

Preliminary Design of Semi-Batch Reactor for Synthesis 1,3-Dichloro-2-Propanol Using Aspen Plus

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Abstract

Glycerin is a key byproduct from the biodiesel production process. Due to the rapid growth in biodiesel production, the market has been flooded with the crude natural glycerin. This crude glycerin (glycerol) has a very low value because of its impurities, and consequently, a great interest has emerged in the development of technology for alternative uses of glycerol. Among the various possibilities, a technology to convert glycerol to 1,3-dichloro-2-propanol has caught our attention. This compound can be subsequently converted into epichlorohydrin, which is an important intermediate in the production of epoxy resins. 1,3-dichloro-2-propanol is currently being synthesized from propylene via allyl chloride route. However, our technology uses crude natural glycerin, the byproduct of biodiesel production plant, as the starting material and hydrochloric acid as the reagent. The present paper discusses the simulation work on the semi-batch reactor for the production of 1,3-dichloro-2-propanol using ASPEN PLUS. The simulation results were then compared with the experimental data.

Keywords: Aspen plus, Dichloropropanol, Epichlorohydrin, Semi-batch, Design

1. Introduction

Biodiesel as an alternative, environmentally friendly, and renewable energy has been produced on a large scale. However one of the main problems in the production of biodiesel is the formation of significantly amount of glycerol (10 wt%) as a by-product (McCoy, 2006; Zheng, Chen, & Shen, 2008). This has resulted in the over supply of glycerol in the industrial market and decrease the commercial value of glycerol. This scenario has attracted attention from many researchers to develop alternative routes to utilize crude glycerol in the production of useful intermediates or final products. One of the promising methods to convert glycerol to high-value chemicals is the chlorination reaction for preparing 1,3-dichloro-2-propanol or α,γ -Dichlorohydrin (α,γ -DCH), which is the an important intermediate in the process for synthesizing epichlorohydrin (Krafft, Gilbeau, Balthasart, & Paganin, 2008; Kubicek, 2005; Ma, Zhu, Yuan, & Yue, 2007; Siano et al., 2006; Tesser, Santacesaria, Di Serio, Di Nuzzi, & Fiandra, 2007). Since this compound is highly toxic, harmful if inhaled, and reported as causing cancer, this compound must be handled with care (Giri, 1997).

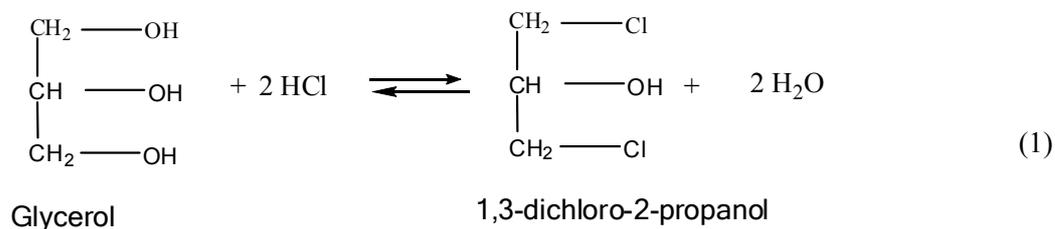
Tesser et al had carried out chlorination reactions experimentally for preparing α,γ -DCH from glycerol and gaseous hydrochloric acid. Their experiment focused on the determination of the reaction kinetics. The reaction was performed in the presence of malonic acid, as a catalyst, and the temperature range was set at 80-120°C. The HCL flow rate, glycerol loaded, and catalyst concentration were kept constant at 24 g/min, 200 g, and 8% (mol/mol) respectively. Based on the literature, the HCL flow rate and catalyst concentration have marked effects on the reaction selectivity of the chlorination reaction but the extent of the effect has not been reported (F.Kastanek, J.Zahradnik, J.Kratochvil, & J.Cermak., 1993). Therefore, investigating the effect of HCL flow rate and catalyst concentration on the preparation of α,γ -DCH would become the initial step taken in this study.

Consequently, the aim of this paper is to present the simulation results obtained from Aspen Plus simulator software carried out on the semi-batch stirred tank reactor by considering the effects of both HCL flow rate and catalyst concentration on reaction selectivity and yield for α,γ -DCH. The reactor block utilized in the simulation was RBatch which is suitable for a semi-batch reactor process (AspenTech., 1999)

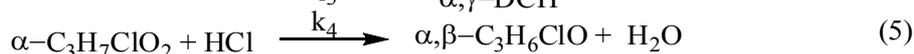
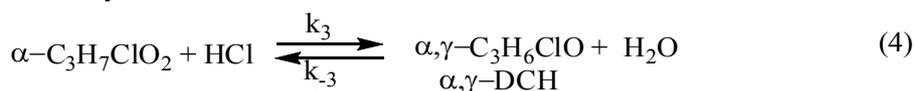
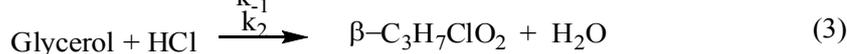
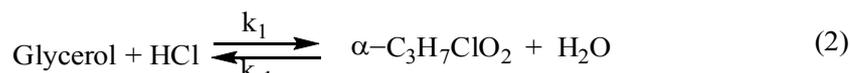
2. Modeling Approach

2.1. Chemical Reactions and Kinetic Parameters

Tesser et al. (2007) have reported that the overall reaction scheme for preparing α,γ -DCH, starting from glycerol and hydrochloric acid, is as follows:



This reaction starts with the chlorination of the glycerol, which mostly forms α -monochlorohydrin (α -MCH) and water, with small quantity of β -monochlorohydrin (β -MCH), followed by a second chlorination from which the required product, α,γ -DCH was mainly obtained and very small amounts of α,β -DCH. Relation 1 can be broken down into four distinct reactions, which are as follows:



The kinetic parameters of the reactions are shown in Table 1 (Tesser,2007).

2.2 Aspen plus Simulation

Table 2 shows the reactor characteristic and feed materials used in the Aspen Plus simulation.

In this work, both parameters HCL flow rate and catalyst concentration (% by moles of glycerol loaded into the reactor), were varied as presented in Table 2. The simulation analyzed the effects of the parameters mentioned above on selectivity and yield of reaction. The following equations were used for selectivity and yield calculation (Felder & W, 2004):

$$\text{selectivity for } \alpha,\gamma\text{-DCH} = \frac{\text{moles of } \alpha,\gamma\text{-DCH produced}}{\text{total moles of } \alpha\text{-MCH, } \beta\text{-MCH, and } \alpha,\beta\text{-DCH produced}}$$

$$\text{Yield for } \alpha,\gamma\text{-DCH} = \frac{\text{moles of } \alpha,\gamma\text{-DCH produced}}{\text{moles of glycerol fed}}$$

3. Simulation Result and Model Validation

3.1 Model Validation

In order to validate the proposed model, experimental data from glycerol chlorination in a lab-scale semi-batch stirred tank reactor reported by Tesser et.al (2007) was used to validate the simulation. Tables 1 and 2 show the kinetic parameters and reactor characteristics used in the simulation. The simulation results in terms of reaction selectivity and glycerol conversion are compared with the experimental data. The results are shown below.

<Figure 1-Figure 3>

Figures 1 and 2 show the simulation results as compared to the experimental data for glycerol conversion and reaction selectivity at five different temperatures in the range of 80 – 120°C. Simulation results and experimental data for products composition versus time of the reaction is shown in Figure 3. These figures show that there is a strong agreement between Aspen Plus simulation results and experimental data. Thus, we can conclude that the

Aspen Plus simulation can indeed be used in our study to guide us in the analysis of the performance of the chlorination reaction using the crude glycerol.

<Figure 4>

Furthermore, several simulation runs had also been carried out in order to investigate effect of HCL flow rate and catalyst concentration on selectivity and yield for α,γ -DCH preparation. Selectivity and yield of α,γ -DCH decreased over the HCL flow rate range from 4 to 24 g/min as shown in Figure 4. It is in good agreement compared qualitatively to data from the literature. Rose (1981) reported that the gas feed rate to the stirred tank should be not more than what is called flood point of the impeller in order to prevent spinning of agitator in a bubble of the gas that have marked on the reaction (L.M.Rose, 1981). In contrast, catalyst concentration does not significantly affect the selectivity and yield for α,γ -DCH preparation as depicted in Figure 5.

<Figure 5>

4. Conclusion

In the present paper, a simulation study was carried out on the α,γ -DCH preparation in a semi batch stirred tank reactor (SBSTR) using the Aspen Plus simulation software. The resulting simulation results were used to predict the performance of SBSTR in terms of selectivity and yield. Effect of both HCL flow rate and catalyst concentration had also been investigated. While lower HCL flow rate improves the chlorination process on both the selectivity and yield of α,γ -DCH, the catalyst concentration does not have significant effect on the process. The findings from these simulation results can be used in our experimental work to develop the technology to convert crude glycerol to 1,3-dichloro-2-propanol and subsequently into epichlorohydrin, which is an important intermediate in the production of epoxy resins.

Acknowledgement

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Table 1. Kinetic parameters

T (°C)	K_1^a	k_2^a	K_3^a	K_4^a	K_1	K_3
80	7667±940	450±41	714±227	8±3	3846	194
100	13274±1692	1089±87	1784±407	26±7	2470	146
120	27411±2861	2215±170	2179±685	31±13	1660	113

^a Kinetic constant are expressed in $\text{cm}^3/(\text{mol min})$

Table 2. Set up Parameters used in the Simulation

Reactor Block	RBatch
Base Method	Wilson
Input Variable	
Temperature (°C)	110
Pressure (bar)	1.05
Chemical reactions	Reaction 2 to 5
Kinetics rate constant	From Table 1
Feed of Reactor	
HCL flow rate (g/min)	4, 8, 12, 16, 20, 24
Concentration of malonic acid catalyst (%)	2,4,6,8,10

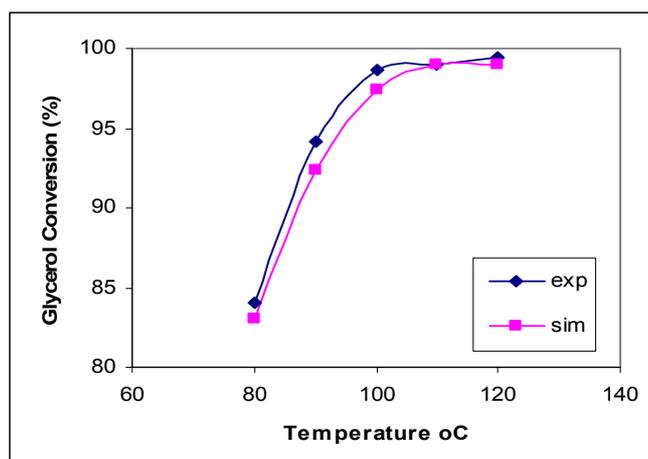


Figure 1. Effect of Temperature on Glycerol conversion. Glycerol loaded: 200g; HCL flow rate: 24 g/min; Catalyst concentration: 8% by moles; reaction time: 2.5 h

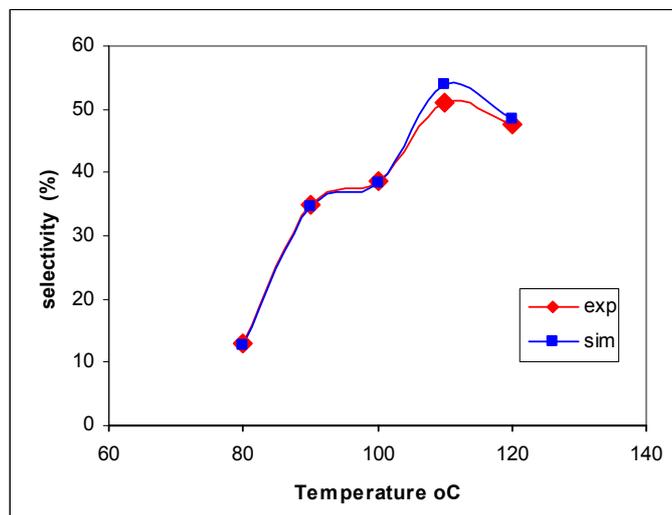


Figure 2. Effect of Temperature on reaction selectivity. Glycerol loaded: 200g; HCL flow rate: 24 g/min; Catalyst concentration: 8% by moles; reaction time: 2.5 h

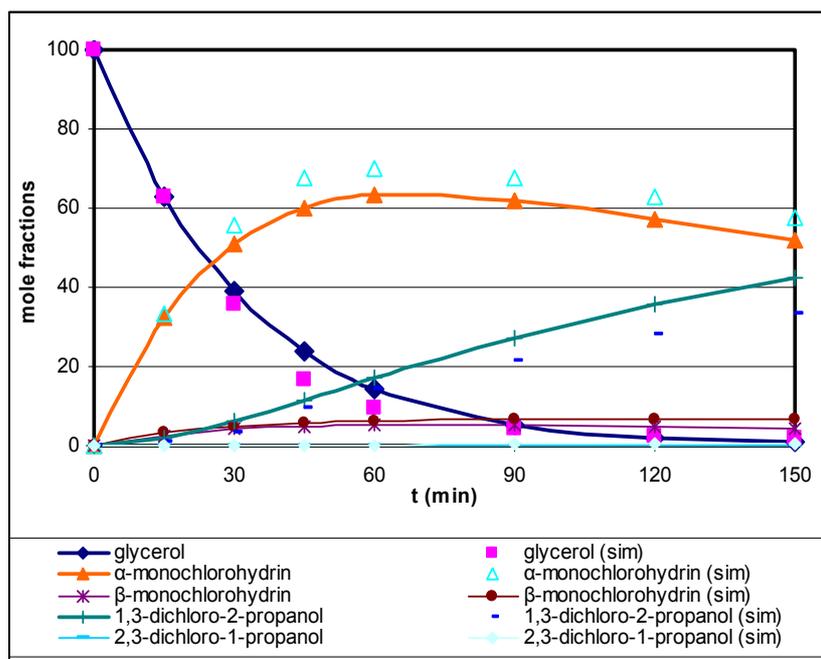


Figure 3. Evolution in time of Products composition. Glycerol loaded: 200g; HCL flow rate: 24g/min; Catalyst concentration: 8% by moles; reaction temperature: 110°C

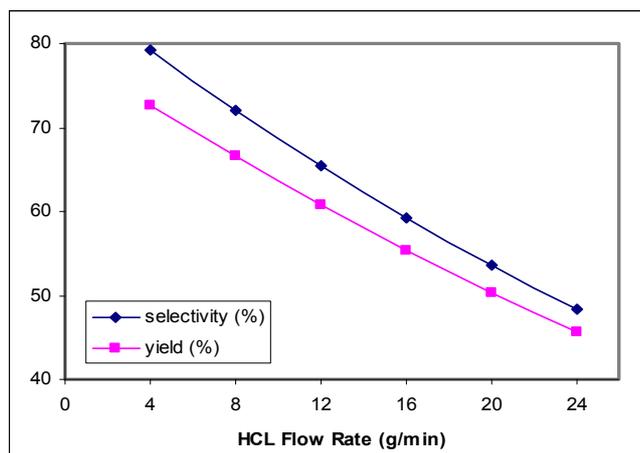


Figure 4. Effect of HCL flow rate on selectivity and yield predicted by the simulation. Glycerol loaded: 200g; Catalyst concentration: 8% by moles; reaction temperature: 110°C; reaction time: 2.5 h

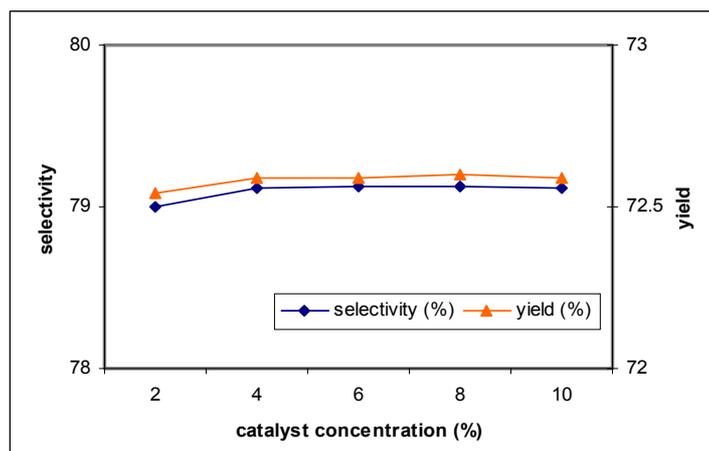


Figure 5. Effect of catalyst concentration on selectivity and yield predicted by the simulation. Glycerol loaded: 200g; HCL flow rate: 4 g/min; reaction temperature: 110°C; reaction time: 2.5 h