

Modeling and Simulating Complete Extractive Distillation Process of Ethanol-Water Mixture Using Equilibrium-Stage Distillation Model and Efficiency Correlations (Barros & Wolf) on EMSO Platform

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This paper envelops the steady-state simulation of the complete process of extractive distillation for the production of anhydrous ethanol and pure water from the azeotropic mixture of ethanol-water. A system of two connected distillation columns was modelled and simulated with the first column used for the extractive distillation of ethanol and the second column for the recovery of the solvent that made the extractive distillation possible, which is then recycled back to the first column. Anhydrous ethanol as the distillate product leaving the first column and very pure water and ethylene glycol leaving the second column as the distillate and bottoms products, respectively, were the aim of the simulations. These simulations were carried out by a custom equilibrium-stage distillation model programmed and running on EMSO (Environment for Modelling, Simulation, and Optimisation). Their results were compared with those obtained from equivalent simulations performed in Aspen Plus as a way to evaluate the reliability and viability of the custom model, since Aspen Plus has proven its utility and reliability through its usage in industry and research. Results from the EMSO equilibrium-stage model simulations were compared with those from equilibrium-stage Aspen Plus distillation simulations, but in order to compare EMSO results with non-equilibrium stage Aspen Plus distillation results, Barros & Wolf correlations were programmed into the EMSO equilibrium-stage model and used to calculate stage-by-stage efficiencies that were then used by the EMSO model with the aim of approximating the Aspen Plus non-equilibrium stage model results. The comparison of results produced by both EMSO and Aspen Plus simulating equivalent processes showed that, for equilibrium-stage distillation, both simulators were able to produce anhydrous ethanol in the first column and very pure water and ethylene glycol in the second column, with very similar results for both simulators across the entire system. Results for EMSO simulations using Barros & Wolf efficiency correlations and Aspen Plus non-equilibrium stage simulations also showed great similarity between them across the columns.

1. Introduction

The production of ethanol through fermentation yields ethanol dissolved in water. Because ethanol and water form an azeotrope when mixed, any process to separate the two components needs to eliminate the azeotrope in order for the process to be able to produce high-purity ethanol. One such process—and the focus of this paper—is extractive distillation, which, unlike the conventional distillation of a binary mixture, includes a third component called the ‘solvent’ or ‘entrainer’ (Lei et al., 2005). The solvent is fed separately from the azeotropic mixture and its purpose is to modify the relative volatility of the two components that form the azeotropic mixture (Hoffman, 1977), which are ethanol and water in this case.

The design of an extractive distillation process can be complex due to the necessity of studying a number of process variables and operation parameters, and, as such, the best way to approach any such design is through computer simulations of the process. Simulation is an important and powerful tool, especially with the

wide scale use of simulators, such as Aspen Plus or PRO/II, in education, research, and industry. There are many commercial simulators available that can be used to simulate extractive distillation, but this study utilizes EMSO (Environment for Modelling, Simulation, and Optimisation) for the simulation of the extractive distillation processes.

EMSO has a graphical environment where a user can, as with commercial simulators such as Aspen Plus, build and organize processes graphically in blocks and streams, but EMSO also has a programming environment in which users can use and edit the models from the EMSO Model Library (EML) or build their own models using EMSO's own modeling language (Soares and Secchi, 2003). Using EMSO, the aim of this study was to simulate, in steady state, the complete process of extractive distillation for the separation of the ethanol-water azeotropic mixture, using ethylene glycol as solvent, and to implement the Barros & Wolf efficiency correlations into the model.

2. Methodology

The EMSO model obtained for use in this study was designed and programmed by Prof. Rafael de Pelegrini Soares, one of the developers of EMSO, in order to simulate distillation in steady state and was modified and expanded upon to suit the purposes of this study. The use of this model was necessary since the standard distillation model currently in the EMSO Model Library only functions adequately for dynamic regime simulations. One of the objectives of this study was the evaluation of the steady state distillation in EMSO, which required the new model, and it was done through comparison with results obtained from equivalent Aspen Plus (version 7.3) simulations.

A 'complete process of extractive distillation', as it was previously called, is a process in which not only is the ethanol separated from the water to produce a high-purity ethanol distillate, but also envelops the separation of the solvent from the water, such that the solvent can later be recycled and reused for the extractive distillation. This can be done through the use of a single distillation column with a dividing wall (Kiss et al., 2013), or, as in this study, using a two-column setup. Figure 1 shows a two-column setup, where the first column, called the extractive column, is fed the azeotropic mixture as well as the solvent and produces high-purity ethanol as its distillate product and a non-azeotropic mixture of water and ethylene glycol (the solvent for this study) as the bottoms product. This bottoms product stream of the extractive column then feeds a conventional distillation column, wherein the water and the ethylene glycol are separated, producing pure ethylene glycol as the sole bottoms product to then be fed back into the extractive column.

The EMSO model is an equilibrium-stage distillation model based on the MESH equations, which is short for Material balances, Equilibrium relations, Summation equations, and Heat/energy balances (Wang and Henke, 1966). In reality, liquid and vapor leaving a plate in a distillation column are not necessarily in equilibrium, and non-equilibrium stage distillation models deal with the nonexistence of equilibrium between the liquid and vapor phases leaving any specific plate in a column. Simulations made with non-equilibrium stage distillation models approximate real behavior more closely than equilibrium-stage distillation simulations (Pescarini, 1999), so, in order to deal with this 'imperfection' in equilibrium-stage models, traditionally efficiencies are implemented, like Hausen efficiencies or, most commonly, Murphree efficiencies (Taylor et al., 2003).

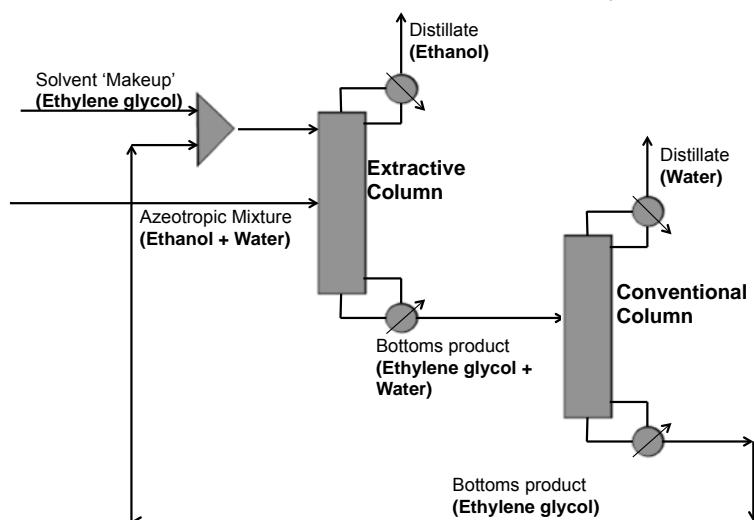


Figure 1: Simple diagram of two-column configuration for complete process of extractive distillation.

In EMSO, the Barros & Wolf efficiency correlations (Barros, 1997) are implemented in order to approximate reality and non-equilibrium stage simulations more closely. These efficiency correlations have been shown to be able to provide reasonably similar results to those from non-equilibrium stage distillation simulations in other studies (Junqueira, 2010; Reis, 2006). Eq(1) and Eq(2) are Barros & Wolf correlations for conventional distillation columns and extractive distillation columns, respectively, and are calculated with the thermal conductivity (k , W/(m*K)), density (ρ , kg/m³), diffusivity (D , m²/s), molar mass (MW), heat capacity (C_p , J/(kmol*K)), and absolute viscosity (μ , Pa*s) of each individual stage, i , within the column, meaning that these efficiency correlations are individual per plate and not global. In order to minimize data external to EMSO and VRTherm (the EMSO plugin that provides all the thermodynamic and component data for pure components and mixtures) for the EMSO simulations, all these values were generated within EMSO through VRTherm, with the exception of diffusivity, which was obtained, for this study, from Aspen Plus.

$$Eff(i) = 38.5309 \left[\frac{k(i)\rho(i)D(i)MW(i)}{C_p(i)\mu^2(i)} \right]^{-0.04516} \quad (1)$$

$$Eff(i) = 19.37272 \left[\frac{k(i)\rho(i)D(i)MW(i)}{C_p(i)\mu^2(i)} \right]^{-0.109588} \quad (2)$$

For the evaluation of steady state results using the EMSO model for the complete process of extractive distillation, comparisons were made with simulation results obtained from RADFRAC distillation columns in Aspen Plus, performing the simulations with equilibrium-stage distillation. For the evaluation of the steady state results produced by the EMSO model for extractive and conventional distillation using Barros & Wolf efficiency correlations, comparisons were made with results also obtained from RADFRAC simulations, performing the simulations with non-equilibrium "rate-based" distillation. Both simulators used UNIFAC for the calculation of activity coefficients and Redlich-Kwong for the vapor-phase fugacity coefficients.

3. Results

3.1 Complete process of extractive distillation

EMSO simulations were made for several complete extractive distillation processes, taking into account both a solvent recycle stream and a makeup stream to replenish whatever small amount of solvent may have been lost in the distillate product of the conventional column. This makeup stream was a necessity in order to obtain convergence when including a recycle stream. Specifications for an instance of this process can be found in Table 1 (where stage 1 is the top of the column, condenser and reboiler are considered stages, and "Bottoms product of extractive column" are values obtained from the bottoms product stream of the extractive column), where desired values specified by the user in the simulators were 309.6 kmol/h in the extractive column (the total amount of ethanol fed, desired as the distillate product) and 240 kmol/h in the conventional column (the total amount of ethylene glycol fed into the extractive column), and the reflux ratio of both columns. The results for this simulation can be seen in Figures 2 and 3, for the extractive and conventional columns, respectively.

Table 1: Specifications of a complete system of extractive distillation.

	Extractive Column	Conventional Column
Number of Stages	32	18
Feed Stage	24	9
Feed Stage (solvent)	3	-
Reflux Ratio	2	2
Feed Flowrate (kmol/h)	387.02	Bottoms product of extractive column
Temperature (K)	350	Bottoms product of extractive column
Pressure (atm)	1	Bottoms product of extractive column
Mol. Fraction (x) Ethanol	0.8	Bottoms product of extractive column
Mol. Fraction (x) Water	0.2	Bottoms product of extractive column
Mol. Fraction (x) Ethylene glycol	-	Bottoms product of extractive column
Solvent (Ethylene glycol) Feed (kmol/h)	240	-
Temperature (K)	351	-
Pressure (atm)	1	-
Stage 1 Pressure (atm)	1	0.5
Pressure drop per stage (kPa)	0	0

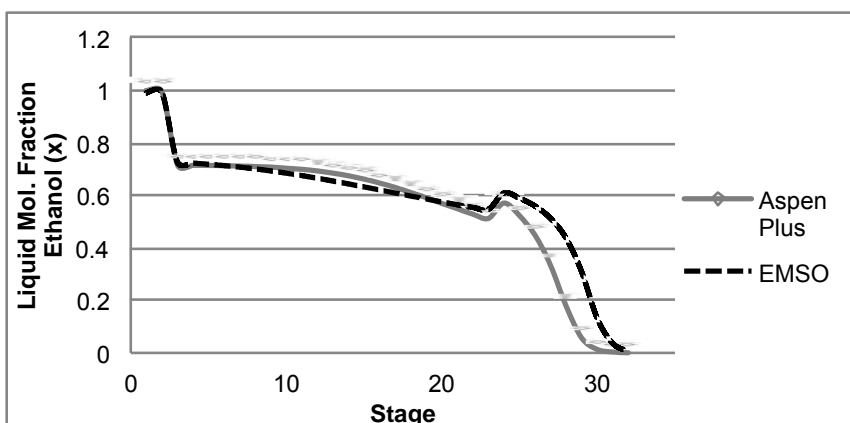


Figure 2: Liquid mole fraction of ethanol throughout extractive column detailed in Table 1.

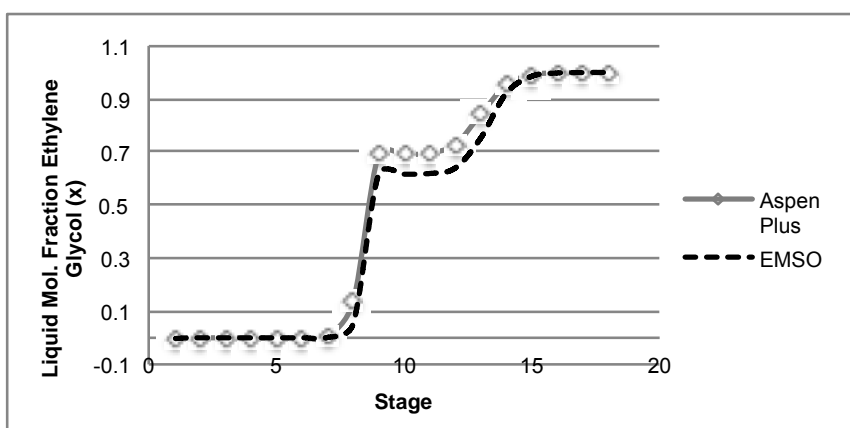


Figure 3: Liquid mole fraction of ethylene glycol throughout conventional column detailed in Table 1.

Figures 2 and 3 show the mole fraction of ethanol and ethylene glycol across the entire columns, for equilibrium-stage distillation. The distillate product of the extractive column has ethanol 99.4 % pure in the EMSO simulation and 99.9 % pure in the Aspen Plus simulation. Across the columns, it can be seen that the EMSO model produces results with great similarity to those from Aspen Plus. There is, though, a difference between the simulators, both throughout the columns and in the product stream. However, what is important to note is that both simulators produce ethanol of +99 % purity for this process, properly performing the job of the extractive column and demonstrating that the EMSO model cannot only eliminate the azeotrope correctly with the addition of the solvent into the column, but both simulators can also produce ethylene glycol of +99 % purity, yielding solvent pure enough to be recycled. The similarity between the results is important in the evaluation of the EMSO model because of the trustworthiness of Aspen Plus results, due to it being a simulator widely used in research and industry.

3.2 Barros & Wolf correlations

In order to obtain results for both the extractive and conventional columns of the complete process with the Barros & Wolf efficiency correlations in the EMSO model, the columns must be simulated individually and not connected as part of a 'complete process'. This is due to the much increased difficulty in obtaining simulation convergence when simulating both columns simultaneously with the efficiency correlations being calculated and applied at the same time, in steady state.

The calculation of the efficiency correlations is done iteratively, where the first simulation of a column is performed with an ideal efficiency of '1' across the entire column. This simulation also calculates the Barros & Wolf efficiency correlations for each stage as part of the results, and these values must then be applied as per-stage efficiencies in a following simulation, with every column parameter remaining the same. This second simulation once again calculates the Barros & Wolf correlations, which, if they are within a certain tolerance from the previously calculated correlations (1.5 % for this study), give the final result. If they are outside of that

tolerance, they are then applied into a new simulation and the process is repeated until the newly-calculated correlations of the most recent iteration have a difference from the previous iteration's correlations that falls within the aforementioned tolerance.

Figures 4 and 5 show the results of the Barros & Wolf correlations applied to the extractive column in Table 1, but, for the purpose of making Figure 6, this is done in four distinct simulations with four different reflux ratios (RR): 1.05, 2, 4, and 10. Due to the variation in reflux ratios being done only to the extractive column, only one result is shown for the conventional column, in Figure 5, fed by the extractive column with reflux ratio of 2. This is done since, regardless of the reflux ratio of the extractive column (within the system from Table 1 and the group of reflux ratios mentioned above), the bottoms product of the extractive column and, as such, the feed flow rate and compositions of the conventional column are all approximately the same. The curves from Figure 5 show the similarity between the EMSO model using Barros & Wolf correlations and Aspen Plus non-equilibrium results, but there is also a noticeable difference in the midsection of the column.

Figure 4 shows a progression of EMSO results compared to Aspen Plus results of the same system while varying reflux ratios. It can be noted here that using Barros & Wolf efficiency correlations in simulations of the EMSO model yields results with a high degree of similarity to those produced by equivalent 'rate based' non-equilibrium simulations performed by Aspen Plus. Figure 2, for equilibrium distillation, showed greater difference in results between simulators in the column interior than non-equilibrium and Barros & Wolf results from Figure 4 (also with reflux ratio of 2), but these Figure 4 results have slightly greater difference between simulators in distillate compositions than Figure 2 results. In addition, Figure 6 shows that, for this particular system, an increase in reflux ratio means that, across the simulated columns, efficiencies tend to decrease.

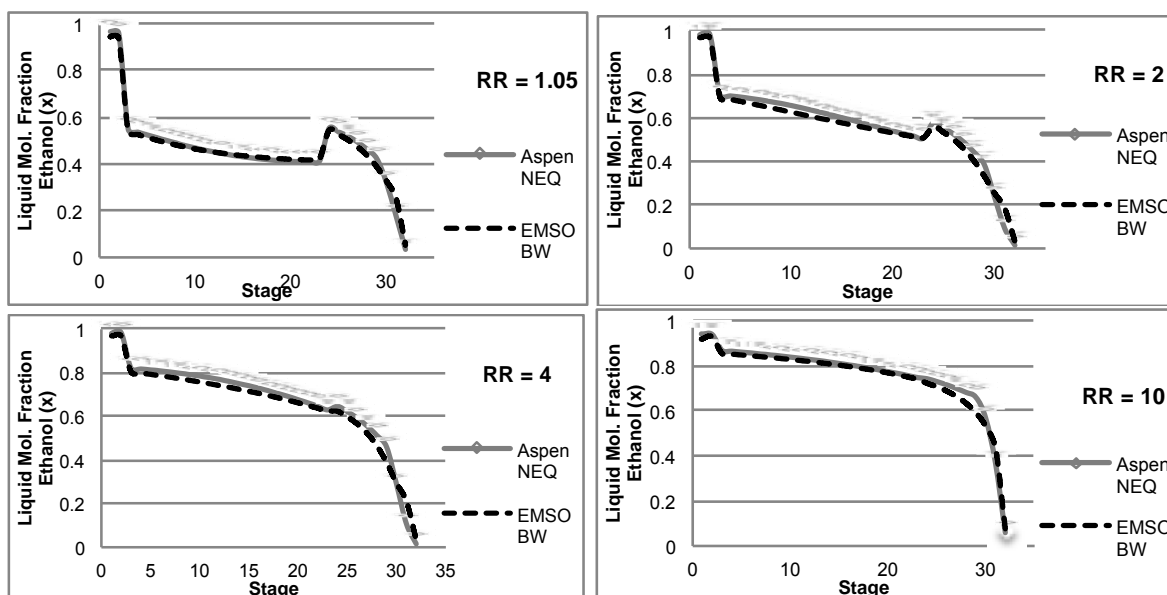


Figure 4: Liquid mole fraction of ethanol throughout extractive column detailed in Table 1 with varying reflux ratios (RR). EMSO BW is EMSO simulation using Barros & Wolf, Aspen NEQ is non-equilibrium Aspen Plus.

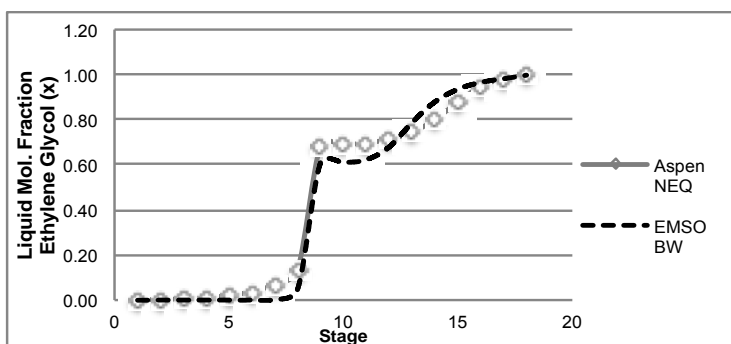


Figure 5: Liquid mole fraction of ethylene glycol throughout conventional column detailed in Table 1. EMSO BW is EMSO simulation using Barros & Wolf, Aspen NEQ is non-equilibrium Aspen Plus.

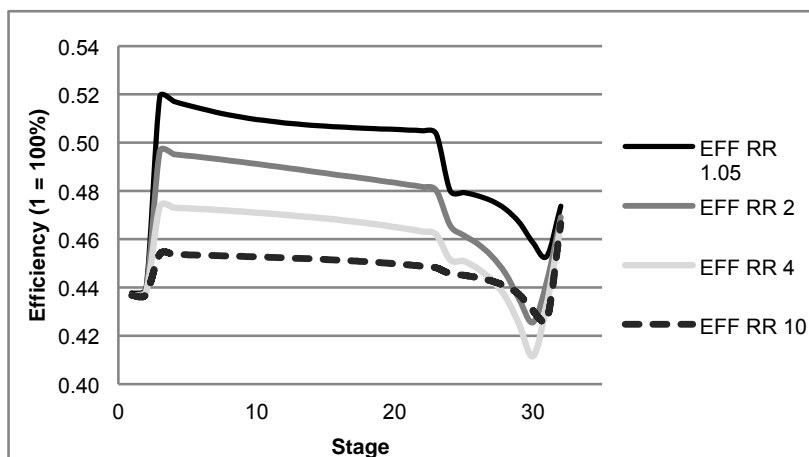


Figure 6: Calculated efficiency per stage for extractive column from Table 1 with varying reflux ratio. 'EFF RR 2' means it's the efficiency for the column with a reflux ratio of 2.

4. Conclusions

The utilized EMSO model has been shown to be able to produce results that bear close resemblance with results produced by equivalent Aspen Plus simulations. High-purity ethanol is produced as the distillate product of the extractive column and high-purity ethylene glycol is produced as the bottoms product of the conventional column, both linked together in a complete process in both EMSO and Aspen Plus, which shows the utility of EMSO in the simulation of the complete process of extractive distillation for the production of anhydrous ethanol. In terms of individual columns, the use of Barros & Wolf efficiency correlations with the EMSO model showed a fair degree of similarity in the conventional column when compared to the non-equilibrium distillation simulation in Aspen Plus, but greater similarity across a variety of reflux ratios for the extractive column. These results for the Barros & Wolf efficiency correlations are compatible with results from literature and further demonstrate the utility of the EMSO model.

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