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The partial heat-integrated pressure-swing reactive distillation process for transesterification of methyl acetate with isopropanol

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ABSTRACT

A novel partial heat-integrated pressure-swing reactive distillation process is designed for the transesterification reaction of methyl acetate and isopropanol. Aspen Plus is used to investigate the steady state for obtaining the optimal configurations of the processes. The partial heat-integrated pressure-swing reactive distillation process can save 33.41% energy consumption and 27.16% total TAC in comparison with conventional reactive distillation process. The basic and improved control structures for the partial heat-integrated pressure-swing reactive distillation process are studied using Aspen Dynamic. The improved control structure can deal with the feed disturbances very well and maintain product purities with acceptable transient deviations and settling times.

1. Introduction

There is a great amount of methyl acetate in production of purified terephthalic acid and polyvinyl alcohol [1]. In industry, methyl acetate is generally applied to the production of acetic acid and methanol via hydrolysis. An alternative method to take advantage of methyl acetate is the synthesis of isopropyl acetate via the transesterification reaction of methyl acetate and isopropanol, which is comparatively more attractive [2].

Reactive distillation (RD) is an innovative process which integrates physical separation and chemical reaction into one unit with less needing of capital investments and operating costs. It has attracted much more attention recently, because it is a process intensification method relying on its capacity of improving reaction conversion and simplifying separation process by means of reacting away azeotropes and removing products simultaneously. For reversible reactions, the removal of products can drive the reaction toward the direction of forward reactions. That is beneficial for improving conversion. Reports about reactive distillation have grown rapidly recently, and the researches covers several sides including process design, steady-state description and control strategies. In the book of Sundmacher, more than one hundred industrial and potential chemical reactions for RD applications were surveyed [3]. Luyben and Yu proposed numbers of reaction systems designed using RD and hundreds of publications and patents in past decades [4]. Transesterification is a slow process which can make an ester transformed into another ester by the interchange of an alkoxy group [5]. And like the esterification reaction, the transesterification reaction is a typical reaction which is equilibrium limited, for the reason of which, RD can be applied into transesterification reaction to improve reaction conversion [6]. Therefore, the RD can be applied into the transesterification of methyl acetate with isopropanol. In conventional RD, there is only conventional distillation column to be considered. But there are three azeotropes involved in this transesterification reactive system. Consequently, a recycle column should be used in RD process. In the recycle column, azeotropes can be easily separated. Wang et al. proposed a flowsheet composed of a reactive distillation column (RD column) and a recycle distillation column (RC column) to produce *n*-butyl acetate by transesterification reaction of methyl acetate and *n*-butanol [7]. The distillate product containing of methyl acetate-methanol mixture in the RD column was fed into the RC column for separating the high-purity methanol from the methyl acetate-methanol mixture. Then the methyl acetate-methanol mixture rich in methyl acetate in the distillate of the RC column was recycled back to the RD column and is further reacted with *n*-butanol. Thus, the high-purity methanol could be obtained in the bottom product and recovered in the RC column. Meanwhile, the reaction conversation was improved.

With the applying of RD, the higher reaction conversation and recirculation of reactants are realized. It should be mentioned that

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Nomenclature

MEOAC	Methyl acetate
IPA	Isopropanol
IPAC	Isopropyl acetate
MEOH	Methanol
RD	Reactive distillation
PSD	Pressure-swing distillation
PSRD	Pressure-swing reactive distillation
RC	Recycle distillation column
RR	Reflux ratio
NF_{IPA}	Feed location of IPA
NF_{MEOAC}	Feed location of MEOAC
Nr	Stage number of rectifying section in RD column
Nrex	Stage number of reactive section in RD column
Ns	Stage number of stripping section in RD column
NT	Total stage number of RC column
NF	Feed location of RC column
D1	Distillate stream in the top of RD column, kmol/hr
D2	Distillate stream in the top of RC column, kmol/hr
B1	Bottom stream of RD column, kmol/hr
B2	Bottom stream of RC column, kmol/hr
K_a	Equilibrium constant of the reaction in terms of activity
k_r	Reverse reactive rate constant, mol/g of dry resin·min
T	Reaction temperature, K
TAC	Total annual cost, $/year
F	the fresh feed, kmol/hr
TC	Temperature controller
P_I	Proportional and integral
K_U	Ultimate gains, %/%
P_U	Ultimate periods, min
K_C	Gain, %/%
τ_I	Integral time, min

a minimum-boiling homogeneous azeotrope will be formed between methyl acetate and methanol in the reaction system. Pressure-swing distillation (PSD) is one efficient way for separating the homogeneous azeotropes based on the shift of the relative volatilities and azeotropic compositions as change of the system pressure [8,9]. Better separation efficiency usually can be achieved with using of different operating pressures in two columns. In recent years, the PSD has gained more and more widespread attention. Repke et al. studied the separation of the homogeneous azeotropic mixture of acetonitrile-water system with PSD [10]. The separation of tetrahydrofuran-water mixture was studied by Hamad A in steady state design with the global energy optimization strategies [11]. The results showed that the PSD process had more than 60% reduction on energy requirements compared with conventional distillation process. Wang Y et al. investigated the PSD process to separate binary azeotropic mixture of tetrahydrofuran-methanol [12]. The results showed that the PSD process had greater reduction on total annual cost compared with the traditional distillation process. In addition, the PSD can also be used to deal with the homogeneous azeotropic mixture in the RD process. Thus, the pressure-swing reactive distillation (PSRD) is proposed for the transesterification of methyl acetate with isopropanol. Modla G suggested a new double-column system by applying reactive pressure swing batch distillation for the production of ethyl-acetate through the reaction of ethanol with acetic-acid in the presence of an acid catalyst [13]. The reactive column was operated at the higher pressure of 10 bar and the non-reactive column for removing water was operated at the lower pressure of 1.01 bar. The research was studied by rigorous simulation and stated that the reduction of the number of the plates was impossible without an increase in the heating requirement. With the PSD applied, the heat-integration technology is a nice choice for improving economic performance of the conventional RD process [14–16]. The basic idea of the heat-integration technology is to use the overhead vapor from one column as a heat source in another column. Due to that different operating pressures are used for two columns, there is a reasonable different temperature driving force for heat transfer in heat exchanger as the condenser of high-pressure column and the reboiler of low-pressure column, and thus, the heat-integration between two columns can be realized, and much more energy consumption can be saved with heat-integration technology. Any differences between the heat duties of two columns require the use of an auxiliary condenser and reboiler, which can also improve the dynamic controllability at the same time. Jana A K summarized the heat-integration technology applications in some distillation process [17]. Abushwireb F firstly investigated the operational feasibility of several heat-integrated extractive distillation technologies [18]. However, the development of current work about the transesterification reaction between methyl acetate and isopropanol is not very comprehensive in academic work so far, and the explorations about the heat-integrated pressure-swing reactive distillation (the heat-integrated PSRD) process are also scarce. In the industrial, the significance of recycling and reusing of methyl acetate and isopropyl acetate are becoming more and more outstanding. For this reason, there are special needs to design and research an effective process of the studied system for practical application.

The control strategies for RD process have been discussed in so many papers. [19–22] Chung Y H researched the associated control strategies for the manufacture of *n*-butyl levulinate using RD process [23]. Two feasible control structures are presented: single-point temperature control and dual-point temperature control. A series of simulations shows that both control strategies can reject throughput disturbances quite well and achieve necessary control performance in face of feed composition disturbances. The studies of dynamic control for azeotropes separation with the heat-integrated distillation process are rarely discussed in the literatures. Luyben W L studied steady-stage designs and dynamic controls for the separation of azeotropic mixtures and proposed some control structures for the heat-integrated PSD process [24–26]. The investments pointed out that due to the variation of operating pressure, the dynamic control of the PSD process with heat-integration performs much more complicated in comparison with usual distillation process without heat-integration. And the control of heat-integrated PSD process can be realized by adding the flow sheet equations in the dynamic. However, the control of the heat-integrated PSRD process is seldom researched at present. In the industrial, there are no practical applications on the control of the studied reactive system. And in the open literatures, the steady and dynamic simulations with equilibrium modeling are uncommon and required to be further completed.

The purpose of this work is to get a novel partial heat-integrated PSRD process of the transesterification reaction of methyl acetate and isopropanol. And the economical optimization is analyzed for screening the best configuration of this novel process. The energy saving potential of the partial heat-integrated PSRD process is investigated by comparison with that of a conventional RD process. Moreover, the two different control structures of this novel heat-integrated PSRD process are also proposed to maintain the molar fractions of products with the feed flow rate and feed composition disturbances being introduced. Few reports about design and control of the partial heat-integrated PSRD process for