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Innovative single step bioethanol dehydration in an extractive dividing-wall column

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ABSTRACT

The large-scale production of bioethanol fuel requires energy demanding distillation steps to concentrate the diluted streams from the fermentation step and to overcome the azeotropic behavior of the ethanol–water mixture. The conventional separation sequence consists of three distillation columns performing several tasks with high energy penalties: pre-concentration of ethanol, extractive distillation and solvent recovery. Despite the novel recent developments in pervaporation and adsorption with molecular sieves, the industrial production of anhydrous bioethanol is still dominated by extractive distillation as the separation method of choice.

This study proposes an innovative distillation setup – based on a novel extractive dividing-wall column (E-DWC) – that is able to concentrate and dehydrate bioethanol in a single step, by integrating all units of the conventional sequence into only one distillation column. In this work, a mixture of 10 wt% ethanol (100 ktpy plant) is concentrated and dehydrated using ethylene glycol as mass separating agent. Rigorous simulations were carried out in Aspen Plus, and for a fair comparison all alternatives were optimized using the reliable sequential quadratic programming (SQP) method. The results show that energy savings of 17%, and a similar decrease in CapEx, are possible for the novel E-DWC alternative, while using a significantly reduced footprint as compared to the conventional separation process.

1. Introduction

Bioethanol is so far the most promising alternative and sustainable biofuel [47,3,18]. A key advantage of bioethanol over other fuel alternatives, such as hydrogen, is that it can be easily integrated in the existing fuel systems as a 5–85% mixture with gasoline that does not need any modification of the current engines. Bioethanol fuel is widely used in Brazil and United States, and together both countries were responsible for 88% of the world's ethanol fuel production in 2010 [29]. Remarkable, the bioethanol production can be also conveniently integrated with the biodiesel production [21], especially in Brazil – a top producer of both biofuels.

The bioethanol production at industrial scale relies on several processes, such as: corn-to-ethanol, sugarcane-to-ethanol, basic and integrated lignocellulosic biomass-to-ethanol [3]. Basically, the raw materials undergo several pre-treatment steps and then enter the fermentation stage where bioethanol is produced. Fig. 1 conveniently illustrates the technological scheme of the bioethanol production process from various feedstock [45,17,11,13]. A common feature of all bioethanol technologies is the production of diluted bioethanol – in the range of 5–12 wt% ethanol – that needs to be further concentrated [45,17,13]. According to the current international bioethanol standards, the maximum allowed water content is 0.2 vol% (EN 15376, Europe), 0.4 vol% (ANP No. 36/2005, Brazil) or 1.0 vol% (ASTM D 4806, USA).

Several energy demanding separation steps are required to reach the purity target, mainly due to the presence of the well known binary azeotrope ethanol–water (95.63 wt% ethanol). The first step is typically carried out in a *pre-concentration* distillation column that concentrates bioethanol from 5–12% up to 92.4–94 wt% [47,45,17,13]. A recently proposed alternative for this step is using cyclic distillation – a method promising energy efficiency at low investment costs [32]. The second step is the *ethanol dehydration* up to higher concentrations above the azeotropic composition, hence it is more complex and of greater interest (Fig. 2). Several alternatives are available and well described in the literature: pervaporation, adsorption, pressure-swing distillation, extractive distillation (ED), azeotropic distillation (AD), as well as hybrid methods combining these options [19,31,30,8,17,18,45,13]. However, all of them reach their limits and are not cost effective in case of large scale separations [45,13]. Extractive distillation (ED) presents relatively high energy costs but is still the option of choice in case of large scale production of bioethanol fuel [45,15,13]. Usually, ED is performed in a sequence of two columns, first of them separating ethanol while the other one recovering the mass separating agent (MSA) that is recycled back.

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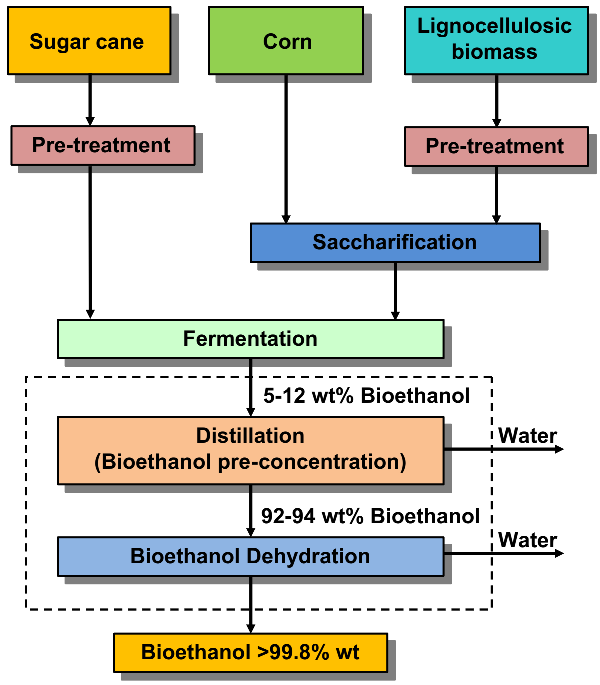

Fig. 1. Block flow diagram of the bioethanol production from various feedstock.

An innovative solution to overcome the drawback of energy intensive distillation is using advanced process intensification and integration techniques, such as thermally coupled distillation columns, dividing-wall columns (DWC), heat-integrated distillation columns, or cyclic distillation [35,14,2,9,32]. Notably, DWC is one of the best examples of proven process intensification technology in distillation, as it allows significantly lower investment and operating costs while also reducing the equipment and carbon footprint [49]. Several excellent reviews and research papers were published on this topic, covering the process design and simulation, dynamics and process control, optimal operation and applications of DWC [43,40,46,41,37,2,9,12,49,22,23,39]. Remarkable, the DWC technology is not limited to ternary separations alone, but it can be used also in azeotropic separations [26,27,44], extractive distillation [7], and even reactive distillation [33,20,16,25,26,27]. Recent studies proposed the use of DWC for azeotropic and extractive distillation of ethanol [26,27,44], but they were limited only to the dehydration step, leaving out the pre-concentration stage of the process, which is in fact the most energy intensive step.

This study proposes an innovative distillation setup (Fig. 6) – based on a novel extractive DWC – that is able to concentrate and dehydrate bioethanol in a single step, by integrating all units of the conventional sequence into only one distillation column. In a 100 ktpy plant, a mixture of 10 wt% ethanol – typical to the production of bioethanol from sugarcane or corn – is concentrated and dehydrated using ethylene glycol as solvent. Rigorous simulations were carried out in Aspen Plus, and – for a fair comparison – all alternatives considered here were optimized using the sequential quadratic programming (SQP) method.

2. Problem statement

For the use as fuel or additive, bioethanol must have a purity of min. 99–99.8 wt%, according to the current standards (EN 15376, ASTM D 4806). Most of the water present in the diluted ethanol/water mixture (5–12 wt%) from the fermentation step is removed by ordinary distillation, but the bioethanol purity is limited to max. 95.6 wt% due to the presence of a binary azeotrope with water. Cyclic distillation was recently described as an energy efficient alternative for ethanol concentration, but this method is also limited by the azeotropic composition [32]. The industrial processes currently used to remove water from ethanol involve pervaporation, adsorption, pressure-swing distillation, extractive and azeotropic distillation, or a combination of these – none of them suitable for very large scale production.

The problem of all these methods is the high energy requirements and/or equipment costs leading to penalties in the OpEx

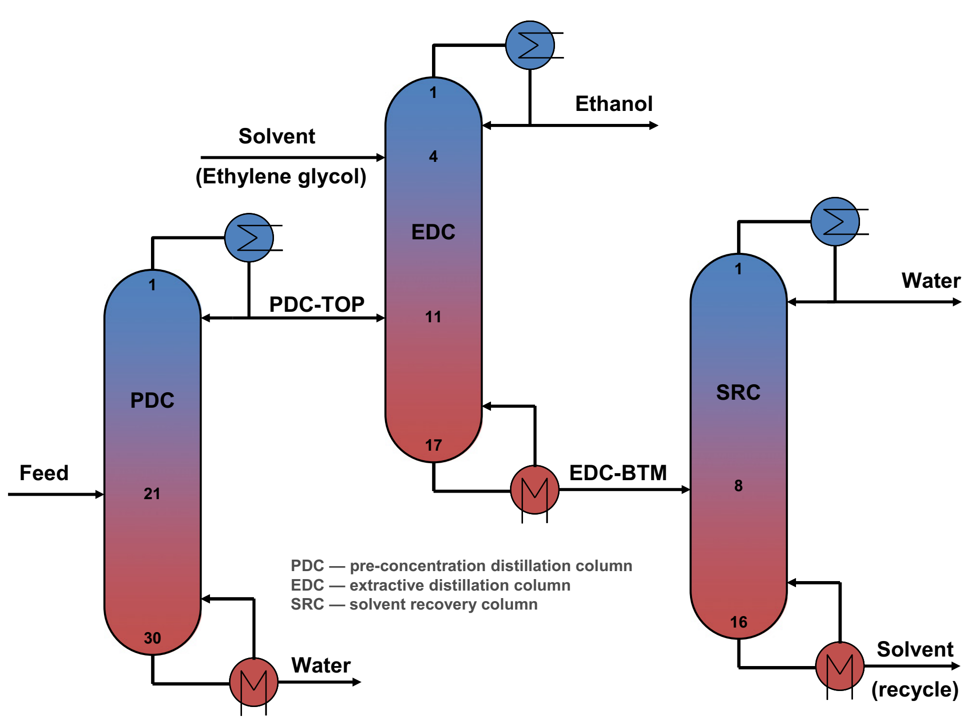

Fig. 2. Conventional sequence for the bioethanol pre-concentration and dehydration by extractive distillation.