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Dynamics and control of entrainer enhanced reactive distillation using an extraneous entrainer for the production of butyl acetate

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ABSTRACT

This paper introduces the dynamics and control of entrainer-enhanced reactive distillation(ERD) for the efficient production of n-butyl acetate via esterification reaction of butanol and acetic acid. It was recently reported that using an extraneous instead of the internal entrainer (butyl acetate) could considerably improve the process efficiency (Cho et al., 2014). In the ERD system, different multiplicities were found to appear depending on whether the azeotrope that the entrainer forms with water is binary or ternary. In the case of binary azeotrope formation, the extraneous entrainer only takes the role of entrainer if the liquid level of the organic phase in the decanter is controlled. However, in the case of ternary azeotrope formation, both the extraneous entrainer and butyl acetate can take the role of entrainer. Keeping a proper inventory of the extraneous entrainer in the column was crucial for ensuring that the system was at a high conversion steady state, leading to a high butyl acetate yield. This is mainly because the presence of too much extraneous entrainer in the reactive distillation column results in a drop in the reaction yield. We propose two different control schemes depending on the type of azeotrope that the extraneous entrainer forms with the reaction mixture. The proposed control schemes were demonstrated to be effective in maintaining a high reaction yield and product purity.

1. Introduction

n-Butyl acetate is commonly used as a solvent in the chemical industry and its production is typically made by the esterification of acetic acid (HOAc) with n-butanol (BuOH). Esterification is an equilibrium limited reaction in the presence of water, which leads to low conversion and low product yield. Reactive distillation (RD) can be employed to deal with the low efficiency caused by the equilibrium limitation by shifting the chemical equilibrium in the favorable direction to the forward reaction through continuous removal of water from the reactive section. However, the produced water forms a minimum boiling azeotrope with butanol so that butanol is removed with water as a distillate. This problem can be solved by using a mass separation agent or entrainer. The entrainer forms a new azeotrope with water and improves water removal efficiency. The reactive distillation process which uses an entrainer to improve its performance is called an entrainer-enhanced RD (ERD) system. Reactive distillation system using an entrainer has been studied by several researchers [1–7]. Dimian et al. [1] used entrainer-based reactive distillation for the synthesis of fatty esters and provide a guide for selecting suitable entrainers for the ERD. Suman et al. [2] proposed ERD for the esterification of ethylene glycol with acetic acid and reported that entrainer controls the reaction temperature so that the catalyst can be free from possible thermal degradation.

n-Butyl acetate, which is also a product of the esterification reaction, forms an azeotrope with water and can be used as an internal entrainer in the ERD. Reactive distillation systems which employs n-butyl acetate as an internal entrainer has been studied [8–16]. Steinigeweg and Gmeling [13] and Gangadwala et al. [14–16] reported that a configuration consisting of a prereactor and a column with a reactive distillation is most suitable for the synthesis of butyl acetate. All these studies have not explored the possibility of using extraneous entrainer instead of the internal entrainer. Cho et al. [17] recently proposed a reactive distillation system without a pre-reactor, which uses an extraneous entrainer instead of butyl acetate for the synthesis of butyl acetate. A more efficient removal of water and butyl acetate from the reactive section was achieved, giving more appropriate column composition profile for higher product yield with lower energy consumption. However, the use of extraneous entrainer can lead the ERD column into operational and control difficulties.

ERD shows complex dynamics such as multiple steady states, and nonlinear dynamics. Only one study on the control strategy of the ERD is given in open literature. Wang and Wong [18] studied

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Nomenclature

HOAc	Acetic acid
BuOAc	n-Butyl acetate
BuOH	Butanol
a_i	Activity coefficient of component i
$E_{A,i}$	Activation energy of component i
r_{BuOAc}	Rate of reaction for BuOAc formation (kmol/kg s)
k_i	Kinetic constant
k_i^0	Pre-exponential factor
m_{cat}	Mass of catalyst
n_i	Number of moles of component i
R	Gas constant
P	Pressure
T	Temperature
$U_{i,j}$	UNIQUAC interaction parameter between components i and j
ν_i	Stoichiometric coefficient of species i

the dynamics of entrainer-added reactive distillation for fatty ester production. They showed that maintenance of a proper entrainer inventory was crucial for achieving the desired specifications. Control of azeotropic distillation which also uses an entrainer has been actively studied [19–24]. Rovagalio et al. [20] developed a control system using an average temperature for checking a transition from the ethanol environment to the entrainer environment. They emphasized the importance of maintaining the entrainer inventory and the inventory should be measured directly from internal trays, not from an external product. Chien et al. [21] employed a controller using an inverse double temperature for the column

Table 1
Kinetic parameters of esterification for the pseudohomogeneous kinetic model[3].

	i	k_i^0(mol/g s)	E_A(kJ/mol)
Esterification	1	6.1084×10^4	56.67
Hydrolysis	−1	9.8420×10^4	67.66

profile not to be transformed from the desired type to other types. Ulrich and Morari [24] examined the influence of impurities on the operation of heterogeneous azeotropic distillation columns. They reported that top vapor composition was close to a heterogeneous azeotrope and the top composition could move from one azeotrope to another.

In the entrainer enhanced reactive distillation proposed by Cho et al. [17], both the extraneous entrainer and butyl acetate can take the role of entrainer and a new kind of multiple steady states appear. The extraneous entrainer competes with the internal entrainer (butyl acetate) to be the major entrainer for removing water from the reactive section of the RD column. Interaction between the two entrainers causes a complex dynamics of the ERD column, posing a challenging control problem. As far as we know, there have not been any studies regarding column dynamics and control when two different entrainers are used in the ERD system. We studied intriguing column dynamics, such as new multiplicity, caused by interaction between extraneous entrainer and internal entrainer (butyl acetate) and proposed control scheme based on understanding of the column dynamics. The proposed control scheme was shown to be able to handle the control difficulties caused by using an extraneous entrainer.

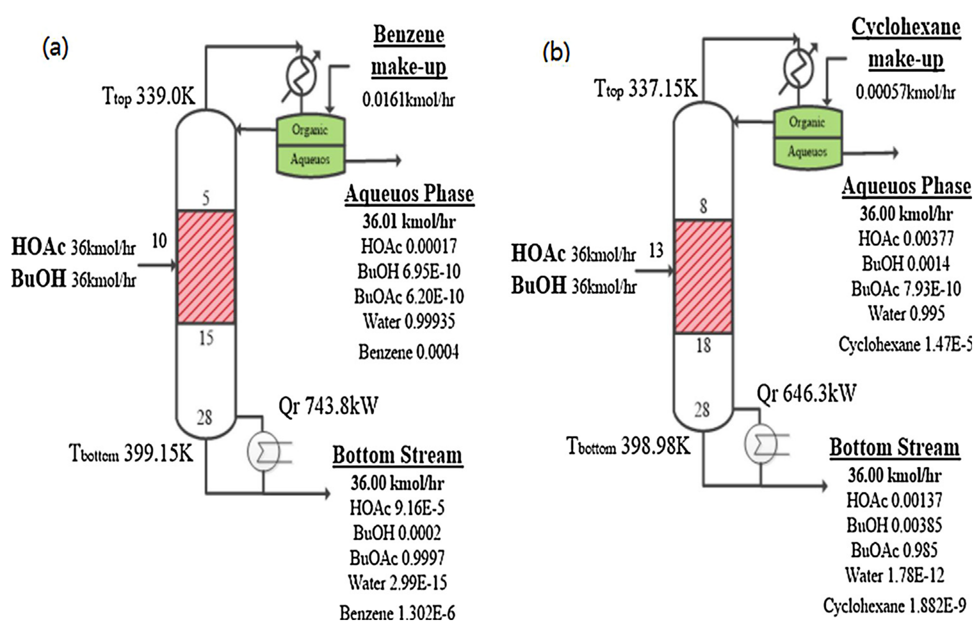

Fig. 1. Steady state column design and simulation results for (a) ERD forming a binary azeotrope using benzene as entrainer; (b) ERD forming a ternary azeotrope using cyclohexane as entrainer.

Table 2
Composition and temperature of the azeotropes involved in the system at atmospheric pressure.

Components	Water	BuOH	BuOAc	Azeotrope Temp.(K)	Azeotrope
Water-BuOAc	0.7072		0.2928	334.05	Heterogeneous
Water-BuOH	0.7517	0.2483		365.76	Heterogeneous
Water-BuOAc-BuOH	0.6892	0.1013	0.2095	363.23	Heterogeneous
BuOH-BuOAc		0.7802	0.2198	390.13	Homogeneous