enhance DCP conversion effectively.

In recent years, microreactors have shown numerous advantages over traditional reactors, such as enhanced mixing and mass transport, controlled hydrodynamic flow and good inherent safety [14–16]. They have been used as effective tools for intensifying fast reactions dependent on careful controls. Examples included rapid precipitation for nanoparticle preparation [17,18], and fast and strongly exothermic reactions for chemical intermediates synthesis [19–21]. Microreactors have the potential to carry out an improved ECH synthesis.

In our previous work, the kinetic parameters of dehydrochlorination of 1,2-DCP were determined in a microchemical system consisting of a micromixer, a delay loop and a microneutralizer [22]. However, an industrial case using microchemical system as the core unit may need

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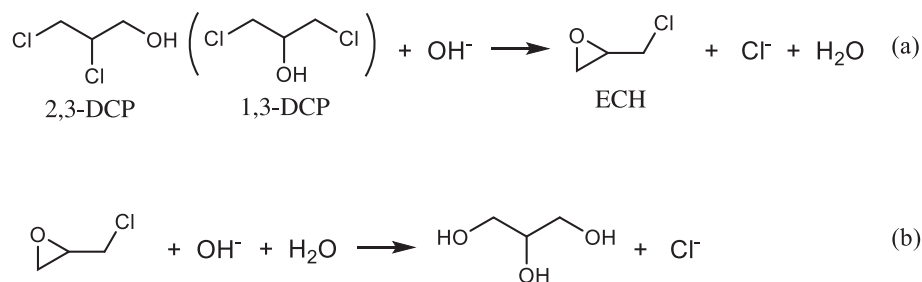


Fig. 1. Synthesis of ECH. (a) Desired reaction; (b) a typical following side reaction.

more considerations and evaluations because the starting material is a mixture of DCP isomers and the ECH product must eventually be separated from reaction system instead of inhibiting the hydrolysis temporarily. In this work, the reaction performance of mixed DCP (1,3-DCP/2,3-DCP: 1/2) aqueous solution with sodium hydroxide solution in the microchemical system on various time scales was investigated and the kinetic characteristics of varieties of side reactions were explored to propose proper reaction conditions and to schedule the integration of reaction and separation for ECH synthesis enhancement. Compared with the traditional reactive distillation process, this new strategy for ECH synthesis exploited microchemical system and decoupled the reaction and separation, therefore, higher productivity and better reliability in scaling up were worth expectation.

2. Experimental

2.1. Reagents

1,3-Dichloro-2-propanol (1,3-DCP, 99% in mass) and 2,3-dichloro-1-propanol (2,3-DCP, 97% in mass) were purchased from J&K Scientific Ltd. (Beijing). Sodium dihydrogen phosphate dihydrate (99.5% in mass), disodium hydrogen phosphate anhydrous (99.0% in mass), sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from Beijing Chemical Works. Epichlorohydrin (ECH, 99.5% in mass) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. All the reagents were of analytical grade and used directly without further purification. Deionized water was used throughout the experiments.

2.2. Experimental setup

The microchemical setup, as shown in Fig. 2, can be found elsewhere [22,23]. Briefly, DCP solution (Feed 1) and NaOH solution (Feed 2) were delivered by two metering pumps (LB-80, Beijing Satellite Co. Ltd.) into the feeding tubes, respectively. The two solutions were preheated to the reaction temperature and then mixed in Microreactor 1 to start the reaction. The preheating zone, Microreactor 1 and most of the delay loop were placed in Thermostat 1 (SC-15, Ningbo Xinzhi) to guarantee a thermostatic reaction process. At the end of the delay loop, the process was extended to a low-temperature thermostat (Thermostat 2, SC-15, Ningbo

Xinzhi), in which phosphate buffer solution (pH = 7.0) delivered by another metering pump was introduced into the reaction system through Microreactor 2. Due to the sudden decrease of temperature and concentration of hydroxyl ions, all the reactions were assumed to be quenched during the sample processing and analysis. In this microchemical system, the nominal reaction time was dependent on the length of the delay loop.

2.3. Analysis

The sample collected from the outlet of Microreactor 2 was diluted with ethanol, and then 0.5 μl of sample was injected into a gas chromatograph (Shimadzu GC-2014). The GC analysis used AB-InoWax (30 m \times 0.25 mm \times 0.25 μm) for the column and polyethylene glycol for the stationary phase. The GC conditions included: carrier gas, N_2 ; injection temperature, 220 $^\circ\text{C}$; column temperature, 70 $^\circ\text{C}$ to 200 $^\circ\text{C}$ (30 $^\circ\text{C}\cdot\text{min}^{-1}$); and detector, flame ionization detector (FID) at 280 $^\circ\text{C}$. The quantitative analysis by GC was based on the internal standard method. 1-Octanol was used as the internal standard. The dichloropropanol conversion (X) and selectivity (S) are calculated with the following equations.

$$X = 1 - \frac{W_{\text{DCP}} \times M_{\text{pro}}}{F_{\text{DCP}}} \quad (1)$$

$$S = \frac{W_{\text{ECH}} \times M_{\text{pro}}}{F_{\text{DCP}} - W_{\text{DCP}} \times M_{\text{pro}}} \quad (2)$$

where W_{DCP} and W_{ECH} are the mass fraction of DCP and ECH in the sample, respectively. M_{pro} (g) is the sampling mass, and F_{DCP} (g) the feeding mass of DCP during sampling. The determination errors of W_{DCP} and W_{ECH} were about 0.5% and 2.4%, respectively.

3. Results and Discussion

3.1. Reaction performance on the time scale of seconds

A microchemical system can provide a resolution of residence time in the sub-second range. For a reaction which nears completion within seconds, this is quite a valuable characteristic for process control. Our previous research showed that the dehydrochlorination of 2,3-DCP,

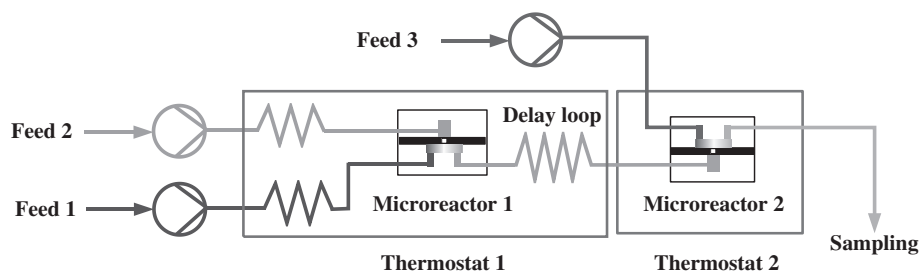


Fig. 2. Schematic of the microchemical system for ECH synthesis.

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