

Comparison of Complete Extractive and Azeotropic Distillation Processes for Anhydrous Ethanol Production using Aspen Plus™ Simulator

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Performance of the extractive and azeotropic distillation processes using ethylene glycol and cyclohexane as solvents, respectively, for anhydrous ethanol production, were investigated using 02 RadFrac columns each and solvent recycling streams via simulation in Aspen Plus™ Simulator. Both operate at 1 atm, and feed flow rate equals to 100 kmol.h^{-1} (ethanol – 0.896 and water – 0.104 in mole fractions at the azeotropic point). The NRTL-RK was the model used for extractive and azeotropic distillations. The anhydrous ethanol purity from top of the 1st column of the extractive distillation (22 stages) was 99.50 % (on a mole basis) and water with 99.20 % of purity at the top of the 2nd column. On the other hand, in the azeotropic distillation, the 1st column (30 stages) had a bottom product of anhydrous ethanol purity of 99.99 % and water with 99.99 % of purity in the 2nd column, also at the bottom. Both processes produced anhydrous ethanol with a high-grade purity required by the standard norms ASTM D4806, EN 15376, and ANP 36. However, the extractive distillation spent 1,928.2 kW in the reboilers against 4,680.3 kW in the azeotropic distillation, demonstrating extractive distillation is the most economical option. Consequently, the energy consumption is an essential analysis for choosing the type of distillation, when an azeotropic mixture needs a good separation task. Finally, the extractive distillation demonstrated to be much more competitive than azeotropic distillation for this type of mixture although azeotropic distillation obtained a higher purity of anhydrous ethanol.

1. Introduction

The production of ethanol has increased over the years, mainly considering the growing world energy demand. The ethanol, a biofuel, is commonly produced via sugar fermentation (ANP, 2019), from different raw materials, such as corn in North America, sugar-beet in Europe, and sugarcane in South America, mainly in Brazil. There are two types of ethanol produced in the industries: hydrated and anhydrous. The hydrated ethanol is directly used in Otto cycle engines. On the other hand, anhydrous ethanol is used as a gasoline additive (ANP, 2019); (Lara-Montañó et al., 2019), which requires very high-grade ethanol in most countries, which classifies the anhydrous ethanol as one of the most important fuels in the industries. Three main standard norms regulate the minimum grade of anhydrous ethanol for commercialization: ASTM D4806 (2019) – American, EN 15376 (2014) – European, and ANP Resolution No. 19 (2015) – Brazilian. ASTM D4806 (2019) establishes the minimum ethanol content for anhydrous fuel ethanol as 92.10 % in volume, EN 15376 (2014) states 98.70 % in mass, and finally, ANP Resolution No. 19 (2015) requires 99.30 % in mass. Brazil, as the country with the strictest minimum grade limits for anhydrous ethanol, comes as the second-largest producer of ethanol in the world (ANP, 2019), only behind the USA. In order to achieve these limits, some special separation techniques (e.g., unconventional distillations) must be used to be capable of separating the undesired water from the ethanol. The problem of this binary mixture is the formation of an azeotrope, complicating the purification process because simple distillation processes are incapable of separating the components of this mixture (Raosaheb, 2015). The most common techniques used to separate azeotropes are the following: extractive distillation, azeotropic distillation, distillation using salts, pressure swing distillation, and reactive distillation (Raosaheb, 2015); (Guzmán-Martínez et al., 2019). Among them, the extractive and

azeotropic distillation processes are the most used in the industries to separate ethanol from water. The presence of a decanter in the azeotropic distillation process is to make the liquid-liquid thermodynamic phase separation since the azeotropic distillation makes use of heterogeneous phase equilibrium. The decanter is necessary after the 1st column to accommodate the two liquid phases formed after steam condensation, and thus, it may be possible to recycle the solvent. Both processes require a suitable solvent to modify the activity coefficient and relative volatility of the components (extractive) (Raosaheb, 2015) or to form new ternary heterogeneous azeotrope (azeotropic). Then, several solvents have been tested, focusing on the efficiency improvement of these processes and less toxicity, generating high grades of ethanol and consuming less energy. Cyclohexane has replaced benzene over the years in the azeotropic distillation for being much less toxic. In the extractive distillation, the most common solvent is ethylene glycol (Sprakel et al., 2018). The literature has already demonstrated the capability of both processes to achieve high-grade ethanol (Vasconcelos, 1999); (Bastidas et al., 2010); (Gil et al., 2014); (Shang et al., 2019). Consequently, the main objective of this work was comparing the performance of the extractive distillation with ethylene glycol as a solvent and the azeotropic distillation with cyclohexane as an entrainer concerning the reboiler heat duties and the purity of the anhydrous ethanol produced.

2. Methodology

The complete extractive and azeotropic distillation processes for anhydrous ethanol production were simulated using the Aspen Plus™ simulator V10.0 at a steady state. Extractive distillation is fed with a mixture of ethanol and water at atmospheric pressure, where a minimum-boiling homogeneous azeotrope is formed at 78.16 °C (Table 1). The NRTL-RK was the physical property model chosen to describe the nonideality of both processes, in which the NRTL activity model was used for the liquid phase and the Redlich-Kwong equation of state for the vapor phase. In azeotropic distillation, a new azeotrope (ternary and heterogeneous) must be formed, generating in most cases two liquid phases and one vapor phase in the upper plates of the column. Figure 1 represents the simulation of the extractive distillation. Both processes use 02 RadFrac columns.

Table 1: Azeotrope only in the ethanol-water mixture with ethylene glycol in molar basis

	Temperature (°C)	Classification	Type	Number of components	Ethanol	Water	Ethylene glycol
1	78.16	Unstable node	Homogeneous	2	0.896	0.104	0.000

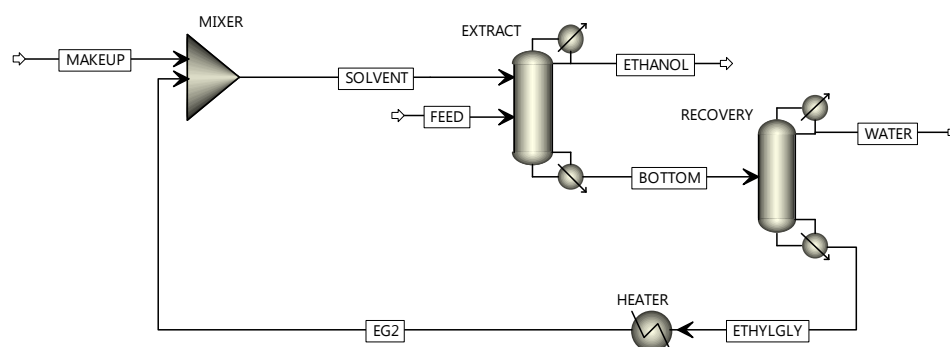


Figure 1: Extractive distillation simulation flowsheet

In the extractive distillation, a heavy solvent with a high boiling point, the ethylene glycol (SOLVENT), is continuously added at the top to separate the FEED, composed of ethanol and water, in the 1st column, producing high-grade ethanol (ETHANOL) in the top of the 1st column. The BOTTOM of the 1st column is mainly composed of the solvent and little amount of water, which enters the 2nd column to recover the WATER at the top and to recycle the solvent (ETHYLGLY and EG2 – solvent at 80 °C) into the 1st column to keep the continuous feed. This solvent can alter the relative volatility of the components, having a higher affinity to one of them, thus extracting it (Sprakel et al., 2018). In this case, ethylene glycol has a greater affinity with water. The HEATER was kept at 80 °C to avoid spending much more energy with the junction of the streams. The MAKEUP stream closes the molar balance. Azeotropic distillation also works with a mixture of ethanol and water at atmospheric pressure, having the same minimum-boiling homogeneous azeotrope at 78.16 °C (Table 2), but the heterogeneity comes from the ternary azeotrope formed between ethanol, water, and the solvent (cyclohexane). The cyclohexane was chosen as the entrainer due to its less toxicity when compared to

benzene, the former entrainer used in this type of simulation. Figure 2 shows the flowsheet of the azeotropic distillation simulation, in which the flowsheet was created based on the literature (AspenTech, 2012).

Table 2: Azeotrope in the ethanol-water mixture with cyclohexane in the azeotropic distillation in molar basis

	Temperature (°C)	Classification	Type	Number of components	Ethanol	Water	Cyclohexane
1	69.26	Saddle	Heterogeneous	2	0.000	0.299	0.701
2	62.14	Unstable node	Heterogeneous	3	0.317	0.152	0.530
3	78.16	Saddle	Homogeneous	2	0.896	0.104	0.000
4	64.78	Saddle	Homogeneous	2	0.438	0.000	0.562

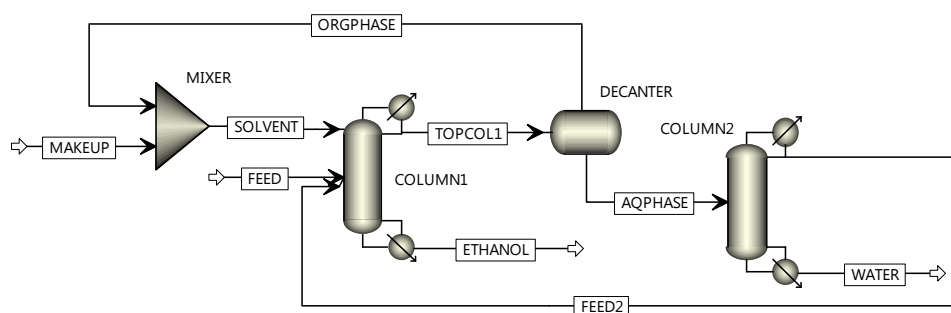


Figure 2: Azeotropic distillation simulation flowsheet

The azeotropic distillation brings a difference from the extractive process, which is the presence of a DECANTER to separate the top of the 1st column (TOPCOL1) into organic (ORGPASE) and aqueous (AQPHASE) phases. The organic phase is rich with solvent, which is recycled to the 1st column, which means there is no continuous feed of solvent into this process other than the MAKEUP stream. The aqueous phase was supposed to have water as the main component, but it has ethanol due to the solvent used. Then, it is important to state that the solvent benzene is much more predictable and easier to work in terms of distillation operating behavior since the aqueous phase is richer in water in the decanter, in all suitable temperature ranges. The cyclohexane makes the distillation column much more “nervous” because of the different distribution of components in the aqueous phase, richer in ethanol, which is a thermodynamic phenomenological behavior. This replacement of solvents is nowadays mandatory for environmental reasons. The aqueous phase goes to the 2nd column to produce WATER in the bottom, and the top (FEED2) is recycled to the 1st column to close the mass balance of the process. Table 3 demonstrates the operating conditions of the extractive and azeotropic distillation processes. Both processes considered the pressure of 1 atm.

Table 3: Operating conditions of the extractive and azeotropic distillation processes

Parameter	Extractive Distillation		Azeotropic Distillation	
	Value	Temperature (°C)	Value	Temperature (°C)
Makeup flow rate (kmol.h ⁻¹)	10 ^{-5a}	25	10 ^{-5b}	25
Molar fraction of solvent in makeup flow	1 ^a	25	1 ^b	25
Feed flow rate (kmol.h ⁻¹)	100	78	100	–
Molar fraction of ethanol in the feed flow	0.8960	78	0.8960	–
Molar fraction of water in the feed flow	0.1040	78	0.1040	–
Solvent flow rate (kmol.h ⁻¹)	70.01 ^a	80	360 ^b	–
Molar fraction of ethanol in the solvent flow	0	80	0.0704	–
Molar fraction of water in the solvent flow	0	80	0.0013	–
Molar fraction of solvent in the solvent flow	1 ^a	80	0.9283 ^b	–

^a ethylene glycol; ^b cyclohexane; – the simulator calculates the ideal temperature for the process

In Table 3, the value of the makeup flow rate is to initiate the simulation, and its balance is made through a convergence block in the simulator. After defining the streams of the process, the characteristics of the extractive and azeotropic distillation columns are established (Table 4). The number of stages, feed stage, and solvent stage of the extractive distillation columns were possible to be optimized through sensitivity

analysis, reaching the number of stages here considered. The distillate flow rate and reflux ratio for this process were also optimized in the simulator. In the case of the azeotropic distillation columns, the high purity defined by the user causes the range of column operating conditions to be limited, not being possible to optimize through sensitivity analysis. The optimization of the reflux ratios, feed stages, and solvent stages were manually made in the simulator to reach the high purity desired. Then, only the bottom flow rates were possible to be optimized in the simulator through design specs. Also, it is essential to mention that most works of extractive and azeotropic distillation processes in the literature use the range of 20 to 50 stages (Raosaheb, 2015); (Le, 2014); (Bastidas et al., 2010); (Vasconcelos, 1999). Then, it was considered for the optimization of the azeotropic distillation by the user, since the extractive distillation has the number of stages optimized by sensitivity analysis.

Table 4: Characteristics of the extractive and azeotropic distillation columns

Parameter	Extractive Distillation		Azeotropic Distillation	
	1 st column	2 nd column	1 st column	2 nd column
Number of stages	22	32	30	25
Condenser	Total	Total	Total	Total
Reboiler	Kettle	Kettle	Kettle	Kettle
Valid phases	Vapor-Liquid	Vapor-Liquid	Vapor-Liquid-Liquid	Vapor-Liquid-Liquid
Distillate flow rate (kmol.h ⁻¹)	89.97	10.04	–	–
Reflux ratio	0.38	0.60	0.50	0.30
Bottoms flow rate (kmol.h ⁻¹)	–	–	89.60	10.40
Feed stage	14	17	11	10
Solvent stage	4	–	1	–
2 nd feed stage*	–	–	11	–

* The recycle of the top of the 2nd column into the 1st column

Since the azeotropic distillation is a 3-phase process, water was considered the 2nd liquid phase in the simulator. The 1st column of extractive distillation (22 stages) had a distillate rate of 89.97 kmol.h⁻¹ and a reflux ratio of 0.38, agreeing with Bastidas et al. (2010) for the number of stages and reflux ratio. The feed and solvent stages were on the 14th and 4th, respectively. Then, the bottom entered on the 17th stage in the 2nd column (32 stages), which had 0.60 of the reflux ratio and 10.04 kmol.h⁻¹ of distillate flow rate. Ethylene glycol left at the last stage and entered in a mixer for its recycling. On the other hand, azeotropic distillation had the 1st column (30 stages) with a bottom rate at 89.60 kmol.h⁻¹ and a reflux ratio of 0.50. In this case, the feed stage was on the 11th stage and the solvent at the 1st stage. Also, this column has feed recycling at the 11th stage. The decanter is necessary after this column to accommodate the two liquid phases formed after steam condensation coming from the top, recycling the cyclohexane into the 1st column. The 2nd column (25 stages) had a reflux ratio of 0.30 and bottom rate as 10.40 kmol.h⁻¹. The bottom of the decanter enters the 2nd column on the 10th stage, recycling the top of the 2nd column into the 1st column, closing the mass balance.

3. Results and discussion

Tables 5 and 6 bring the results of the simulations of both processes for anhydrous ethanol production. These tables demonstrate the flow rate, molar fractions of ethanol, water, and solvent, and temperature of all streams of both processes.

Table 5: Results of the extractive distillation

Stream	Solvent	Feed	Ethanol	Bottom	Water	Ethylgly	Eg2	Makeup
Flow rate (kmol.h ⁻¹)	70.02	100.00	89.97	80.05	10.04	70.01	70.01	0.01
Molar fraction of ethanol	3.21x10 ⁻¹⁷	0.896	0.9949	0.001	0.008	3.43x10 ⁻¹⁷	3.43x10 ⁻¹⁷	0
Molar fraction of water	9.99x10 ⁻⁵	0.104	0.0048	0.1246	0.9920	0.0001	0.0001	0
Molar fraction of solvent	0.9999	0	0.0002	0.8744	3.29x10 ⁻¹⁶	0.9999	0.9999	1
Temperature (°C)	80.00	78.00	78.30	159.00	97.68	197.04	80.00	25.00

The ethanol stream indicates a high purity of anhydrous ethanol as a product (99.49 %). For the water stream, high purity is also observed (99.20 %). The recycling of the solvent ethylene glycol allowed a high purity of the solvent (99.99 %), which required only a small flow rate of solvent makeup (0.01 kmol.h⁻¹). The solvent to feed ratio (S/F) was 0.70, which was similar to the one used by Gil et al. (2014). It is important to highlight that

ethanol and water mole fractions appear on the solvent stream due to the necessity of reflecting the ETHYLGly and EG2 streams into the process again. These values were obtained after the first simulation without these values. After that, it was possible to close the molar balance. Table 6 shows the results of the azeotropic distillation for the comparison proposed.

Table 6: Results of the azeotropic distillation

Stream	Solvent	Feed	Topcol1	Ethanol	Orgphase ¹	Aqphase ²	Water	Feed2	Makeup
Flow rate (kmol.h ⁻¹)	360.01	100.00	461.08	89.60	360.01	101.07	10.39	90.67	1x10 ⁻⁵
Molar fraction of ethanol	0.0704	0.896	0.1959	0.9999	0.0704	0.6432	0.0001	0.7169	0
Molar fraction of water	0.0013	0.104	0.0666	9.68x10 ⁻⁵	0.0013	0.2990	0.9999	0.2187	0
Molar fraction of solvent	0.9282	0	0.7374	3.18x10 ⁻⁶	0.9282	0.0578	1.12x10 ⁻²³	0.0644	1
Temperature (°C)	25.00	77.82	61.80	77.98	25.00	25.00	99.62	66.21	25.00

¹ 1st liquid phase (upper) of the decanter

² 2nd liquid phase (lower) of the decanter

The ethanol stream in the azeotropic distillation demonstrated higher purity of anhydrous ethanol (99.99 %) when compared to the extractive distillation. However, to be able to achieve this purity, a decanter is necessary besides the 1st column in the azeotropic distillation. The decanter can separate the two liquid phases. The 1st liquid phase (upper phase) (ORGPPhase stream in Figure 2 and Table 6) was primarily consisted of solvent, returning to the azeotropic column as a reflux ratio. Furthermore, to achieve this high-grade ethanol, the solvent to feed ratio required value of 1.90. The 2nd liquid phase (AQPhase stream), on the other hand, is mostly composed of ethanol and water, which requires to pass through the 2nd column to produce high purity water. In this type of distillation, the recycling of solvent in the simulation and feeding in the 1st stage is to demonstrate that the solvent is kept inside the column, and it did not have a continuous feed flow rate. Table 6 brings that the makeup flow of the solvent was 10⁻⁵ kmol.h⁻¹, which indicates the low required replacement. Although the solvent feed flow rate is high, the recycling with the decanter and feeding at the 1st stage ensure that the only continuous feeding comes from the makeup stream. Also, water and solvent purities were very efficient. Besides assessing the purity of distillation products, energy spending in condensers and reboilers should also be evaluated (Table 7). The decanter was kept at 25 °C.

Table 7: Results of the condensers and reboilers of the 1st and 2nd columns on extractive and azeotropic distillation processes

Parameter	Extractive Distillation				Azeotropic Distillation			
	1 st column		2 nd column		1 st column		2 nd column	
	Condenser	Reboiler	Condenser	Reboiler	Condenser	Reboiler	Condenser	Reboiler
Temperature (°C)	78.30	158.99	97.68	197.04	61.80	77.98	66.21	99.62
Heat duty (kW)	-1,351.4	1,621.5	-182.1	306.7	-2,618.8	3,220.8	-1,314.8	1,459.5
Distillate flow rate (kmol.h ⁻¹)	89.97	–	10.04	–	461.08	–	90.68	–
Reflux flow rate (kmol.h ⁻¹)	34.11	–	6.00	–	230.54	–	27.20	–
Reflux ratio	0.38	–	0.60	–	0.50	–	0.30	–
Bottoms flow rate (kmol.h ⁻¹)	–	80.05	–	70.01	–	89.60	–	10.39
Boilup flow rate (kmol.h ⁻¹)	–	110.39	–	20.58	–	295.73	–	128.97
Boilup ratio	–	1.38	–	0.29	–	3.30	–	12.41

Remarkably, energy spending is always higher on the condenser and reboiler of the first columns on both processes, which happens due to the energy spending to break the azeotrope between the water and ethanol, with the solvent aid in the first columns. In the extractive distillation process, the reflux rate is 5.7 times higher in the 1st column, while in the azeotropic distillation is 8.5 times higher in the 1st column. The boilup ratio is higher on the azeotropic distillation, which needs to be high to achieve the anhydrous ethanol purity, making it have the reboiler heat duty 2.4 times higher than the extractive distillation, spending 4,680.3 kW on the reboilers on the azeotropic distillation against 1,928.2 kW in the extractive distillation. Koczka et al. (2007) also affirmed that the azeotropic distillation is the one that demonstrates the highest energy consumption, and Bastidas et al. (2010) confirmed stating that extractive distillation stands out for being more economically favorable. Some authors have found similar reboiler heat duties, but a bit higher than those found in this work (Vasconcelos, 1999); (Bastidas et al., 2010). The decanter in the azeotropic distillation spent -743.2 kW, and the heater in the extractive distillation also spent low energy (-391.4 kW), keeping the same proportion of heat duties when added to the total. Figure 3 represents the vapor molar composition of the ternary mixture of ethanol, water, and cyclohexane through the column stages to demonstrate that there is no formation of

plateau (constant values) in two different vapor molar composition in the first stages of the column, confirming that the process does not have the vapor-liquid-liquid equilibrium (VLE).

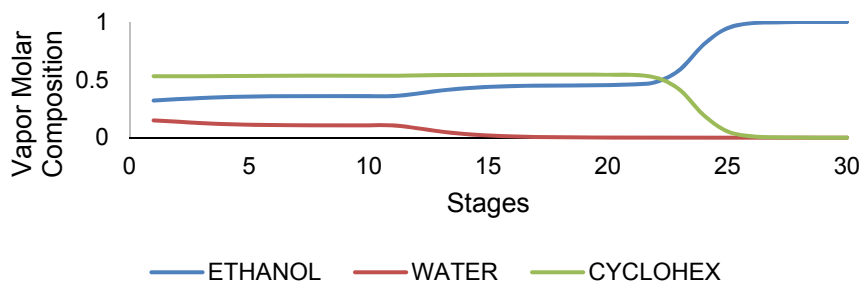


Figure 3: Vapor molar composition of the ternary mixture through the column stages

4. Conclusions

This work assessed the use of extractive and azeotropic distillation processes to produce anhydrous ethanol. Both processes demonstrated to be efficient regarding the purity of the anhydrous ethanol, achieving purities of 99.49 and 99.99 % of ethanol in the extractive and azeotropic distillations, respectively. Nevertheless, when comparing both processes, the extractive is more advantageous than the azeotropic distillation concerning the reboiler heat duty, which the latter was 2.4 times higher. Both processes achieved the purities required for the anhydrous ethanol by the standard norms ASTM D4806, EN 15376, and ANP 36. The results were compared to the theoretical data in the open literature. One of the important contributions of this work was to build up the simulation involving recycles, convergence strategy, and the consideration of liquid-liquid equilibrium in the condenser.

Acknowledgments

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