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A new hybrid membrane separation process for enhanced ethanol recovery: Process description and numerical studies

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ABSTRACT

Ethanol is a biofuel, produced through the fermentation of sugars derived from biomass. Its usefulness as a fuel is limited by the energy intensive nature of the ethanol separation process. The ethanol recovery process is inefficient due to the dilute nature of the fermentation product and the presence of the ethanol – water azeotrope. This investigation presents a new hybrid separation process for energy efficient ethanol recovery. The new process is a hybrid of distillation and pervaporation. However, as opposed to most other hybrid processes, the distillation and pervaporation processes are combined into single unit. An overview of the proposed system was provided and differences to the conventional separation process were highlighted. A mathematical model was derived to explain the transport phenomena occurring in the hybrid process. The model was then used to compare the process to distillation. It was shown that the hybrid process is capable of breaking the ethanol-water azeotrope. It was also demonstrated that the pervaporation process, which is associated with both material and energy transfer, induces partial condensation of the vapor and thereby affects the efficiency of vapor – liquid contacting. Simulations were presented to show the impact of reflux ratio and pervaporation flux on the performance of the process.

1. Introduction

Ethanol is a biofuel that can be produced through the fermentation of saccharides found in biomass. However, the utility of ethanol as a biofuel is limited due to the energy intensive nature of its production process. Ethanol separation from water is a particularly energy intensive part of the production process, usually accounting for more than half of the total process energy requirement. Further, only anhydrous ethanol can be blended with gasoline and used in conventional gasoline burning engines. The requirement to produce anhydrous ethanol complicates the production process because ethanol and water form an azeotrope, making it impossible to recover pure ethanol through simple distillation. A special dehydration process is therefore required to recover anhydrous ethanol. The most commonly used methods for ethanol dehydration are currently extractive distillation, pressure swing adsorption of water on molecular sieves and pervaporation or vapor permeation of water through hydrophilic membranes (Cardona and Sánchez, 2007).

In the conventional ethanol separation process, the fermentation mixture is first passed through a beer column. This column essentially behaves as a steam stripping column and produces a vapor stream having an ethanol composition between 40% and 60% by mass (although this can vary). The bottoms stream leaving the beer column is composed mainly of water, with some residual solids. The vapor stream leaving the beer column usually enters another column, which operates as the enriching section of a distillation column. The bottoms product leaving the enriching column can go to a separate stripping column or be returned to the beer column. The distillate leaving the enriching column is normally near the azeotropic composition (approximately 90% ethanol by mass). This distillate stream then undergoes dehydration to produce an anhydrous ethanol product (Cardona and Sánchez, 2007; Vane, 2008).

Dephlegmation is a process in which a vapor, flowing upwards along a solid surface, is partially condensed. Liquid condensate is then allowed to flow in a countercurrent fashion to the vapor through the action of gravity. Similar to distillation, countercurrent contacting leads to the accumulation of the more volatile species in the vapor and the less volatile species in the liquid (Vane et al., 2004). If this process is augmented with an external reflux, it becomes non-adiabatic distillation. A number of studies have shown the potential thermodynamic benefits of adding or removing varying quantities of heat from stages in a distillation column (Kjelstrup Ratkje et al., 1995; Sauar et al., 1997; de Koeijer et al., 2004; Rivero, 2001; Demirel, 2004). The addition or removal

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of heat modifies the temperature and composition profiles, which allows for the minimization of the entropy production rate, thereby improving the thermodynamic efficiency of the column.

The ultimate goal of an ongoing set of studies is to synthesize a more efficient hybrid separation system to replace the enriching column and dehydration section of the ethanol recovery process. The proposed system is a hybrid of pervaporation, distillation and dephlegmation processes. In this study, an overview of the proposed system is provided along with a comparison to the conventional separation process. A mathematical model is then developed to describe the process and explain the transport phenomena governing its performance. Model results are then used to compare the theoretical performance of the system to the wetted-wall distillation process. The geometry used to study the process is that of a real, commercially available NaA zeolite membrane. A literature model is used to describe transport through the membrane.

2. Process description

To put the description of the proposed separation process into perspective, an overview of the conventional ethanol recovery process is first presented. Fig. 1 presents a schematic overview of the conventional separation process. In reality, the feedstock pretreatment and fermentation steps of the ethanol production process are usually quite complicated. However, these are not the focus of this study and are therefore not discussed. The fermentation step produces a stream that usually contains at most 10% ethanol by mass, if conventional substrates are used and at most 5% ethanol by mass if cellulosic biomass is used. The fermentation broth then undergoes a separation step to remove insoluble solids. After solids separation, the dilute mixture is usually sent to a steam stripping column (beer column). The steam stripping column can operate with a reboiler or direct steam injection. In either case, ethanol is stripped from the feed stream to generate a vapor phase distillate stream that usually contains between 40% and 60% ethanol by mass. The concentration of this distillate stream depends on the design of the beer column as well as the feed composition. The vapor stream exiting the beer column is then normally sent to a rectifying column, which increases the ethanol concentration to near the ethanol-water azeotrope. The concentration of the distillate stream leaving the rectifying column varies depending on the design of the column (i.e. reflux ratio and number of stages), but cannot exceed the composition of the ethanol–water azeotrope ($\sim$ 95.6% by mass). Commonly the distillate concentration is between 90% and 94% ethanol by mass. Normally, this distillate stream then goes to a dehydration system (commonly Pressure Swing Adsorption, Pervaporation or Vapor Permeation), which produces anhydrous ethanol. The bottoms leaving the rectifying column is either recycled to the beer column or sent to a separate side stripping column to maintain a high ethanol recovery.

This study proposes a new hybrid pervaporation–distillation process. These types of hybrid processes have been the subject of a large number of investigations. To provide some background, a brief summary of the most relevant studies is provided here. Generally, two types of hybrid processes have been investigated. Several studies have attempted to generate optimal designs for using pervaporation as the dehydration stage following distillation. Other studies have integrated the pervaporation process directly with other separation processes, using complex recycle streams and energy integration. Lipnizki et al. (1999) presented a review of hybrid pervaporation processes. Included in their paper is a discussion of different approaches to integrate pervaporation with distillation in the ethanol production process. Frolkova and Raeva (2010) provided a comprehensive review of methods available for ethanol dehydration. Their discussion also included a hybrid pervaporation–distillation process for breaking the ethanol–water azeotrope. Szitkai et al. (2002) attempted to optimize the performance of a hybrid distillation–pervaporation process for ethanol separation. Their study employed a Mixed-Integer Nonlinear Programming (MINLP) approach to minimize the total annual cost.

Vane (2005) reviewed various approaches to integrate pervaporation into the recovery of products from biomass fermentation. Ethanol production was one of the main topics covered. The review also presented several original processes employing both hydrophobic and hydrophilic membranes in conjunction with distillation to improve process efficiency. More recently, this group proposed an innovative process, which combines distillation and vapor permeation to improve process energy efficiency (Vane and Alvarez, 2008; Huang et al., 2010; Vane et al., 2010). Several variations were

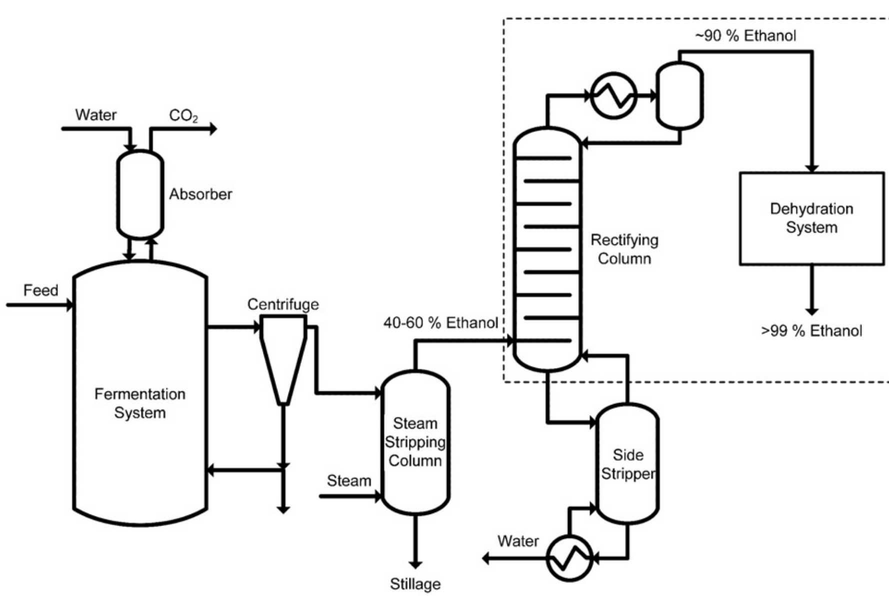

Fig. 1. Overview of the conventional ethanol recovery process.