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Reactive distillation with pervaporation hybrid configuration for enhanced ethyl levulinate production

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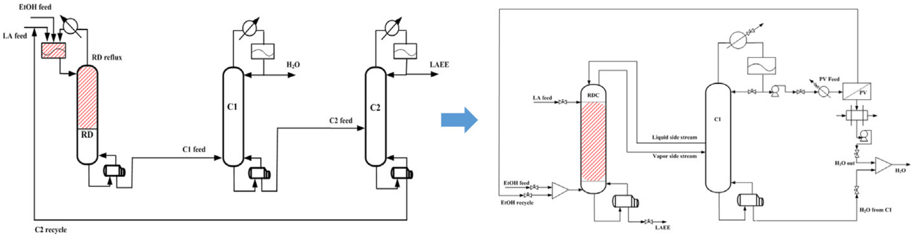
HIGHLIGHTS

- A novel RD combined with PV process was proposed for enhanced LAEE production.
- The excess EtOH reactant showed a significant advantage over the excess LA case.
- The proposed hybrid configuration reduced the energy and TAC remarkably.
- Thermal coupling enhanced the efficiency of the hybrid process successfully.
- Series PV arrangement was suitable for LAEE production process.

GRAPHICAL ABSTRACT

Thermally coupled reactive distillation-pervaporation ($TCRD_{SS}$-PV) hybrid configuration saves the energy requirement of LAEE production process remarkably up to 73.0%.



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ABSTRACT

A hybrid process design based on reactive distillation (RD) combined with pervaporation membrane systems was proposed for the production of ethyl levulinate (LAEE) via esterification. In the proposed hybrid configuration, LAEE is produced from the bottom stream of the RD column while the ethanol/water mixture from the overhead is fed to an additional column. The azeotropic mixture in the overhead of the additional column is separated in the pervaporation unit, and the ethanol-rich stream is recycled to the RD column. An RD-only configuration with excess ethanol reactant was also examined to investigate the benefit of excess ethanol reactant and the azeotrope mixture separation. The proposed RD with pervaporation hybrid configuration provided 61.0% and 71.0% reductions of the total annual cost and energy, respectively, compared to the conventional RD configuration with excess levulinic acid (LA) reactant and 6.0% and 13.0%, respectively, as compared to the conventional RD configuration with excess ethanol reactant. The results demonstrated the advantage of the proposed hybrid RD process using pervaporation for lowering the cost and improving the energy efficiency of LAEE production. Different pervaporation arrangements (such as series and parallel arrangements) were discussed in connection with the two main variables (operating temperature and concentration gradient) affecting the membrane flux. The series arrangement was more suitable for the LAEE hybrid process because the influence of the operating temperature is dominant in this process. Thermal intensification in the RD-pervaporation was also examined for exploring further energy reduction. This thermally coupled RD-pervaporation hybrid configuration

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Abbreviations: LAEE, ethyl levulinate; LA, levulinic acid; PV, pervaporation; RD, reactive distillation; RD_{LA}, reactive distillation using an excess LA reactant; $RDEt_{OH}$, reactive distillation using an excess EtOH reactant; TAC, total annual cost; TCD, thermally-coupled distillation; TCRD, thermally-coupled reactive distillation; $TCRD_{SS}$, thermally-coupled reactive distillation with a side-stripper; $TCRD_{SS}$-PV, thermally-coupled reactive distillation–pervaporation.

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provided further reductions in total annual cost and energy by 63.0% and 73.0%, respectively, compared to the conventional RD configuration with excess LA reactant.

1. Introduction

Ethyl levulinate (LAEE), which is one of main derivatives of levulinic acid (LA), has attracted considerable interest as a next-generation fuel additive with its many advantages such as higher engine efficiency and lower CO and NO_x emissions (Fagan and Manzer, 2006; Joshi et al., 2011). The global LAEE market is expected to reach USD 11.8 million by 2022 (Grand View Research, 2016). Because the global LAEE industry is still in its nascent stage, research has focused primarily on R&D for a novel commercial LAEE production technology. Unlu and Hilmioglu (2016) mentioned that the synthesis of LAEE can be generally carried out using a homogeneous catalyst in a conventional batch reactor. However, Huber et al. (2006) reported that ester levulinates, including LAEE, are normally produced in two reaction steps: LA is dehydrated to angelica lactone and then mixed with an alcohol to form levulinate. However, the two reaction steps make the process complicated and expensive. To address the problem associated with the two reaction steps, Nandiwale et al. (2013) carried out an esterification experiment, in which LA reacted directly with alcohol to form levulinates. Because the esterification process is a reversible reaction where high conversion can only be achieved if the backward reaction is minimized, they employed excess ethanol (EtOH) to reach the high conversion of LA in the esterification reaction. Recently, to overcome the equilibrium limitation in the esterification of LA more efficiently, Novita et al. (2017) applied a reactive distillation (RD) technique to the LAEE production process and proposed several reactive distillation configurations with excess LA reactant.

Reactive distillation is an important example of combined reaction and separation in a single column, and is especially useful for equilibrium-limited reaction systems (Buchaly et al., 2007; Taylor and Krishna, 2000). Reactive distillation offers numerous advantages, such as improved yield and selectivity, decreased energy requirements, and avoidance of hot spots (Novita et al., 2015). These advantages are promising for the application of reactive distillation columns in esterification, where the conventional process has an equilibrium limitation and high operating costs.

Thermally-coupled distillation (TCD), where either the condenser or the reboiler, or both, in one column are replaced by additional thermal links (an interconnecting vapor liquid stream) to the other columns, is an attractive alternative that offers lower energy consumption in distillation processes (Triantafyllou and Smith, 1992). Both reactive distillation and thermally-coupled distillation are further developments of the conventional distillation unit (Wang et al., 2010) but represent two different methods of integration. However, reactive distillation and thermally-coupled distillation can be combined to create a new process integration concept termed "thermally-coupled reactive distillation" (TCRD). By implementing thermally-coupled reactive distillation, the advantages of both processes (reactive distillation and thermally-coupled distillation) can be harnessed and enhanced, and further cost reduction is possible compared to the conventional distillation unit. In particular, thermally-coupled reactive distillation is suitable to particular reaction-separation systems in which the unreacted components and products are integrated in at least a ternary mixture (Galindo et al., 2011).

Along with the distillation system, membrane systems are now recognized as a possible alternative to traditional energy intensive separation methods such as distillation. Membrane systems often offer lower capital and utility costs and can be used for a wide range of separations (Verhoef et al., 2008). Pervaporation (PV) membrane is most suitable if the liquid mixtures form an azeotrope or contain thermally-unstable components and/or have components with close boiling points (Nagai, 2010). In pervaporation, the feed and retentate are in the liquid-state on the high-pressure side of the membrane, while the permeate is removed as a vapor on the low-pressure side of the membrane. Pervaporation has been the subject of many papers for several decades as mentioned by Luyben (2009). As a stand-alone process, pervaporation is probably not economically feasible. However, in a hybrid or combined process, such as when coupled with a distillation unit or a reactor, the overall efficiency of pervaporation can be improved (Lipnitzki et al., 1999; Verhoef et al., 2008; Singh and Rangaiah, 2017). Based on the advantages of membrane and distillation systems, their combination with pervaporation is anticipated to find increasing application in the future (Aiouache and Goto, 2003). Recently, the research effort for distillation-membrane hybrid systems was expanded to combine it with more complicated distillation systems such as thermally coupled and reactive distillation (Lee et al., 2016; Harvianto et al., 2017a, 2017b).

In this paper, a novel hybrid process combining reactive distillation and pervaporation is proposed for the enhanced production of LAEE via esterification. To force the forward reaction in the esterification of LA to LAEE, an LA or ethanol reactant needs to be provided in excess to the reactive distillation column while the product H_2O recycled to the reactive distillation column, if any, is minimized. In the proposed hybrid process, an excess EtOH reactant configuration was chosen to utilize a highly selective membrane unit for EtOH/H_2O separation. A reactive distillation-only configuration with the excess EtOH reactant, where the EtOH/H_2O azeotrope mixture is recycled to the reactive distillation column without further separation, was also examined to investigate the effect of different excess reactants and the azeotrope mixture separation on overall process performance. Thermal intensification was also investigated for exploring further energy and cost reductions in the RD–pervaporation hybrid process. The arrangements of the pervaporation unit are also discussed to highlight its significance in real applications of membrane hybrid configuration.

2. Model development

2.1. Thermodynamic and kinetic models

There are four components in the studied system, i.e., two reactants (EtOH and LA) and two products (LAEE and H_2O). The non-random two liquid (NRTL) model was used to calculate the liquid activity coefficient, and the Hayden and O'Connell (HOC) model was used to account for association in the vapor phase (Novita et al., 2017). The EtOH and H_2O pairing parameters were obtained from the Aspen Plus built-in database, and the remaining parameters refer to the regressed results from Resk's paper (Resk et al., 2014).

The reversible esterification reaction for the studied system is represented as:

$$C_5H_8O_3 + C_2H_5OH \underset{k_2}{\overset{k_1}{\Longleftrightarrow}} C_7H_{12}O_3 + H_2O \tag{1}$$

(LA) (EtOH) (LAEE) (H_2O)