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Advanced millireactor technology for the kinetic investigation of very rapid reactions: Dehydrochlorination of 1,3-dichloro-2-propanol to epichlorohydrin

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HIGHLIGHTS

- Use of millireactor technology in the study of the kinetics of fast reactions.
- Proper sampling procedure for rapid dehydrochlorination reaction.
- αγ-DCP dehydrochlorination over wide range of temperature and concentrations.
- Estimation of reliable kinetic parameters for rapid dehydrochlorination reaction.

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ABSTRACT

Epichlorohydrin is an important chemical intermediate, which can be obtained by valorisation of glycerol, an inexpensive raw material obtained as a stoichiometric co-product from biodiesel production. A continuous milliscale tubular reactor was developed to conduct the synthesis of epichlorohydrin and to measure the very rapid reaction kinetics. 1,3-dichloro-2-propanol (αγ-DCP) was dehydrochlorinated with sodium hydroxide at 30–70 °C. The residence times in the millireactor system were less than 25 s. The kinetic data were interpreted with a plug flow model and a rate equation based on a plausible reaction mechanism. The model – the rate equation and the plug flow concept – gave a perfect description of the experimental data.

1. Introduction

In recent years, increasing attention has been paid on the use of biomass-derived raw materials for the production of fuels and chemicals (Naik et al., 2010; Tuck et al., 2012). Following this trend, glycerol has emerged as a potential platform molecule for the production of several value-added chemicals, such as light olefins, epichlorohydrin, acrolein, glycerol ethers and glycerol carbonate, 1,3-propanediol, propylene glycol, glycidol and hydrogen (Tuck et al., 2012; Pagliaro et al., 2007; Zakaria et al., 2012; Katryniok et al., 2009; Gu et al., 2008; Teng et al., 2014; Adhikari et al., 2009; Markočič et al., 2013; Rabello et al., 2013). Glycerol is a stoichiometric by-product of the biodiesel production via transesterification reaction (Leung et al., 2010); in fact, it constitutes ca. 10 wt% of the crude biodiesel produced.

Epichlorohydrin is a valuable chemical used in the production of epoxy resins and plasticizers (Bell et al., 2008; Santacesaria et al., 2010; Santacesaria et al., 2013) and it can be obtained from glycerol originating from biofuel production instead of fossil raw materials. The Asian-Pacific market for bio-based epichlorohydrin has increased significantly during recent years, reflecting in the start-up of plants by Solvay and Dow Chemicals in China and Thailand (Tuck et al., 2012; Santacesaria et al., 2013). The first step in the production of bio-based epichlorohydrin involves the hydrochlorination of glycerol in the presence of a weak organic acid as a homogeneous catalyst (de Araujo Filho et al., 2014). Typical catalysts are acetic acid, propionic acid, malonic acid and adipic acid. The reaction scheme of glycerol hydrochlorination gives 3-chloro-1,2-propanediol (α-MCP) and 2-chloro-1,3-propanediol (β-MCP) as primary products and 1,3-dichloro-2-propanol (αγ-DCP) and 1,2-dichloro-3-propanol (αβ-DCP) as secondary

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Notation

α-MCP	3-chloro-1,2-propanediol
β-MCP	2-chloro-1,3-propanediol
αβ-DCP	1,2-dichloro-3-propanol
αγ-DCP, αγ	1,3-dichloro-2-propanol
c	concentration [mmol/L] or [mol/m^3]
D	internal diameter [mm]
Ea	activation energy [kJ/mol]
epy	epichlorohydrin, chloromethyloxirane
k	rate constant [L/mmol/s] or [m^3/mol/s]
L	length of the tube [m]
Q	objective function [mmol^2/L^2] or [mol^2/m^6]
R	degree of explanation [%]
R	ideal gas constant [J/mol/K]
r	reaction rate [mmol/L/s] or [mol/m^3/s]
τ	residence time [s]
T	temperature [K]
V	volume [mL]
$\dot{V}$	volumetric flow rate mL/s

products. Typically, α-MCP and αγ-DCP are very dominant among the products. Both αγ-DCP and αβ-DCP can be transformed to epichlorohydrin by dehydrochlorination in the presence of alkali.

Krzyżanowska and Milchert (2013) and Krzyżanowska et al. (2013) present an interesting analysis of the dehydrochlorination of αγ-DCP using calcium hydroxide in a reaction-stripping column. An extensive discussion is provided in which the influence of several reaction parameters are analysed. Furthermore, the work presents the most complete analysis of the side reactions that might occur in the dehydrochlorination system. Nevertheless, no kinetic model was proposed by the authors (Gu et al., 2008; Krzyżanowska et al., 2013).

Carrà et al. (1979) wrote the first report of a kinetic investigation of the dehydrochlorination reaction using dichlorohydrins. Batch reactor experiments were carried out, investigating the kinetics of both αγ-DCP and αβ-DCP, separately. Calcium hydroxide was used as reactant. This work was very important because it brought the first quantitative explanation for why αβ-DCP was less reactive than αγ-DCP in the dehydrochlorination process. Nevertheless, the use of calcium hydroxide in large scale is discouraged due to its ability to form complexes and promote encrustation of equipment and pipelines.

Ma et al. (2007) is the only source in the open literature that provides kinetic data for the dehydrochlorination of αγ-DCP using sodium hydroxide. However, the data presented in Ma et al. (2007) is of questionable reliability, because it presents two very distinct activation energies (41 kJ/mol and 123 kJ/mol) for the hydrochlorination reaction within the relatively narrow temperature range of 20–60 °C. Surprisingly, no discussion was provided for explaining this double dependence on the activation energy in such narrow temperature range.

Zhang et al. (2012) investigated the kinetics of dehydrochlorination of αβ-DCP using sodium hydroxide in a microreactor. The work presents an excellent discussion about the dehydrochlorination mechanism; however, the kinetic model proposed was based on empirical observations rather than on a proposed reaction mechanism. The experimental approach presented for the hydrochlorination system in Zhang et al. (2012) is the most adequate one published in the literature so far and the activation energy estimated show a good identifiability.

The limited literature sources available on the dehydrochlorination kinetics of dichlorohydrins have often worked under conditions favouring side reactions (Carrà et al., 1979; Ma et al., 2007). In addition, classic batch reactors have been used in these investigations, even though the reaction is reported to be completed in tens of seconds; that may promote the formation of temperature and concentration gradients inside the reactor, affecting the local reaction rate. Therefore, the use of a micro/millireactor is suggested for studying this reaction. Furthermore, the production of dichlorohydrins from glycerol yields a mixture with high contents of αγ-DCP and almost none αβ-DCP, therefore, the literature lacks reliable kinetic parameters for αγ-DCP dehydrochlorination with sodium hydroxide.

The present study aims to determine the kinetics of αγ-DCP dehydrochlorination using sodium hydroxide in a continuous millireactor constructed by our research group. In order to suppress the occurrence of side reactions, diluted solutions of the reactants were used. Experiments were conducted at different temperatures (30, 40, 50, 60 and 70 °C) and different reactants ratio (1:1, 1:3 and 3:1). A reaction mechanism proposed in literature is assumed and the kinetic equations are derived based on it. A plug flow model is used for the reactor mass balance. Numerical regression of the experimental data showed an excellent fit of the model with the obtained experimental results. Reliable kinetic constants were estimated and the millireactor apparatus developed by our research group was proven suitable for the study of liquid phase fast reactions.

2. Materials and methods

2.1. *Experimental apparatus*

The millireactor consisted of four stainless steel tubes of different internal diameters (0.5, 0.7, 1.0 and 1.7 mm) connected in series. Each tube had a length of 1 m. At the very beginning of the reaction zone and at the intersection of each tube, sampling valves were placed, allowing sampling at different residence times. The total volume estimated for the reaction zone was 3.693 cm^3. Before the first sampling valve, the reactants travelled through separate 1-m long pre-heating tubes before being mixed in the static mixer. Between the static mixer and the first sampling valve, a small pipeline was placed in which reaction already took place. For this reason, the first sampling valve is assumed to represent “time zero” and the product (epichlorohydrin) is already present at that point, for the reaction is very fast. The pre-heating and reaction zones were immersed in a water bath of ca. 45 l. Three temperature probes were placed along the reactor to assure isothermal conditions. HPLC pumps provided a precise flow of the liquids. The reaction apparatus is depicted in Fig. 1.

2.2. *Analytical methods and sampling procedure*

The concentrations of αγ-DCP and epichlorohydrin were analysed by using a gas chromatograph (Agilent Technologies 6890 N) equipped with a capillary column (JW Scientific DB-WAX, 30 m × 0.250 mm × 0.25 μm) and a flame ionization detector (FID). Helium was used as a carrier gas. The samples were diluted with methanol at a ratio of 1:4 and the injection volume was 1 μl. The initial temperature of the column was 55 °C and it was kept for 2 min, after which it was increased to 160 °C at a rate of 15 °C/min and held for 3 min, then the temperature was increased to 240 °C at a rate of 25 °C/min and held at this temperature for 6 min. The injector temperature was 250 °C while the detector temperature was 280 °C.