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Integrated reaction and separation in a continuous middle vessel column for enhancing indirect hydration of cyclohexene to cyclohexanol

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ABSTRACT

This study introduced economically-viable continuous reactive distillation (RD) design alternatives for cyclohexanol production through the indirect hydration of cyclohexene. The feasibility concept of batch RD was employed for generating the new design alternatives. The first alternative process utilized a continuous stripper for recovering the stable node product of cyclohexyl formate in the esterification reaction and then employed a continuous middle vessel column (MVC) for recovering the stable and unstable node products of cyclohexanol and formic acid in the hydrolysis reaction. The second design had a single MVC-type column having the reactive rectifying zone and the middle vessel reactor for the two respective reactions. The simulation results showed the two alternative sequences required less energy duty than the previously proposed RD process. However, compared to the prior RD process, the life cycle cost (LCC) of the first alternative design increased about 30% due to high equipment costs and the LCC of the second process decreased nearly 40% because of low equipment costs and energy requirements.

1. Introduction

Cyclohexanol is an intermediate component for synthesizing polymers and it is widely used in the nylon production industry [1,2]. There are several ways to produce cyclohexanol. The hydrogenation of phenol was suggested for producing cyclohexanol [3,4]. The direct oxidation of cyclohexane is a typical process for producing cyclohexanol and a liquid-phase oxidation process was also developed [5,6]. A direct hydration of cyclohexene was considered and the process using a heterogeneous catalyst was proposed [7–9]. A hybrid reactive distillation (RD) column sequence improved the efficiency of direct hydration process [10]. More recently, the RD process utilizing excess water was proposed for a complete conversion of cyclohexene [11]. However, the phenol hydrogenation was regarded as an uneconomical process due to the high cost of raw material.

The oxidation process has several disadvantages such as low selectivity of cyclohexanol, formation of by-products, and safety concern during the oxidation operation. In the direct hydration of cyclohexene, a low mutual solubility between cyclohexene and water has been pointed out as a problem to be solved. To solve this problem, a co-solvent such as 1,4-dioxane was adopted for the direct hydration of

cyclohexene [12]. However, the indirect hydration of cyclohexene was also considered for producing cyclohexanol to overcome the low miscibility between cyclohexene and water and RD was proposed as an effective solution for the reaction. RD is one of the most widely applied technologies in the chemical industry and numerous studies have introduced the benefits of the RD process [13–16]. Using thermodynamic and kinetic data obtained by experiments, a two-RD column process was proposed for the indirect hydration of cyclohexene to cyclohexanol [17–19].

This study aims at introducing cost-effective RD column sequences for the indirect hydration of cyclohexene to cyclohexanol by employing the feasibility concept of batch reactive distillation (BRD) [20–23] and life cycle cost analyses. The batch reactive rectifier consisting of a still reactor and a non-reactive rectifying column can produce an unstable node (UN) product with high purity and full conversion if the product can be reachable from any distillation region in the residue curve map (RCM) regardless of the number of azeotropes and distillation boundaries. A batch reactive stripper has an inverted configuration of the batch rectifier with the reaction region in the overhead drum. The batch reactive stripper is an appropriate choice when the desired product of the reaction has a stable node (SN) product (maximum boiling point)

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Nomenclature

| | |
|----------------|-----------------------------|
| AZ | Azeotrope |
| BRD | Batch reactive distillation |
| CAPEX | Capital expenditure |
| C-ENE | Cyclohexene |
| C-FORM | Cyclohexyl formate |
| C-HXOL | Cyclohexanol |
| FA | Formic acid |
| H | Liquid level |
| H ₀ | Initial liquid level |
| LCC | Life cycle cost |
| LH | Langmuir-Hinshelwood |
| MVC | Middle vessel column |

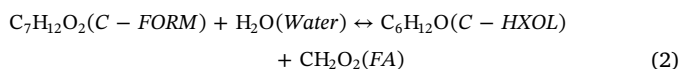
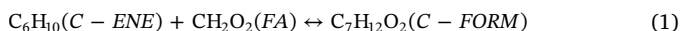
| | |
|----------------|---|
| NRTL | Non-random two-liquid |
| OPEX | Operating expenditure |
| PFD | Process flow diagram |
| RCM | Residue curve map |
| RD | Reactive distillation |
| S | Saddle point |
| SN | Stable node |
| t | Time |
| t ₀ | Process initial time |
| UN | Unstable node |
| UNIFAC | Universal quasi-chemical functional-group activity coefficients |
| VLE | Vapor-liquid equilibrium |
| VLLE | Vapor-liquid-liquid equilibrium |

that can be reachable from any distillation region in the RCM because the removal of the product at the bottom of the column can shift the reaction equilibrium to the forward reaction. A reactive middle vessel column (MVC) is a combined process of batch rectifier and stripper with reaction taking place in the middle vessel. In the MVC, products can be separated continuously from the opposite side of the product stream at the top and bottom of the column. To produce pure products with full reaction conversion, the products must have maximum (SN in the RCM) and minimum (UN in the RCM) boiling points.

The purpose of this study is to propose RD design alternative column sequences for the indirect hydration of cyclohexene by modifying the batch configuration of stripper and MVC to the continuous form of the RD columns. The simulation will be conducted by using Aspen Plus™ to verify the feasibility of the proposed column sequences. The life cycle cost (LCC) of the column sequences will be estimated for an economic evaluation and will show that the single MVC configuration improves the economic feasibility more than the conventional two-RD column process.

2. Thermodynamic and kinetic data

The indirect hydration of cyclohexene to cyclohexanol is shown in Eqs. (1) and (2). Initially, cyclohexyl formate (C-FORM) is produced from the esterification of cyclohexene (C-ENE) with formic acid (FA). Then, cyclohexanol (C-HXOL) and FA are generated after the hydrolysis of C-FORM with water. The esterification reaction is moderately fast and exothermic, but the ester hydrolysis reaction is relatively slow compared to the first esterification reaction [24].



The UNIFAC thermodynamic model in a prior work [25] is used for calculating the vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE). The parameters of UNIFAC model are borrowed from another reference [26]. A previous study used a NRTL thermodynamic model for the phase equilibrium calculation [27]. However, when applying the NRTL model during the simulation, it cannot detect azeotropes in the system and thus this study uses the UNIFAC model. Before the simulation, we confirmed that the thermodynamic characteristics and the shape of the residue curve map (RCM) shown in Fig. 1 is similar to those of the previous literature [19]. To avoid the decomposition of FA above 60 °C, we set the operating pressure of the process to 0.1 bar [19]. Table 1 shows the dynamic properties of the components and azeotrope in the esterification reaction system. Here, S denotes a saddle point, SN is for a stable node, and UN represents an unstable node. The RCM of the esterification system is shown in Fig. 1. Only one UN binary minimum-boiling azeotrope exists in the system.

Table 2 shows the thermodynamic properties of the components in the ester hydrolysis system and Fig. 2 represents the RCM of the system. Three binary azeotropes exist in the system and these azeotropes are all saddle points. Because the target product, C-HXOL, has the highest boiling point (SN) and FA has the minimum boiling point, this system can utilize a reactive MVC configuration for the complete separation of the products and the full conversion of the hydrolysis reaction.

The Langmuir-Hinshelwood (LH) type reaction kinetic model is adopted to calculate the reaction rate.



$$R = \left[m_{cat} k_{forward}^{het} \frac{K_{ads}^A K_{ads}^B}{(1 + K_{ads}^A a_A + K_{ads}^B a_B + K_{ads}^C a_C + K_{ads}^D a_D)^2} + n_{hom} k_{forward}^{hom} \right] \times \left[a_A a_B - \frac{a_C a_D}{K_{eq}} \right] \quad (4)$$

$$k_{forward}^{het} = k_{forward,0}^{het} \times e^{-\frac{E_A^{het}}{R_u T}} \quad (5)$$

$$k_{forward}^{hom} = k_{forward,0}^{hom} \times e^{-\frac{E_A^{hom}}{R_u T}} \quad (6)$$

In Eq. (4)–(6), m_{cat} is the amount of catalyst, $k_{forward}^{het}$ and $k_{forward}^{hom}$ are the forward reaction rate constant of the heterogeneous and homogeneous reactions. K_{ads}^i is the adsorption equilibrium constant for species i in a corresponding reaction and a_i is the liquid activity coefficient of the chemical species i . n_{hom} is the molar amount of FA which is a homogeneous catalyst in the esterification reaction and K_{eq} is the chemical equilibrium constant.

The kinetic parameters [19] in the LH model are described in Table 3. The LH type kinetic model for RD was implemented in Aspen

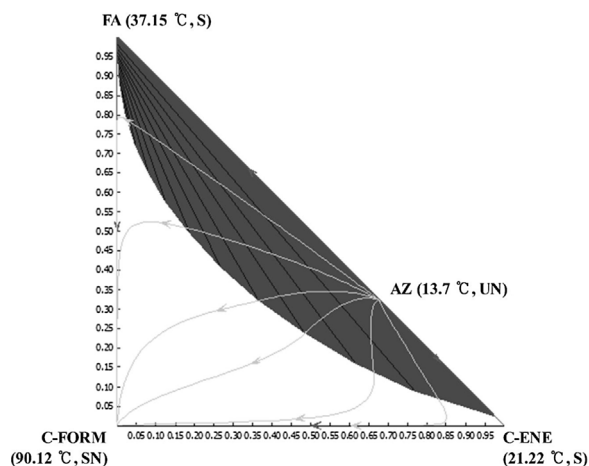


Fig. 1. RCM of the esterification system (0.1 bar).

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