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Modeling and analysis of solid catalyzed reactive HiGee stripping

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HIGHLIGHTS

- Concept of solid catalyzed reactive HiGee stripper (SCRHS) is introduced.
- Interdependent esterification and etherification reaction system is analyzed.
- Modeling, simulation and parametric analysis of SCRHS is performed.
- Catalyst modeling and component-based effectiveness factor are included.
- Better mass transfer and conversion are achieved in SCRHS over conventional reactors.

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ABSTRACT

Increasing emphasis on process intensification for enhancing industrial chemical processes opens up many promising opportunities for an integrated rather than sequential (the onion-model approach) process synthesis and design. The present article introduces the concept of solid catalyzed reactive HiGee stripper (SCRHS) where reaction and stripping are integrated in a solid catalytic rotating packed bed. SCRHS is modeled for an esterification reaction, and analyzed in detail. Rotation of reactive stripper offers several advantages such as faster mass-transfer and higher product concentration over conventional reactors. Intraparticle diffusion-based modeling, component-based effectiveness factor, and instantaneous selectivity provide several insights into the proposed integrated process. Obtained results are encouraging and show that SCRHS is a promising candidate for future esterification plants.

1. Introduction

Integration of reaction and separation in a single unit results in considerable reduction in the size of a plant and accompanied by benefits such as increased conversion, reduced recycles and increased safety. Reactive distillation (RD), reactive stripping (RS) and reactive absorption are few of the many examples of such integration (Sundmacher et al., 2005). Although RD has received industrial acceptance, it is found to be applicable and beneficial only when the operating regimes for reaction and the separation window overlaps. However, the approach of RD may not be beneficial when heat-sensitive reactants or products are present within the system. RS is a better alternative for such situations. It also provides greater operational freedom by allowing the engineer to manipulate both temperature and pressure, independent of each other for reaction and separation. Schembecker and Tlatlik (2003) reported that energy consumption for the production of high boiling esters is lower for RS compared to RD for partial conversion in a one-pass configuration.

Although RS has several advantages, mass transfer in conventional RS beds is slow resulting in tall and bulky columns. Moreover, although countercurrent RS is beneficial over cocurrent RS in terms of conversion, gas/liquid flow rates in the former are constrained to a narrow range to avoid the problem of flooding. This further limits the reactor to operate at lower capacities. The present article introduces the concept of a solid catalyzed reactive HiGee (high gravity) stripper (SCRHS) with esterification reaction as an illustrative application. Esterification reactions are of prime relevance to the process industries with ethyl acetate, butyl acetate and amyl lactate being a few out of the many important examples. To the authors' knowledge, only a single work on liquid catalyzed reactive HiGee stripping (LCRHS) has been reported till now for industrial production of hypochlorous acid (HOCl) by Dow Chemical (Trent and Quaderer, 1999). No further work or analysis is available in the open literature until now.

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The general form of an esterification reaction involves reaction of acid and alcohol to form ester as the main product:

$$\text{Acid} + \text{Alcohol} \Leftrightarrow \text{Ester} + \text{Water}$$

These reactions are reversible in nature, and are often mass-transfer limited. Catalysts used for esterification reactions are generally mineral acids in liquid state. Kinetics of these reactions is reasonably fast but the mixing of the reactants is slow and non-uniform. For solid-catalyzed esterification reactions, constant removal of water is necessary as its presence poisons the catalyst. The major benefits of solid catalyzed esterification include reduction in corrosive waste streams and downstream separation costs. The solid catalyst used for these reactions is generally encapsulated within a specially designed structured packing, or the catalyst itself is coated over the inert packing of the column.

Modeling and analysis of an intensified SCRHS for minimizing the thermodynamic and mass-transfer limitations encountered in conventional packed beds is the focus of the current work. Mathematical modeling of SCRHS is performed using first-principles approach, and its performance results are discussed in detail. Component-based effectiveness factor as a measure of overall diffusional resistance within the porous catalyst is also studied. Influence of the centrifugal field on the ester formation and any variation on the catalyst effectiveness factor is further analyzed to gain more insights into the proposed SCRHS process. The obtained results are encouraging and show that SCRHS is promising for the future esterification plants.

2. Proposed solid catalyzed reactive HiGee stripper (SCRHS)

HiGee (acronym for high gravity) involves the rotation of a torus packed bed under high centrifugal force, thereby achieving increased overall gas–liquid mass transfer (Ramshaw and Mallison, 1981). The packing within the HiGee packed bed generally consists of inert material with characteristics of high specific surface area to volume ratio. Because of its low tendency of flooding, HiGee can be operated at a higher gas/liquid flow ratios when compared to conventional packed beds. With about 60% of process operations in chemical industries involving multiple phases, HiGee represents an important technique for achieving highly intensified operations (Burns et al., 2000). Studies, which explored HiGee for different mass-transfer processes, are for absorption (Agarwal et al., 2010; Chen and Liu, 2002; Jassim et al., 2007; Reddy et al., 2006), stripping (Chen et al., 2005; Singh et al., 1992), distillation (Agarwal et al., 2010; Kelleher and Fair, 1996; Li et al., 2008; Lin et al., 2002; Nascimento et al., 2009), adsorption (Lin and Liu, 1999; Lin et al., 2004), desorption (Tan and Lee, 2008), reaction (Chen et al., 2010; Dhiman et al., 2005) and nanoparticle preparation (Chen and Shao, 2003).

Fig. 1 shows the schematic of an SCRHS system. The modification for SCRHS is that the inert packing material within the conventional HiGee is replaced by porous solid catalytic packing. The packing within the multiphase reactor thus acts as both a catalyst surface and a mass transfer surface, over which the inert gas phase and reactive liquid phase contact each other in counter–current direction. Reaction kinetics used for the analysis of SCRHS is from the work of Schildhauer et al. (2009) where the esterification of 1-octanol with hexanoic acid was studied. Reasons for selecting this reaction system are its similarity to several industrial processes and its ability to demonstrate the interdependencies of activity, selectivity and mass transfer in reactive separations (Schildhauer et al., 2005a). The esterification

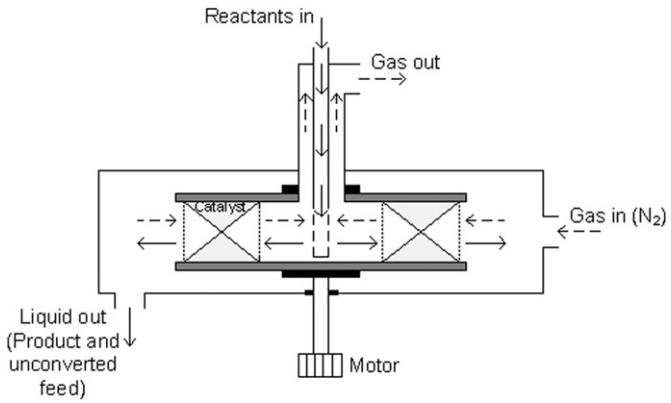

Fig. 1. Schematic of a solid catalyzed reactive HiGee stripper (SCRHS).

Table 1
Vapor pressures of pure components at 150 °C (Mueller et al., 2007).

Component	Vapor pressure (bar)
Water	4.75
Cumene	0.95
1-octanol	0.24
Hexanoic acid	0.15
Octyl-hexanoate	0.02
Dioctyl ether	0.01

and etherification reaction of hexanoic acid and 1-octanol is as follows:

$$1-\text{Octanol} + \text{Hexanoic acid} \Leftrightarrow \text{Octyl}-\text{hexanoate} + \text{Water} \quad (1a)$$

$$2(1-\text{Octanol}) \Leftrightarrow \text{Dioctyl ether} + \text{Water} \quad (1b)$$

1-octanol reacting with hexanoic acid to form octyl-hexanoate (Eq. (1a)) is the main reaction of interest. A side reaction where 1-octanol forms a dimer of dioctyl ether and water is shown in Eq. (1b). The system analyzed here is the integrated octyl-hexanoate esterification followed by stripping of water by nitrogen from a multi-component mixture of solvent (cumene), ester, ether, 1-octanol and hexanoic acid at 5 bar and 160 °C.

Some of the many parameters used for the present analysis of SCRHS are obtained from the works of Ramshaw and Mallison (1981) and Schildhauer et al. (2005b). Due care is given for the selection of bed porosity, specific surface area of packing and dimensions of HiGee (Ramshaw and Mallison, 1981). Bulk density for granular shaped Zeolite (Aluminum silicate) catalyst is obtained from Perry's Chemical Engineers' Handbook (Green et al., 2008). The reactants (hexanoic acid and 1-octanol), each mixed in solvent (cumene) with equimolar concentration of 100 gmol/m^3, are fed into the inner radius of the HiGee bed by coaxial distributors placed at the eye of the rotor. Simultaneously, gas (here, nitrogen) enters from the casing of the SCRHS, and the enhanced gas–liquid–solid contacting occurs within the catalyst zone of packed bed. Under high centrifugal force-field, reactants will travel in the form of thin films over the catalyst surfaces, resulting in efficient reaction and mass-transfer. Since water has the minimum boiling point and highest vapor pressure among other components in the liquid phase (Table 1), it can be removed easily from the reaction mixture as soon as it is formed. Inert gas (nitrogen) is used as the stripping agent to remove water from the