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Design and control of entrainer-assisted reactive distillation for *N*-propyl propionate production

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ABSTRACT

An entrainer-assisted reactive distillation process is proposed to produce high-purity *N*-propyl propionate from propionic acid and *N*-propanol. The E-RD process can take advantages of both the heterogeneous azeotropic distillation (HAD) and reactive distillation (RD). Cyclohexane is selected as the proper entrainer in the E-RD process. And the E-RD process is optimized by calculating the minimum total annual cost (TAC). The optimal results reveal that the E-RD process can save 46.11% of TAC and 41.40% of reboiler duty compared with the two-column process. Furthermore, two control structures for the E-RD process are considered. The dynamic performances demonstrate that the improved control structure (CS2) can solve the problem of disturbances and maintain the product purities close to the set points with small deviations and short settling times.

1. Introduction

N-Propyl propionate (Propro) is a widely used chemical solvent. It has many applications in paints, coatings, and other industrial products. Propro can be produced by the liquid-phase esterification of *N*-propanol (POH) and propionic acid (ProAc) (Altman et al., 2012; Buchaly et al., 2012; Gooch, 2007). The esterification reaction is a kind of reversible reaction and it is limited by chemical equilibrium. Propro is produced in a batch or continuous reactor in a homogeneous or heterogeneous system catalyzed by acids followed by several distillation columns (Cruz-Díaz et al., 2012; Duarte et al., 2006). It has many problems: it has low conversion rate; it consumes large capital and energy cost and the corrosion of the equipment is serious. Hence, reactive distillation (RD) is an effective method to solve the problems. RD is an integration of reaction and separation into a single column. It allows the simultaneous production and removal of the products, it can also improve the productivity and reduce capital costs and energy consumption (Kiss, 2013). It has been applied to the industrial production of MTBE, ETBE and TAME (Al-Arfaj and Luyben, 2004; Domingues et al., 2014; Huang et al., 2008).

Several studies reported the production of Propro in a reactive distillation column (RDC). Kotora et al. (2008) studied the experiment for the Propro production in a pilot-scale RDC, the purity of Propro in the process is 0.698; Keller et al. (2011) studied the experiment of the production of Propro in a pilot-scale RDC assisted with a liquid–liquid phase separator. The purity of Propro in the process is 0.521. Based on the processes, the experimental purities of Propro are below 0.7, this is because POH and water form a minimum-boiling azeotrope so that most of POH is removed from the reaction zone of the RDC. Since POH is not totally reacted in the reactive section, and the chemical equilibrium of the esterification is limited, an extra separation unit is necessary to recover and recycle the unreacted alcohol. Xu et al. (2014) proposed a two-column process to synthesize Propro, they concluded that it is hard to produce high-purity Propro in a single RDC because it could not operate 'neat'. The two-column process feathers a RDC coupled with a decanter and a recovery column (RC). Consequently, the purity of Propro in the process is 0.9975.

Though high-purity Propro can be obtained in the two-column process, the two-column process needs larger capital cost and energy consumption. To reduce the capital cost and energy consumption, Dimian et al. (2002) introduced a novel entrainer-assisted RD process by adding an entrainer to the reactive distillation system. The entrainer is able to form a minimum ternary heterogeneous azeotrope with alcohol and H_2O. The formation of azeotrope can enhance water removal and improve the concentration of reactants. A second column is unnecessary for alcohol recovery. Recently, some researchers studied the entrainer-assisted reactive distillation process. Wang and Huang (2011)

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Nomenclature

E-RD	Entrainer-assisted reactive distillation
Propro	*N*-Propyl propionate
POH	*N*-Propanol
ProAc	Propionic acid
HAD	Heterogeneous azeotropic distillation
RD	Reactive distillation
RDC	Reactive distillation column
RC	Recovery column
ri	Reaction rate, mol eq^{-1} s^{-1}
a_{ProAc}	Liquid phase activity of the ProAc
a_{Propro}	Liquid phase activity of the propro
a_{water}	Liquid phase activity of the water
a_{POH}	Liquid phase activity of the POH
$m_{cat,dry}$	Mass of the dry catalyst, g
vi	The stoichiometric coefficient of the i^{th} component
c_{cat}	Concentration of active sites on the dry catalyst, eq kg^{-1}
$K_{eq}(T)$	Activity based equilibrium constant, mol eq^{-1} s^{-1}
k_1	Rate constant of the forward reaction, mol eq^{-1} s^{-1}
R	Universal gas constant, J mol^{-1} K^{-1}
TAC	Total annual cost
BP	Boiling points
VLE	Vapor-liquid equilibrium
VLLE	Vapor-liquid–liquid equilibrium
RCM	Residue curve map
TOC	Total operating cost
TCC	Total capital cost
TAC	Total annual cost
PI	Proportional and integral
Q_B	Reboiler duty
Nr	Numbers of the rectifying stages
Nrz	Numbers of the reaction stages
Ns	Number of the stripping stages
Kc	Gain
Ti	Integral time
T_C	Temperature controller
K_U	Ultimate gains
P_U	Ultimate periods

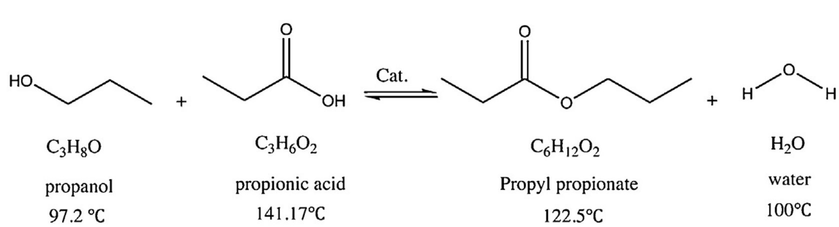
concluded that the entrainer assisted reactive distillation process combines both the advantages of heterogeneous azeotropic distillation (HAD) and RD. De Jong et al. (2008) studied the entrainer assisted RD process and the conventional RD process for the fatty acid esters production. They concluded that the E-RD process is able to reach the required conversion of 99%, and the E-RD process needs fewer reactive stages and energy consumption than that of the conventional RD process. Hu et al. (2011) investigated an entrainer assisted RD process for the ethyl acetate production, in the process, *N*-butyl acetate is selected as the entrainer to carry out H_2O from the RD column. The entrainer assisted reactive distillation process can save 32% of energy consumption compared with the conventional RD process. As is concluded in the literature (De Jong et al., 2008; Dimian et al., 2002; Hu et al., 2011; Wang and Huang, 2011), the entrainer-assisted reactive distillation process can not only produce high purity products, but also reduce capital investment and operation costs. To reduce capital cost and energy consumption of the two-column process, the entrainer-assisted reactive distillation (E-RD) process can be used to produce Propro.

Dynamic control is another important aspect in the E-RD process. The control structure of E-RD process is more complex than the control structures of the RD systems and the azeotropic distillation systems. The control of RDC and the azeotropic distillation column have been deeply investigated by many researchers. But the control structure of the entrainer-assisted reactive distillation column has attracted less attention. Chen et al. (2016) proposed a temperature control structure to control a RD process for the Methyl Valerate production. Based on the control structure, the reboiler duty is utilized to control the tray temperature of the column. In terms of dynamic performance, the control structure was able to deal with disturbances, maintain the methyl valerate purity, and get to steady state very fast. Huang et al. (2004) proposed a temperature control structure to control the heterogeneous reactive distillation process. The ratio scheme between the two reactants is used to keep the balance of reactants and the reboiler heat duty is used to control the tray temperature of the column. The dynamic results show that the control structure can reject throughput disturbances very fast and maintain the product purity. Wang and Wong (2006) investigated a temperature control structure to control the entrainer-added RD process for the fatty ester production. In the process, the tray temperature of the entrainer-added RD is controlled by manipulating the reboiler duty. The dynamic results show that the temperature control scheme has good dynamic performance. Hung et al. (2014) investigated the tray-temperature control strategy to control the triacetin reactive distillation process for the utilization of glycerol. The dynamic results show that the proposed tray-temperature control strategy is able to maintain product purity despite disturbances from throughput and feed composition changes. Since temperature control structure has good dynamic performance of reactive distillation, heterogeneous azeotropic distillation and entrainer-assisted reactive distillation. Thus the temperature control structure can be used to the control the E-RD process for the production of Propro.

Though many researches illustrate the advantages of the E-RD process, the E-RD process hasn't been studied for Propro production, so far. The aim of the research is to investigate the synthesis of Propro by the esterification of POH and ProAc in the E-RD process. A proper entrainer is selected for the E-RD process. And the E-RD process is optimized through calculating the minimum total annual cost (TAC). Moreover, two control structures are proposed to evaluate the stability and controllability of the E-RD process.

2. Kinetics and thermodynamics

Propro is synthetized by the reversible liquid-phase esterification reaction of ProAc and POH, the reaction equation is shown as:



(1)

The esterification reaction is a reversible reaction. It requires to be catalyzed by acidic cation exchange resin (Amberlyst 46^{TM}). Amberlyst 46^{TM} has the maximum operating temperature of 120 °C