Simulation study of direct hydration of cyclohexene to cyclohexanol using isophorone as cosolvent

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ABSTRACT

Cyclohexanol is an important intermediate in the production of adipic acid and ε-caprolactame, and these in turn are used as intermediates for the production of nylons, plasticizers, and pesticides. Traditionally, cyclohexanol is obtained from the oxidation of cyclohexane, however, the process suffer lots of drawbacks including the low selectivity of cyclohexanol, high energy requirement, the explosion risk, and numerous by-products formations. In this paper, a process simulation of reactive distillation using isophorone as cosolvent for the direct hydration of cyclohexene to cyclohexanol was performed. Results showed that the novel process not only got rid of drawbacks owned by the traditional oxidation method, but also improved the conversion and reaction rate of the reactants greatly. Process simulation results also demonstrated that with the increasing Damköhler number (Da), a reactive azeotrope emerged when Da numbers exceeded a critical value of 0.07. Therefore, the reactive distillation could only be practical when Da numbers is below 0.07. During the simulation, the cyclohexene conversion increased with excess water and cosolvent isophorone in the reactive distillation column. Finally, a high-purity cyclohexanol product (99.9 mol.%) can be obtained using a decanter and two distillation columns for reactive distillation, with a high cyclohexene conversion of 99.14%, and the isophorone purity well fitted for recycling, and the energy consumption was studied.

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1. Introduction

Cyclohexanol is an important intermediate in the production of adipic acid and ε-caprolactame, and these in turn are used as intermediates for the production of important polymer such as nylons, plasticizers, and pesticides (Musser, 2003; Misono and Inui, 1999). There are three commercial routes to produce cyclohexanol: (1) the hydrogenation of phenol, (2) the oxidation of cyclohexane, and (3) the direct hydration of cyclohexene. The route of the hydrogenation of phenol (Struijk et al., 1992; Nagahara et al., 1997) is the earliest method among them. However, this process has several disadvantages such as the heavy consumption of hydrogen and the high price of phenol. The oxidation of cyclohexane (Suresh et al., 1988a,b,c) is the main method to produce cyclohexanol currently, but there are several well-known drawbacks that associated with this process including high energy demands, low

selectivity, low conversion, numerous side-product formations, and high risk with oxidizer which leaded to serious concern with its operation safety. The third route using direct hydration of cyclohexene is therefore proposed by researchers from Asahi Chemical Industry Co., Ltd, which has avoided most disadvantages associated with previous process. However, the slow reaction rate and fairly low equilibrium conversion hampered the broader application of the new process. It is of great interest to further investigate this process for more favorable commercial operation.

The history of the innovative direct hydration of cyclohexene process can date back to 1980s. Mitsui and Fukuoka (1986) studied a process for the direct hydration of cyclohexene to produce cyclohexanol, utilizing a zeolite catalyst of HZSM-5. Qi and Sundmacher (2002) and Qi et al. (2002) developed a systematic approach to investigate the feasibility of reactive distillation processes for the systems with

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Nomenclature

x_i^{org}, x_i^{aq}	Mole fraction of component i in organic phase and aqueous phase, respectively
z_i	Average mole fraction of component i in the mixture of the two liquid phases
y_i	Average mole fraction of component i in the mixture of the two liquid phases
k_f	Forward reaction rate constant
$k_{f,ref}$	Forward reaction rate constant at the reference temperature
Da	Damköhler number
r_{NOL}	Reaction rate
p_i^{sat}	Saturated vapor pressure for component i
p	System pressure
K	Chemical equilibrium constant
T	Temperature, K

Greek letters

γ_i	Activity coefficient of component i in aqueous phase
β	Relative liquid mole holdup of aqueous phase
$^{33}\alpha_i^{aq}$	Activity of component i in aqueous phase
ξ_i	Dimensionless time of component i
υ_i	Stoichiometric coefficient of component i
υ_T	Total mole change of reaction
$\Re$	Dimensionless reaction rate

Subscripts

i	Species
ENE	Cyclohexene
H_2O	Water
NOL	Cyclohexanol
Ref	Reference state (point of lowest boiling temperature in the system)

Superscripts

org	Organic phase
aq	Aqueous phase

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liquid phase splitting using residue curve maps, and compared the topologies of pseudohomogeneous and heterogeneous residue curve maps (RCMs) of the direct hydration of cyclohexene. The result showed that the bifurcation behavior in the heterogenous systems is much more complex than in the homogeneous. Taking into account that the direct hydration of cyclohexene is slightly exothermic and is limited to equilibrium, Steyer et al. (2002) proposed a new process that enables the cyclohexene hydration to be carried out in a reactive distillation column, which was the improvement of the process developed by Asahi Chemical Industry Co., Ltd. Furthermore, they also used RCMs to analyze the feasibility of the process. Their results showed that when Damköhler number was below a critical value of 0.109, pure cyclohexanol was conceptually possible as the bottom product. However the process had its own intricate challenges due to the fact that the simultaneous presence of reaction, distillation separation and liquid-phase splitting, because of a very limited mutual miscibility between cyclohexene and water. Khaledi and Bishnoi (2006) simulated the previous process of the direct hydration of cyclohexene. Their results indicated that all of the cyclohexene conversion, cyclohexanol purity in the bottom product, and the phase pattern in the column were dependent on the operating conditions of reactive distillation columns. Steyer and Sundmacher (2007) and Steyer et al. (2008) proposed a reactive distillation process of the indirect hydration of cyclohexene by further research, which used formic acid to form a

reactive intermediate, cyclohexyl ester, subsequently hydrolyzed the formed ester to cyclohexanol and formic acid in a second column and then recycled the formic acid back to the first column as a reactive entrainer. They used the RCMs to prove the feasibility of the process and considered that this process is safer and has less by-products than conventional ones. Katariya et al. (2009) simulated the previous process of the cyclohexene indirect hydration by equilibrium stage simulations, the results showed that the conversion of cyclohexene is almost completed with moderate amounts of catalyst. In Ester hydrolysis column a back-splitting of the ester to cyclohexene and formic acid takes place which makes the operation of this column has to be restricted to a relatively narrow operating window. Qiu et al. (2013) suggested a reactive distillation process with 1,4-dioxane as cosolvent for the production of cyclohexanol from cyclohexene and used residue curve maps to analyzed the feasibility of the proposed process, however, they did not simulate their process. Chen et al. (2014) studied a reactive distillation process for the production of cyclohexanol with excess water, although the conversion of cyclohexene can increase to 99.9%, a high pressure of 3 atm is needed for the reactive distillation column.

Because of the fact that a very low mutual miscibility between cyclohexene and water, which may lead to the low yield of cyclohexanol, some researchers have put forward a way to overcome the drawbacks by adding a verity of organic solvents or additives. A series of Japanese patents (Moriyasu et al., 2016; Takahara et al., 1996a,b) have been reported that used organics including benzoic acid, acetic acid and phenol etc. As a cosolvent for the direct hydration of cyclohexene. Apart from the yield of product was still insufficient, further problems come along. For example, the cosolvents reacted with cyclohexene or cyclohexanol in the hydration reaction system, or the cosolvents were not stable under the hydration reaction conditions, whereby by-products resulting from the cosolvent were produced causing loss of the cosolvents and reduction in purity of the product cyclohexanol. Moreover, some of the cosolvents formed an azeotropic composition with cyclohexanol, which gave rise to be difficult separation of cyclohexanol and cosolvent by distillation. Panneman and Beenackers (1992a,b,c) studied the solvent effects of sulfolane on the cyclohexene hydration by a strong acid ion-exchange resin, and discussed the solvent effects of sulfolane on the kinetics and chemical equilibrium of cyclohexene hydration reaction. Shan et al. (2011) investigated the solvent effect of ethylene glycol on the kinetics and chemical equilibrium of cyclohexene hydration reaction. Both sulfolane and ethylene glycol encountered the same problem of reacting easily with cyclohexene. As a result, these two solvents were not suitable for the reactive distillation process. The U.S. Patent 20030018223 A1 (Takamatsu and Kaneshima, 2003) published a method using the organic solvent of isophorone to enhance the liquid–liquid distribution of cyclohexene with a solid acid as a catalyst in the aqueous phase to improve the yield of cyclohexanol. Isophorone does not form an azeotropic composition with cyclohexanol, which made it easy to separate from the product. What is more, isophorone is stable under the hydration reaction condition.

Based on previous studies, a process using isophorone (IPHO) as cosolvent for the direct hydration of cyclohexene to cyclohexanol with reactive residue curve maps (rRCMs) for feasibility analysis of reactive distillation process is proposed. Such a process should have benefits of several individual unit process reported previously (Qi et al., 2002; Steyer et al., 2002; Khaledi and Bishnoi, 2006; Steyer and Sundmacher, 2007; Steyer et al., 2008; Katariya et al., 2009; Qiu et al., 2013; Chen et al., 2014; Moriyasu et al., 2016; Takahara et al., 1996a,b; Panneman and Beenackers, 1992a,b). Furthermore, a simulation using Aspen Plus Software was performed to verify this process.

2. Theoretical model

2.1. Model of rRCMs

Reaction for direct hydration of cyclohexene is shown in Eq. (1):

The rRCMs first developed by Qi et al. (2002) and Shu (2005) is formed by overlying the reaction and the RCMs with liquid-