

The Simulation of Epichlorohydrin Production Process by using NaOH Instead of $\text{Ca}(\text{OH})_2$ Based on the Reaction Kinetics

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The epichlorohydrin (ECH) were prepared by the method of dichloropropanol (DCH) saponified with $\text{Ca}(\text{OH})_2$, while using $\text{Ca}(\text{OH})_2$ as reactant, it could bring out some disadvantages, such as equipment jam and environment pollution. In this research, NaOH had been used as the alkali instead of $\text{Ca}(\text{OH})_2$ to react with the DCH to resolve the above questions. Firstly, the reaction kinetics of DCH saponification and ECH hydrolysis under NaOH circumstances were obtained by the experiments. Secondly, based on the obtained reaction kinetics and the appropriate thermodynamics, the mathematic models of DCH saponification processes under $\text{Ca}(\text{OH})_2$ and NaOH circumstances were built respectively. Thirdly, with comparison and analysis of the two cases, the operation parameters of DCH saponified in NaOH case had been optimized and gained the appropriate operation parameters. The results showed that, in the NaOH case the reaction speed of DCH saponification and ECH hydrolysis were more quickly compared to $\text{Ca}(\text{OH})_2$ case. So, if taking the NaOH instead of $\text{Ca}(\text{OH})_2$ as alkali, the residence time of reactants must be considered in order to reduce the ECH hydrolysis. Compared to $\text{Ca}(\text{OH})_2$ case, the optimum operating condition in NaOH case were modified. The results showed that in the feasible conditions, using NaOH instead of $\text{Ca}(\text{OH})_2$ as alkali in the saponification process could be achieved. And more, the CODs (Chemical Oxygen Demands) in wastewater was not yet increase, while the yield of ECH increased from 96.21 % (in case of $\text{Ca}(\text{OH})_2$) to 98.44 % (in case of NaOH).

1. Introduction

Epichlorohydrin (ECH) was originally prepared in 1854, and later by Clarke and Hartman (1941), using alkali to hydrolyze the product of reaction between hydrogen chloride and crude glycerol. Nowadays, ECH is produced in many plants using dichloropropanol (DCH) saponified by $\text{Ca}(\text{OH})_2$. While $\text{Ca}(\text{OH})_2$ is a cheaper alkali for saponification, such problems as equipment jam and environment pollution may occur. With the price decreasing, NaOH could be used as alkali to produce ECH. However, NaOH has stronger basicity than $\text{Ca}(\text{OH})_2$, which speeds the reactions of both dehydrochlorination and hydrolysis, so the control of overall conditions becomes more difficult. Only the reactions kinetics of these reaction processes are known well, we can simulate the processes more accurately (Francesco et al., 2016).

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 α -DCH and β -DCH, separately. Calcium hydroxide was used as reactant. This work was very important because it brought the first quantitative explanation for why 2, 3-DCH was less reactive than 1, 3-DCH 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 1, 3-DCH using sodium hydroxide. However, the data presented 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. Moreover, 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 DCH using sodium hydroxide in a micro reactor. 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. Krzyżanowska and Milchert (2013) and Krzyżanowska et al. (2013) present an interesting analysis of the dehydrochlorination of 1, 3-DCH using calcium hydroxide in a reaction-stripping column. An extensive discussion is provided in which the influence of several reaction parameters is analyzed. 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) and more recently by (Krzyżanowska et al., 2013).

Cesar et al. (2016) used a millireactor apparatus for the kinetic investigation of 1, 3-DCH dehydrochlorination with sodium hydroxide. The millireactor used consisted of a continuous isothermal reactor in which sampling valves were placed along its length, allowing sampling at different residence times. Due to the small volume of the reactor, short residence times were achieved. A simple kinetic model was derived from the reaction mechanism.

All above reaction kinetics have not been used to simulate the saponification and ECH hydrolysis processes. And the reaction kinetic of ECH hydrolysis process has not been reported still now. In this research, NaOH was used as the alkali instead of Ca(OH)_2 to react with DCH to resolve the above problems. The reaction kinetics of DCH saponification and ECH hydrolysis under NaOH circumstance were obtained by the experiments, and in case of Ca(OH)_2 , the reaction kinetics was referred to Carra (1979). Based on the two sets of reaction kinetics and the appropriate thermodynamics, mathematic models of DCH saponification under Ca(OH)_2 and NaOH circumstances were built respectively. According to the reaction kinetics equations, operation parameters of DCH saponified in NaOH case were optimized and the appropriate operation parameters were gained.

2. Experiment and reaction kinetics

2.1 Experiment

The kinetics of both dehydrochlorination and hydrolysis reactions was studied in presence of caustic soda using the gas chromatogram to analyze the compositions.

Dehydrochlorination of DCH in aqueous basic solution is a fast reaction with the elimination of hydrogen chloride. The DCH has two isomeric forms of 1, 3-DCH and 2, 3-DCH. As the reaction of 1, 3-DCH and NaOH is very fast, in the process simulation, it could be assumed that the 1, 3-DCH is reacted completely at the start. So here only 2, 3-DCH dehydrochlorination was considered. In 2, 3-DCH dehydrochlorination experiments, 50g of 2, 3-DCH (3.8 wt%) and 0.3 g of n-butanol as the inside standard substance were added to the 100ml reactant bottle simultaneously. When the reaction temperature was reached, 3.24 g of NaOH (20 wt%) was injected into the bottle using a glass syringe. Runs were made in the temperature range of 323 K to 363 K.

Hydrolysis of ECH was implemented with the same instrument. In this experiment, 50 g of ECH (3.0 wt%) and 0.3 g of n-butanol as the inside standard substance were added to the 100 mL reactant bottle simultaneously. When the reaction temperature was reached, 1.3 g of NaOH (20 wt%) was injected into the bottle using a glass syringe. Runs were made in the temperature range of 323 K to 363 K.

The compositions in the reaction solution were analyzed offline using VARIAN GC3900 equipped with a FID detector and a capillary column (60 m long and 0.25 mm o.d. with a 0.25 μm thick film of stationary phase).

2.2 Reaction kinetics

According to the above experiments, the reactions kinetics of 2, 3-DCH dehydrochlorination and ECH hydrolysis under NaOH environment could be obtained, while the two reactions under Ca(OH)_2 were referred to Carra (1979). All results are shown in Table 1, where r_1 , r_2 indicate the reaction speed of DCH dehydrochlorination in case of NaOH and Ca(OH)_2 . And r_{-1} , r_{-2} indicate the reaction speed of ECH hydrolysis in case of NaOH and Ca(OH)_2 , C_1 , C_2 and C_3 indicate the concentration ($\text{mol}\cdot\text{L}^{-1}$) of DCH, ECH and OH^- .

Table 1: Kinetic parameters for the saponification and hydrolysis reaction

Reaction	Adopted kinetic model ($\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$)	
	NaOH	Ca(OH)_2
Dehydrochlorination	$r_1 = 9.17 \times 10^{12} e^{-76.15 \times 10^3 / RT} [C_1][C_3]$	$r_2 = 1.09 \times 10^8 e^{-57.25 \times 10^3 / RT} [C_1]$
Hydrolysis	$r_{-1} = 8.39 \times 10^4 e^{-32.24 \times 10^3 / RT} [C_2][C_3]$	$r_{-2} = 2.9 \times 10^8 e^{-58.1 \times 10^3 / RT} [C_2][C_3]$

3. Simulation of the saponification process

3.1 Process Description

The DCH saponification process is shown schematically in Figure 1. The 3.8 wt% DCH solution (2, 3-DCH: 1, 3-DCH = 3:1) flowing out from the DCH production process is concentrated into slaked lime (20 wt% $\text{Ca}(\text{OH})_2$ or NaOH) in the saponification mixer (V-101). Alkali, water, and DCH are mixed in V101 as pre-reactor to generate ECH where about 30 % of DCH could be transformed to ECH. Then the mixture goes to the saponification column (D101), which is a multistage column with the type of sieve tray. ECH is produced as a top product and is utilized as an energy source for the hot water in reflux condenser (E-102). After being condensed in condenser E-103, the mixture in top of D101 goes to V103. From V103, a part of the mixture goes to distillation units, and the others return back to D101. Steam is recovered from the bottom wastewater in a vacuum drum by steam ejector (P101).

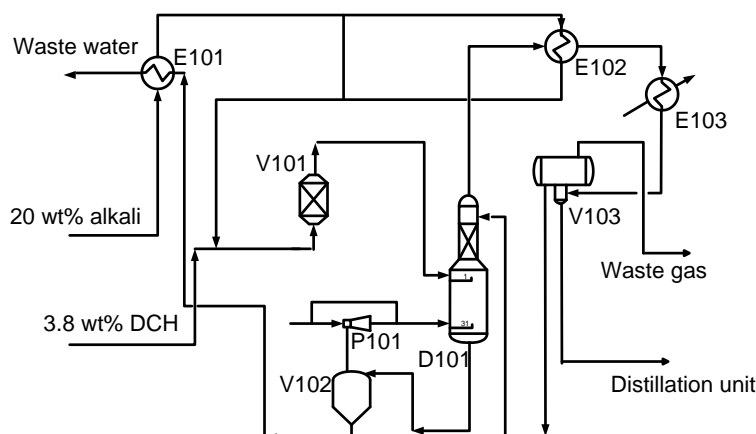


Figure 1: Diagram of DCH saponification process.

3.2 Thermodynamic model

It is well known that the calculated performances are heavily dependent on the accuracy of the thermodynamic model. To improve its accuracy, the equipment modules containing alkali and water e.g., saponification mixer V101, column D101, tank V102 and E101 use ELECNRTL and the others use NRTL activity coefficient model (Srinivas, B., 1995 and Steltenpohl, P., 2008). The ELECNRTL is the most versatile electrolyte property method. It can handle very low and very high concentrations. It can handle aqueous and mixed solvent system. The missing binary interaction parameters in the activity coefficient models were predicted by UNIFAC. The details of thermodynamic model of every unit could be found in Table 2.

3.3 Unit models

With the thermodynamic model and reaction kinetics mentioned above, the DCH saponification process was modeled using ASPEN PLUS. Standard equipment modules were used for modeling exchangers, pumps, separators, the reactive distillation column, etc. In this process, as given in Table 2. Every model was constructed and solved by the sequential modular approach. In V101 and D101, the reaction kinetic equations in Table 1 were used to obtain the reaction results.

Table 2: Models in the saponification process

equipment	model in ASPEN PLUS	thermodynamic model
V101	RPLug	ELECNRTL
V102	Flash2	ELECNRTL
V103	Flash2	NRTL
D101	RadFrac	ELECNRTL
E101	Heater+ Flash2	ELECNRTL
E102	Heater+ Flash2	NRTL
E103	Heater+ Flash2	NRTL
P-101	Mixer	NRTL

3.4 Simulation results

In order to verify the unit and thermodynamic models selected, the process in case of $\text{Ca}(\text{OH})_2$ were simulated. The material and energy balance for the saponification process were computed here. CODs is the amount of oxygen needed when the organic compounds are oxidized to CO_2 and H_2O at the bottom of the tower. The simulation results were analyzed and compared with actual plant operation data, as shown in table 3. The results show that the simulation proposed here is suitable and could be applied to process improvement and optimization.

Table 3: Comparison of the simulation results and the actual operating data

equipment	actual operating data	simulation results
The DCH solution flow rate [kg/h]	150,058.50	150,058.50
Alkali solution flow rate [kg/h]	22,275.00	22,275.00
Top temperature of saponification column [$^{\circ}\text{C}$]	80.00	81.70
Bottom temperature of saponification column [$^{\circ}\text{C}$]	101.70	101.30
Product flow rate (ECH) [kg/h]	4,865.60	4,885.20
The yield for ECH [%]	95.89	96.21
The CODs of wastewater, [mg/l]	1,241.00	1,100.00

4. Reconstruction of Process by using NaOH

As NaOH has stronger basicity than $\text{Ca}(\text{OH})_2$, compared to $\text{Ca}(\text{OH})_2$, NaOH could accelerate not only the dehydrochlorination but also the hydrolysis reaction speed. Since the hydrolysis reaction may lower the yields, the reaction temperature, time, pressure and the configuration of units shall be considered carefully to investigate how these factors influence the process results, such as CODs and the yield of ECH.

4.1 Optimization conditions

Here, using NaOH as alkali, the technical parameters, including saponification column pressure (P), reaction temperature (T), the mole ratio of OH^- to DCH and HCl (B), the fresh steam injection rate into the saponification column (Q) and the equipment parameters including the height of weir (H) and the number of trays (N) for saponification column were investigated in order to find the appropriate condition of the saponification process. The ranges of above factors were given in Table 4.

Table 4: Optimization decisions regarding saponification process

factors	optimization boundary
P [kPaA]	29.40~117.70
T [$^{\circ}\text{C}$]	56.40~70.10
B	1.03~1.10
Q [10^3 kg/h]	8.00~12.00
N	27.00~34.00
H [mm]	50.00~80.00

4.2 Results and Discussion

The influences on the CODs and ECH yield of the six factors, P, T, B, Q, H, N were studied separately. The optimal condition is determined via a COD-based optimization calculation that minimized the CODs of wastewater. Simultaneously, the yield of ECH was calculated. Optimization was accomplished which directs appropriate changes in the independent variables to the executive system. Boundary constraints on the independent variables, shown in Table 4, were checked before performing the computations in the ASPEN PLUS.

Figure 2 shows the influences of six different factors to the CODs and the yield of ECH. As the figure shows, the CODs increase with the pressure P, the ratio B, the temperature T, the height H and the number of tray N increase, and decrease with the steam rate Q increases, while the trend of ECH yields is contrary. Other more, the pressure of top column P and the ratio B affect the CODs and ECH yield observably.

As a result, the optimum operating condition in NaOH case are modified as follows: (1) mole ratio of OH^- to DCH is 1.05; (2) saponification column pressure is 39.2 kPaA; (3) the height of weir is 60 mm; (4) the saponification reaction temperature is 61 $^{\circ}\text{C}$; (5) the fresh steam from the bottom of saponification column is 10 t/h; and (6) the number of trays is 31. Under these conditions, the CODs is 1022.4 ppm, and the yield of ECH is 98.44 %. So, compared to $\text{Ca}(\text{OH})_2$ case, the main changes of system conditions are given in Table 5. The results show that if using NaOH as alkali in order to lower the CODs and improve the ECH yield, all

values of factors should be reduced except the number of trays. Decrease of P and H can shorten the residence time of ECH in the solution, and decrease of factors T and B can weaken the activity of NaOH, making the hydrolysis reaction slower. All those changes could lower the progress of hydrolysis reaction. And more, using NaOH instead of $\text{Ca}(\text{OH})_2$ as alkali, the CODs in wastewater does not increase, while the yield of ECH is increased from 96.21 % (in case of $\text{Ca}(\text{OH})_2$) to 98.44 % (in case of NaOH).

Table 5: The main system conditions in case of $\text{Ca}(\text{OH})_2$ and NaOH

factors	$\text{Ca}(\text{OH})_2$	NaOH
P [kPaA]	48.02	39.20
T [$^{\circ}\text{C}$]	80.00	61.00
B	1.20	1.05
Q [10^3 kg/h]	13.00	10.00
N	31.00	31.00
H [mm]	80.00	60.00
CODs [ppm]	1100.00	1022.40
ECH yield [%]	96.21	98.44

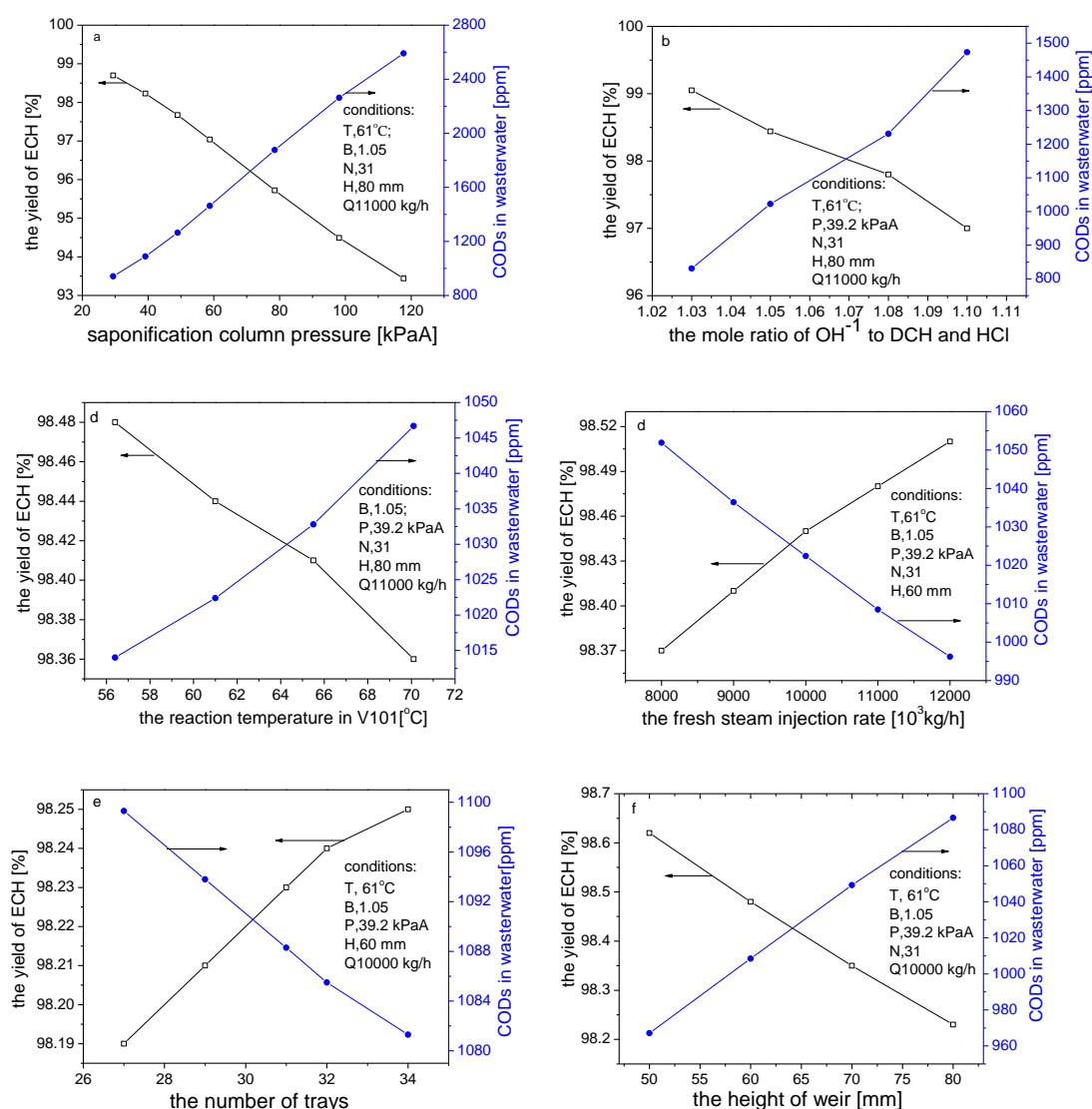


Figure 2: The trends of CODs and ECH yield with the different factors (a, P; b, B; c, T; d, Q; e, N; f, H.)

5. Conclusions

The scheme of reconstruction of ECH production process by using NaOH instead of $\text{Ca}(\text{OH})_2$ based on the reaction kinetics were proposed by the method of simulation. Using NaOH as alkali, in order to lower the CODs and improve the ECH yield, 6 main factors were considered. Through optimizing some of those factors, using NaOH instead of $\text{Ca}(\text{OH})_2$ as alkali in the saponification process could be achieved. And more, the CODs in wastewater does not increase, while the yield of ECH is increased from 96.21 % (in case of $\text{Ca}(\text{OH})_2$) to 98.44% (in case of NaOH).

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References

- Clarke H.T., Hartman W.W., 1941, Epichlorohydrin, *Organic Syntheses Collective*, 1, 233-237.
- Carrà S., Santacesaria E., Morbidelli M., Cavalli L., 1979, Synthesis of Propylene Oxide from Propylene Chlorohydrins-I, *Chemical Engineering Science*, 34, 1123-1132.
- Carrà S., Morbidelli M., 1979, Synthesis of Propylene Oxide from Propylene Chlorohydrins-II: Modeling of the distillation with chemical reaction unit. *Chemical Engineering Science*, 34, 1133-1140.
- Cesar A.de A.F., Shuyana H., Kari E., Tapio S., 2016, Advanced Millireactor Technology for the Kinetic Investigation of Very Rapid Reactions: Dehydrochlorination of 1,3-dichloro-2-propanol to Epichlorohydrin, *Chemical Engineering Science*, 149, 35-41.
- Francesco D., Sergio C., Giacomo M., Matteo B., Luca S., 2016, Design and Simulation of a RF Resonant Reactor for Biochemical Reactions, *Chemical Engineering Transactions*, 52, 1183-1188.
- Gu Y., Azzouzi A., Pouilloux Y., Jérôme F., Barrault J., 2008, Heterogeneously Catalyzed Etherification of Glycerol: New Path Ways for Transformation of Glycerol to More Valuable Chemicals, *Green Chemistry*, 10, 164-167.
- Krzyżanowska A.M., Milchert E., 2013, Continuous Dehydrochlorination of 1,3-dichloropropan-2-ol to Epichlorohydrin: Process Parameters and Byproducts formation, *Chemical Papers*, 67, 1218-1224
- Krzyżanowska A.M., Milchert E., Paździuch W.M., 2013. Technological Parameters of dehydrochlorination of 1,3-dichloropropan-2-ol to epichlorohydrin, *Industry Engineering Chemical Research*, 52, 10890-10895.
- Ma L., Zhu J.W., Yuan X.Q., Yue Q., 2007, Synthesis of Epichlorohydrin from Dichloropropanols: kinetic Aspects of the Process, *Chemical Engineering Research Design*, 85, 1580-1585.
- Srinivas B., Parande M.G., 1995, Liquid-Liquid Equilibrium for the Propylene Oxide + Water + Propylene Dichloride System, *Journal of Chemical Engineering Data*, 40, 927-930.
- Steltenpohl P., Graczová E., 2008, Vapor-Liquid Equilibria of Selected Components in Propylene Oxide Production, *Journal of Chemical Engineering Data*, 53, 1579-1582.
- Zhang J., Lu Y., Jin Q., Wang K., Luo G., 2012, Determination of the Kinetic Parameters of Dehydrochlorination of Dichloropropanol in a Microreactor, *Journal of Chemical Engineering*, 207, 142-147.