

Design and Optimization of Thermally Coupled Distillation Sequences for Purification of Bioethanol

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Abstract

An important problem in the bioethanol production process is the purification of ethanol from a dilute solution, i.e., approximately 10% ethanol in water. The key factor in the purification process is the formation of the ethanol-water binary homogeneous azeotrope, and an additional process is required to obtain high purity ethanol that can be used in motor vehicles. This study examines the design and optimization of three extractive distillation options (two with thermal coupling) for the purification of a representative mixture of ethanol and water. These extractive arrangements can produce ethanol as distillate with the required purity and energy savings, reduction in CO₂ emissions, high thermodynamic efficiencies and good control properties.

Keywords: extractive distillation, thermal coupling, energy savings.

1. Introduction

A large portion of the world economy has been based on processes highly dependent on petroleum; as a consequence, two major problems have arisen: draining of oil reserves, and increasing gas emissions, associated with global warming. Researchers in many areas are working on solutions to mitigate these problems. One option that offers a partial solution is to intensify production and use of biofuels, including biodiesel, bioethanol, biomass, etc. Of these, bioethanol is currently being used in unmodified combustion engines in a mixture of up to 20%. The use of this mixture is important because it enables improved oxidation of hydrocarbons and, as a result, reduction in both hydrocarbon and carbon dioxide emissions (Quintero et al., 2008).

Currently, most bioethanol is produced from sugar cane, with corn in second place. However, a great deal of current research is focused on industrial production from lignocellulosic material such as agricultural and forest residues. In the production process, four main steps can be identified: Treatment of raw material to obtain the cellulosic mass, saccharification to obtain sugars from the cellulosic mass, fermentation of the sugars, and recovery of ethanol. Independently from the raw material and/or the

process used, the product obtained from the fermentation step is a dilute solution of ethanol in water, from which ethanol is separated and purified to the desired concentration. In addition to research efforts in the saccharification and fermentation process, the separation step should also be viewed as a challenge, and studied accordingly, because of the energy it requires. Assuming that the fermentation process produces a dilute solution of ethanol in water (10% in moles of ethanol) requiring treatment in order to obtain high-purity ethanol for mixing with gasoline (Cardona and Sanchez, 2007; Wingren et al., 2008), the production of high-purity ethanol using distillation requires significant quantities of energy and mass separation agents such as ethylene glycol, NaCl, KI or CaCl₂.

The key factor in the purification process is the formation of the ethanol-water binary homogeneous azeotrope. This azeotrope is formed with 96 mass percent of ethanol in water, and an additional process is required to obtain high-purity ethanol to be used in motor vehicles. Several methods can be used: the first is dehydration using a salt, e.g., NaCl, KI, CaCl₂, while a second method involves the use of ethylene glycol as an entrainer. Other option is the use of membranes for dehydration by pervaporation (Jiang et al., 2008). This study examines the design and optimization of three extractive distillation options for the purification of a representative mixture of ethanol and water using ethylene glycol (Figure 1), where two of the options use thermally coupled extractive distillation sequences (thermally coupled extractive distillation sequence, Figure 1b; and extractive Petlyuk column, Figure 1c). The study is complemented by a thermodynamic efficiency analysis, CO₂ emissions calculations and determination of control properties at zero frequency.

As previously mentioned, bioethanol can be used in a mixture with gasoline in current combustion engines (Goldemberg, 2007; Goldemberg and Guardabassi, 2009), and it is the most important biofuel produced at present, with worldwide output of about 32 million tons in 2006, of which 90% was from only two countries, Brazil and the USA (Dimian and Bildea, 2008). If bioethanol were to replace gasoline, emissions of greenhouse gases would be reduced by more than 85%, taking the complete fuel cycle into consideration (Bergeron, 1996).

2. Design of Purification Options

Figure 1 shows the three alternatives for the purification of the mixture. A dilute feed of 100 lb-mol/h ethanol in water (10% in moles of ethanol in water) as saturated liquid at 1 atm is introduced into a conventional distillation column that removes the binary homogeneous azeotrope as distillate. This study focuses on the separation stage for ethanol with a high mass fraction (0.995). The bottoms product of the first distillation column is almost pure water. This conventional distillation column is needed in all three distillation options. The first alternative (Figure 1a) uses an extractive conventional distillation column with ethylene glycol as entrainer; the distillate of the column is ethanol with a mass fraction of 0.995. The bottoms product of the extractive distillation column is a ternary mixture of ethanol, water and ethylene glycol. This mixture is fed to a third distillation column in order to recover the entrainer as bottoms product, where the distillate is a mixture of ethanol and water that can be returned to the first distillation column, where the azeotrope is formed. The second and third options (figures 1b and 1c), in the extractive stage of the separation, use a distillation column coupled to a side rectifier and a Petlyuk column, respectively.

Design and optimization methods for thermally coupled extractive distillation are reported in Gutiérrez-Guerra et al., 2009, and briefly described below: To overcome the complexity of the simultaneous solution of the tray arrangement and energy consumption in a formal optimization algorithm, we decoupled the design problem into two stages: (i) tray configuration; (ii) optimal energy consumption. The first stage of the approach begins with the development of preliminary designs for the complex systems, starting from the design aspects of conventional distillation columns. After the tray arrangement for the complex extractive sequence has been obtained, an optimization procedure is used to minimize the heat duty supplied to the reboilers of the arrangement, taking into account the constraints imposed by the required purity of the product streams. Next, the degrees of freedom that remain after design specifications and tray arrangement are used to determine operating conditions that provide minimum energy consumption. The optimization strategy can be summarized as follows: (a) A base design for the complex scheme is obtained. (b) Values for the extractant stream stage and interconnecting flows are assumed. (c) A rigorous model for the simulation of the complex scheme with the proposed tray arrangement is solved (in this study, Aspen Plus™ was used for this purpose). If product compositions are obtained, then the design is kept; otherwise, appropriate adjustments must be made. (d) One value of interconnecting flow is changed, returning to step (c) until a local minimum in energy consumption for the assumed value of the extractant stream stage is identified. (e) The value of the extractant stream stage is modified, returning to step (c) until the energy consumption is minimum (optimization criterion). This result implies that an optimum value has been identified for the design of the complex scheme.

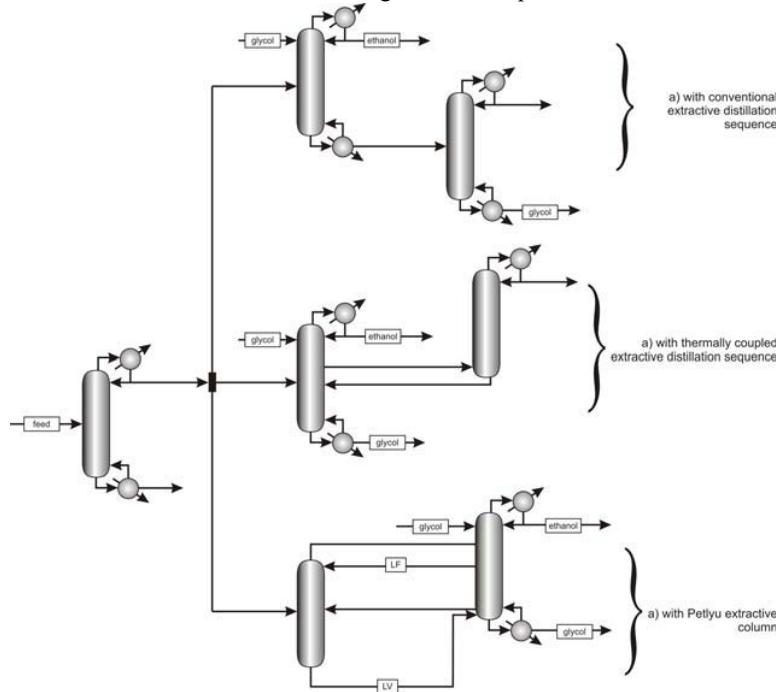


Figure 1. Purification options studied.

Thermodynamic properties of the liquid and vapor phases were calculated using the NRTL model and the Redlich-Kwong equation, respectively. Proper modeling of thermodynamic properties is very important since, in the first stage of the separation procedure, a binary distillation column is required to obtain the binary ethanol-water azeotrope. In this regard, the NRTL model can predict the formation of the binary azeotrope. In all distillation columns, the design pressure for each separation was chosen to ensure the use of cooling water in the condensers. A pressure drop of 10 psi was assumed for each distillation column of the separation sequences.

3. Results

The resulting designs and their performance with respect to optimum solvent to feed ratio (E/F), optimum energy consumption (Q), CO₂ emissions (Gadalla et al., 2005), thermodynamic efficiency (η) and control properties [minimum singular value (σ_*) and condition number (γ) at zero frequency] are discussed. As mentioned previously, the first option (Figure 1a) uses an extractive conventional distillation column with ethylene glycol as entrainer. This option has total energy consumption (including three columns) of 487.63 kW (Table 1) and it is considered a basis for the analysis.

Table 1. Results for the cases of study.

Option	E/F Optimum	Total Energy Consumption (kW)	CO ₂ Emissions (Ton/h)	η (%)	σ_*	γ
With conventional extractive sequence	1.5	487.63	0.105	8.13	0.0296	852
With thermally coupled extractive distillation sequence	1.4	497.32	0.111	7.97	0.125	57.5
With extractive Petlyuk column	1.5	362.30	0.0798	12.5	0.987	45.8

Typical optimization curves for the thermally coupled extractive distillation sequence are shown in Figure 2, where the optimal value for the extractant stage and interconnecting flowrate can be identified in order to guarantee minimum energy consumption. The optimization curves show an interesting effect of the search variables on energy consumption. The design is sensitive, in terms of its energy consumption, to changes in interconnecting flowrates and extractant stage. An implication of this observation has to do with operational considerations (the presence of recycle streams can contribute to good dynamic behavior). For all alternatives, the results can be summarized as follows: (i) the energy savings achieved by the option using a Petlyuk

extractive column are 25.7% over the option using a conventional extractive arrangement; (ii) the least favorable option is the sequence using a thermally coupled extractive distillation sequence, as it shows the highest energy consumption and lowest thermodynamic efficiency; (iii) the second law efficiency (η) of the option using a Petlyuk extractive column is higher than that of the corresponding conventional extractive distillation option; (iv) the reduction in global CO₂ emissions, in the arrangement with the Petlyuk structure, is considerable: 24% over the option using the conventional extractive sequence. The inefficiency of conventional sequences (associated with increased CO₂ emissions) has been reported as a consequence of remixing (Hernández, et al., 2006).

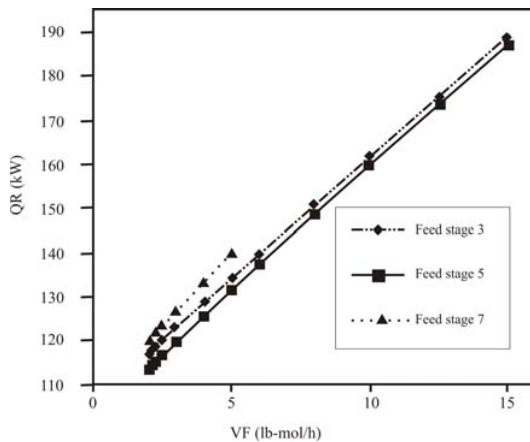


Figure 2. Search for minimum energy consumption in the thermally coupled extractive distillation sequence design.

Therefore, proper optimization of the Petlyuk extractive sequence avoids such a remixing problem. The methodology used generates designs where the effect of the remixing is eliminated. In addition, it is important to analyze the composition profiles in the extractive distillation systems. The option using the conventional extractive column can produce ethanol with a high mass fraction (0.995), with the bottoms product composed of ethylene glycol, water and ethanol. The options using complex extractive columns produce ethanol with the same mass fraction, but it is important to highlight that these complex columns separate the entrainer as the bottoms product and the side rectifier or side stream removes a mixture of ethanol and water.

A final test was carried out on the control properties of the options studied, using the singular value decomposition (SVD) technique at zero frequency. The singular values of the transfer function matrix of a process at zero frequency are the squared roots of the eigenvalues of the product of the transfer function matrix by its transpose and conjugated. Two parameters of interest are the minimum singular value and the ratio of maximum to minimum singular values, or condition number. The systems with higher σ_* values and lower γ values are expected to show the best dynamic performance under feedback control. Table 1 shows the SVD results for the three options analyzed. The arrangement using an extractive Petlyuk column presents the highest minimum singular value; therefore, it can be expected that this complex system will exhibit better closed-loop dynamic behavior than the option using an extractive conventional sequence. Condition number results show that the sequence with the Petlyuk structure offers the

best value. As a result, it can be expected that the complex distillation system is better conditioned to the effect of disturbances than the conventional arrangement.

According to the results, the Petlyuk extractive arrangement is the best scheme option for separation of the binary homogeneous azeotrope of ethanol and water as regards energy consumption, CO₂ emissions, thermodynamic efficiency and control properties. In addition, this complex distillation sequence can reduce capital costs since it can be implemented in a single distillation column using a dividing wall.

4. Conclusions

In this work, the separation of a typical mixture of ethanol and water from a fermentation process was studied, considering an extractive conventional distillation column and two thermally coupled extractive distillation sequences using ethylene glycol as entrainer. The results show that the option using an extractive Petlyuk column can produce energy savings of 25.7% over the option with an extractive conventional distillation arrangement. Moreover, the structure with the Petlyuk scheme shows the best results with regard to CO₂ emissions (associated with energy consumption), thermodynamic efficiency and control properties. In general, the results are important because they indicate that the use of complex extractive distillation systems in the bioethanol purification process is feasible as regards economic, thermodynamic and control aspects.

5. Acknowledgements

We acknowledge the financial support provided by CONACyT, CONCyTEG, Universidad de Guanajuato and Instituto Tecnológico de Aguascalientes (Mexico).

6. References

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