



Dehydration of Bioethanol by Hybrid Process Liquid—Liquid Extraction/Extractive Distillation

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ABSTRACT: Bioethanol is among the most promising of biofuels because it has an energy content similar to gasoline while generating lower pollutant emissions than gasoline. But, in order to be used as an automotive fuel mixed with gasoline, ethanol must have less than 0.5 wt % of water. To achieve required ethanol purity, in light of the fact that the ethanol—water mixture forms an azeotrope, unconventional separation techniques such as extractive distillation or azeotropic distillation are necessary. However, the purification of ethanol using conventional distillation followed by extractive distillation has the disadvantage of high cost of services. Thus, this study proposes alternative hybrid systems using liquid—liquid extraction and extractive distillation. The use of *n*-dodecane as entrainer for liquid—liquid extraction and glycerol as entrainer for extractive distillation has been considered. The proposed systems are analyzed and a comparison is done on their performance in terms of energy and total annual cost. It has been found that the hybrid scheme presents both lower total energy consumption and lower total annual cost as compared to the traditional purification scheme with conventional distillation and extractive distillation.

1. INTRODUCTION

At present, a major concern of humankind is ensuring its energy supply for the future. Energy is used in transportation, industrial processes, heating devices, and so on—an almost limitless number of applications. Traditionally, energy requirements have been satisfied using fossil fuels such as petroleum derivatives. However, in recent years a decline in petroleum production has been observed, and this trend is predicted to continue over the coming decades. Moreover, fossil fuels are partially responsible for the accelerated increase in the concentration of greenhouse gases in the atmosphere, leading to an increase in the Earth's temperature. In response to the above factors, a variety of efforts have been undertaken to find alternative sources of energy, which must be renewable, clean, and inexpensive. Biofuels, which are fuels produced from biomass, meet the first two requirements: they are obtained from renewable sources, and they produce lower emissions than fossil fuels. In the transportation industry the most promising candidate to replace gasoline as fuel for gasoline engines is ethanol. This alcohol has a higher octane number, broader flammability limits, and higher heats of vaporization than gasoline. Furthermore, ethanol can be used mixed with gasoline and also used directly in existing spark-ignition engines, and thus no additional engine modification investment is required. To these performance advantages can be added the lower greenhouse gas emissions of ethanol, as compared to gasoline. The main disadvantages of ethanol as fuel include its lower energy density and lower vapor pressure as compared to gasoline, and its miscibility with water. 1 Ethanol can also be used as a fuel for electric power generation, in fuel cells, and in power cogeneration systems, and also as a raw material in the chemical industry.^{2,3} It has been established that if ethanol replaces gasoline as automotive fuel, greenhouse gas emissions will be reduced by more than 85% when considering the entire fuel life cycle.⁴ In recent years, the countries with the highest production of ethanol worldwide have been Brazil, the United States, and Canada.⁵ Moreover, it has been predicted that, by 2022, a third of energy requirements in the United States will be satisfied by fuels obtained from biomass, and at least half of that proportion will be fulfilled by ethanol.⁶

Bioethanol can be produced from sources with a high content of sugars, or materials that can be converted into sugars, such as corn, sugar cane, sugar beet, and even sweet sorghum. However, since these crops are used for human food, alternative sources are required. A potential solution to this problem is to use lignocellulosic compounds, such as crop residues, sawdust, sludges, and livestock manure, as raw material. Using such nonedible biomass to produce ethanol also reduces the biofuel's cost of production. The production of bioethanol from lignocellulosic materials basically consists of four steps: delignification, depolymerization, fermentation, and purification. The delignification step involves the separation of cellulose, hemicellulose, and lignin, so the molecules of cellulose and hemicelluloses can be further treated to obtain sugars. In the depolymerization step, the lignocellulosic biomass is hydrolyzed with enzymes or acids as catalysts, obtaining sugars such as glucose, xylose, and arabinose. 9

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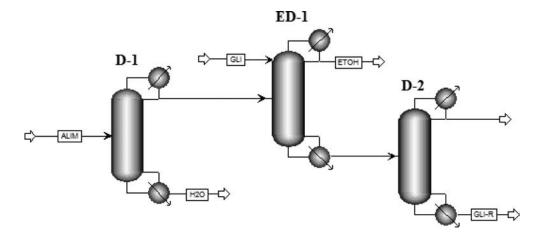


Figure 1. CS-1 conventional separation sequence.

Sugars are then fermented, usually with yeast or bacteria, to obtain mainly ethanol and water. In the purification step, ethanol must be separated from water. The final product must contain less than 0.5 wt % of water in order to be useful as automotive fuel in combination with gasoline, or as oxygenate for gasoline. Nevertheless, purification by conventional distillation is not possible because the ethanol—water mixture forms an azeotrope when a purity of 96 wt % of ethanol is reached. Thus, nonconventional methods are necessary to achieve the required ethanol purity. One alternative to obtain pure ethanol is to use conventional distillation to preconcentrate the ethanol to purity levels close to the azeotrope, and then reach the desired purity by using extractive distillation. The main purpose of extractive distillation is to modify the relative volatilities of the components of a given mixture by using an entrainer. One entrainer used to separate ethanol—water mixtures is ethylene glycol, and recently the use of glycerol has been proposed to separate such mixtures using extractive distillation. Other proposals for the purification of bioethanol include the use of ionic liquids as solvents, ¹² schemes involving pervaporation membranes, ^{13,14} and pressureswing distillation systems.¹⁵ It has been reported that the industrial oil company Sasol Ltd. uses n-dodecane as a solvent to extract light alcohols, such as ethanol and 2-propanol, from water. 16 Liquid—liquid extraction could thus be an alternative to separate ethanol from water. However, liquid-liquid extraction alone is unable to produce the purity levels required for bioethanol. Therefore, in this study we propose the use of hybrid systems of liquid-liquid extraction and extractive distillation to reduce energy consumption and total annual costs for the purification step in the bioethanol production process. The liquid—liquid extraction is done using *n*-dodecane as entrainer, reducing the concentration of water; in a second separation stage, extractive distillation is used to reach the desired ethanol purity using glycerol as entrainer. The performance of the proposed separation strategy is then compared to that of the purification process involving conventional distillation and extractive distillation.

2. METHODOLOGY AND CASES OF STUDY

In this section the three analyzed purification processes will be presented. The design methodology for each set of equipment in

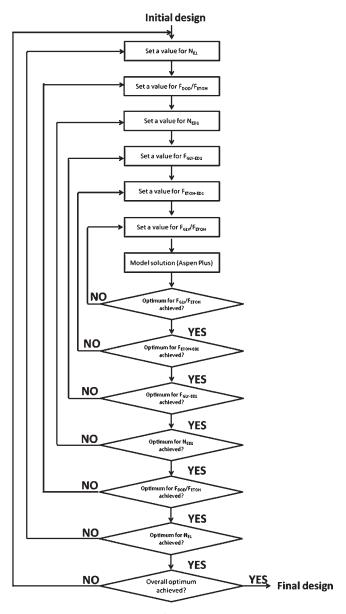


Figure 2. Optimization method for the CS-1 sequence.

the different alternatives will be described, together with the strategy to minimize process energy consumption. The method used to calculate total annual cost is also presented.

2.1. Design Methodology. To analyze the processes under consideration, simulations have been performed in the commercial simulator Aspen Plus. The feed stream for all the alternatives analyzed is 100 lb mol/h with a composition of 90 mol % of water and 10 mol % of ethanol. This is a typical yield for fermentation of sugar cane bagasse. ¹⁷ This stream enters the purification process at 30 °C and 1 atm. The vapor—liquid equilibrium has been calculated using the NRTL equation for determination of the activity coefficients, using the binary parameters provided by the simulator.

Three different processes have been analyzed. First, a conventional separation sequence (CS-1) is considered. A scheme for such a sequence is presented in Figure 1. This separation method

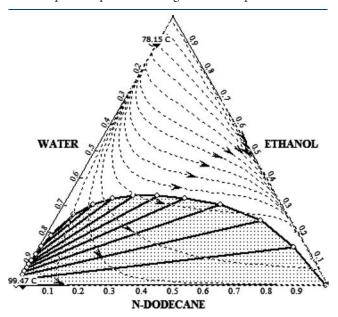


Figure 3. Ternary map for the ethanol/water/n-dodecane mixture.

involves the prepurification of ethanol using conventional distillation until a maximum feasible purity is achieved. This purity will be lower than the composition of the azeotrope. The bottoms stream consists of water with a purity of 99.99 mol %. The concentrated ethanol is then treated in an extractive distillation column, using glycerol as entrainer, aiming for a purity of 99.99% in mole fraction of ethanol. Once the ethanol has been purified, an additional conventional distillation column is used to purify the glycerol so it can be reused. The waste stream resulting from this separation step consists of about 0.99 kmol/h, containing water with small quantities of ethanol and glycerol (around 85 mol % of water). The conventional distillation column is designed using the Winn-Underwood-Gilliland method, and its reflux ratio is manipulated until the maximum feasible purity for ethanol is reached. For the extractive distillation column, an initial design is supposed. This initial design must allow reaching the desired purity for ethanol, with a recovery higher than 98 mol %. Once the design specification for ethanol has been fixed, the degrees of freedom of the column are modified one by one, aiming to reduce the energy requirements for the separation. The methodology used for the optimization of the CS-1 sequence is shown in Figure 2, where $N_{\rm ED}$ is the number of stages in the extractive distillation column, $F_{GLY-ED1}$ is the glycerol feed stage in the extractive distillation column, $F_{\mathrm{ETOH\text{-}ED1}}$ is the ethanol feed stage in the extractive distillation column, and $F_{\rm GLY}/F_{\rm ETOH}$ is the molar flow rate ratio between glycerol and ethanol feed streams. The distillation column where the entrainer is purified is a conventional system, and thus the Winn-Underwood-Gilliland method is once again used to find the design of this column, aiming for a purity of 99 mol % for glycerol.

For the two alternative schemes proposed, the possibility of prepurifying the ethanol by using liquid—liquid extraction with *n*-dodecane as entrainer is considered. To prove the ability of *n*-dodecane to separate water from ethanol by liquid—liquid extraction, Figure 3 shows the ternary diagram for the ethanol/water/*n*-dodecane mixture at 1 atm. The diagram shows two azeotropes, one being the ethanol—water azeotrope and the other an azeotrope between water and *n*-dodecane. This azeotrope, however, occurs at a high purity of water, at a temperature

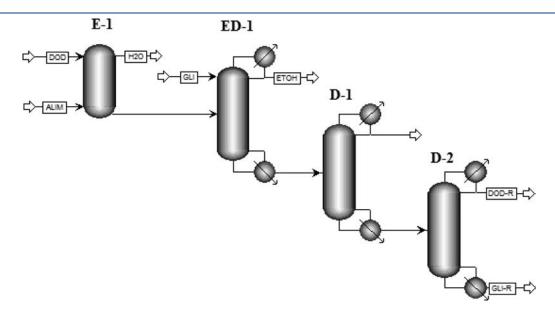


Figure 4. AS-1 alternative separation sequence.

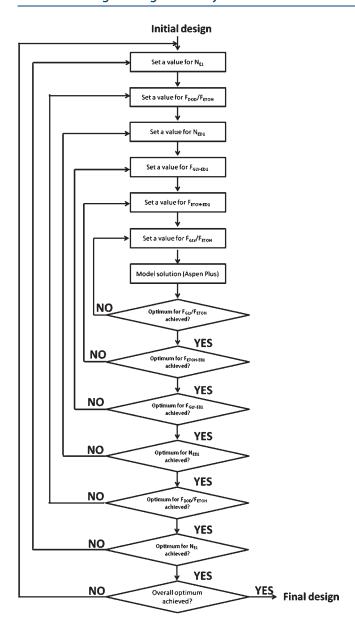


Figure 5. Optimization method for the AS-1 sequence.

of 99.47 °C. From the liquid—liquid envelope, it can be seen that, if *n*-dodecane is used as entrainer, almost pure water can be obtained in one phase, and in the other phase a mixture of ethanol, n-dodecane, and some water is obtained. The quantity of water in the second phase will depend, of course, on the composition of *n*-dodecane. In the context of the ideas discussed above, Figure 4 presents the first alternative purification sequence (AS-1). In this approach, the original mixture enters a liquid—liquid extraction column, where a portion of the water (39.9 kmol/h, with a purity of 99.95 mol %) is separated from ethanol using *n*-dodecane as extraction agent. Then, in an extractive distillation column, the rest of the water is separated from ethanol using glycerol as entrainer, aiming for a purity of 99.99 mol % of ethanol in the distillate stream. The bottoms stream leaving the extractive distillation column enters a distillation column where water is separated from the glycerol and n-dodecane, obtaining at the top of the column a waste stream with a mole flow rate of 1.11 kmol/h, containing water and some of the other components (around 85 mol % of water). In a second distillation column, the entrainers are recovered so they can be reused. To design the liquid-liquid extraction and the extractive distillation columns, an initial guess is first considered, aiming for a global recovery for ethanol higher than 98 mol % and a purity of 99.99 mol % for ethanol at the top of the extractive distillation column. Once the design specifications have been reached, degrees of freedom are manipulated to reduce energy consumption in the extractive distillation column. The optimization methodology used for the sequence AS-1 is shown in Figure 5, where N_{E1} is the number of stages in the liquid—liquid extraction column, $F_{\rm DOD}/F_{\rm ETOH}$ is the molar flow rate of n-dodecane/ethanol, $N_{\rm ED}$ is the number of stages in the extractive distillation column, $\boldsymbol{F}_{\text{GLY-ED1}}$ is the glycerol feed stage in the extractive distillation column, $F_{\text{ETOH-ED1}}$ is the ethanol feed stage in the extractive distillation column, and $F_{\rm GLY}/F_{\rm ETOH}$ is the molar flow rate ratio of glycerol-ethanol. The bottoms stream of the extractive distillation column contains *n*-dodecane, glycerol, and some water. The extraction agents are purified in a conventional distillation train, separating first the water and, in a second column, the *n*-dodecane and the glycerol. Both columns are designed using the Winn-Underwood-Gilliland method, aiming for a purity of 99 mol % for *n*-dodecane and glycerol.

The second purification alternative (AS-2) is shown in Figure 6. In this separation scheme, ethanol is prepurified in a liquid—liquid

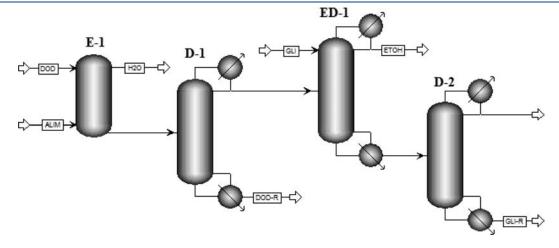
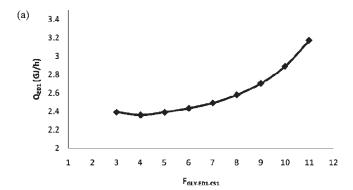


Figure 6. AS-2 alternative separation sequence.



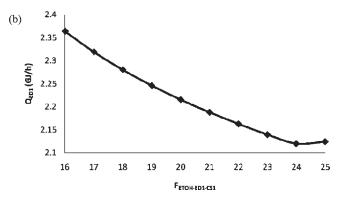


Figure 7. Effect of locations of feed streams on energy consumption of the extractive distillation column for CS-1: (a) glycerol feed stream, (b) ethanol feed stream.

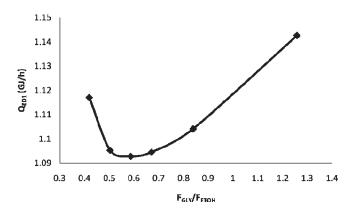


Figure 8. Effect of glycerol/ethanol molar feed ratio on energy consumption of the extractive distillation column for CS-1.

extractive column using *n*-dodecane as extraction agent. Then, the stream containing ethanol, *n*-dodecane, and some water enters a distillation column, where *n*-dodecane is recovered. Ethanol is then obtained with a purity of 99.99 mol % in an extractive distillation column, using glycerol as entrainer. In a final separation stage, glycerol is recovered to be reused as entrainer. To design the liquid—liquid extraction column and the extractive distillation column, an initial guess is required, aiming for a recovery higher than 98 mol % for ethanol and a purity of 99.99 mol % at the top of the extractive distillation column. The conventional distillation column following the liquid—liquid extraction column is designed using the Winn—Underwood—Gilliland method, aiming for a purity of 99 mol % for *n*-dodecane in the bottoms stream. Once the design specifications are reached, an

Table 1. Design Characteristics of Columns in the CS-1 Sequence

	D-1	ED-1	D-2
number of stages	20	26	6
feed stage	10	24	5
entrainer feed stage		4	
feed molar flow (kmol/h)	45.36	5.41	4.15
entrainer molar flow (kmol/h)		3.18	
distillate flow (kmol/h)	5.41	4.44	0.99
bottoms flow (kmol/h)	39.94	4.15	3.15
temperature, top (K)	351.35	351.47	361.05
temperature, bottoms (K)	373.16	439.97	554.25
design pressure (kPa)	101.35	101.35	101.35
reflux ratio	6.1902	1.1341	0.3863
heat duty (GJ/h)	1.78	0.27	0.15

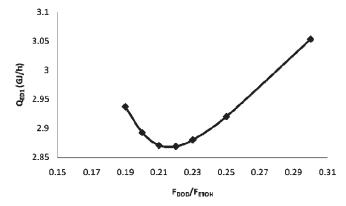


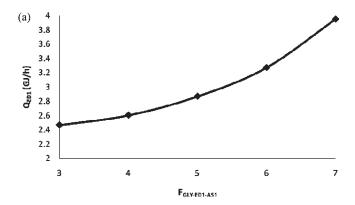
Figure 9. Effect of *n*-dodecane/ethanol molar feed ratio on energy consumption of the extractive distillation column for AS-1.

analysis of the design variables is performed to reduce energy consumption in the conventional distillation column and the extractive distillation column. The optimization method is the same as that used for the AS-1 sequence (Figure 5), but it presents a higher number of degrees of freedom. The next piece of equipment is a conventional distillation column, where glycerol is recovered with a purity of 99 mol %, with a waste stream at the top of the column containing around 99 mol % of water, with a molar flow rate of 0.93 kmol/h. This column is designed using the Winn—Underwood—Gilliland method.

2.2. Costs Calculations and Emissions Analysis. Total annual cost has been calculated for the different purification alternatives under study. To perform such calculations, the Guthrie method¹⁸ has been used. For a given process, the total annual cost (TAC) is thus given by

$$TAC = C_E + C_U \tag{1}$$

where $C_{\rm E}$ is the annualized equipment cost and $C_{\rm U}$ is the cost of the utilities required to keep the process operating. The equipment cost has been annualized considering 5 years as the time to recover the investment. The utilities costs are given by the costs of the cooling water and the costs of the steam used to supply the process with thermal energy. The material for the construction of all the equipment has been considered to be carbon steel, since there are no extreme operating conditions and the components involved in the process are not especially corrosive. In addition,



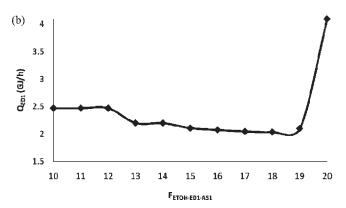


Figure 10. Effect of locations of feed streams on energy consumption of the extractive distillation column for AS-1: (a) glycerol feed stream, (b) ethanol feed stream.

8400 h of operation per year are considered. The calculated costs have been updated using the Chemical Engineering Costs Index. Since energy cost represents the most significant contribution to the total annual cost, ¹⁹ and the solvents are recovered to be reused, thus avoiding the continuous use of fresh entrainers, the cost corresponding to the solvents has not been considered in the costs calculations.

To compliment the performance analysis, emissions of carbon dioxide due to the generation of steam to provide thermal energy to the process are calculated. The methodology used to determine such emissions has been reported by Gadalla et al.²⁰ Natural gas has been considered as fuel to deliver the energy required to produce saturated steam at a pressure of 10 000 kPa. This pressure level has been selected to satisfy the temperature levels at all the reboilers in the process.

3. RESULTS AND DISCUSSION

The first analyzed process is the conventional distillation and extractive distillation sequence. In the first column, ethanol is purified to 92.95 mass % (i.e., 83.76 mol % of ethanol). Once the ethanol has been prepurified, the stream enters the extractive distillation column. The effect of the number of stages on the energy requirements has been analyzed, and it has been found that increasing the number of stages does not have a significant effect on heat duty. Thus, 26 stages have been selected as the number of stages for the column, which allows performing the desired separation with an acceptable number of stages and heat duty. Figure 7 shows the effect of the location of the glycerol feed stream and the location of the ethanol feed stream on the energy

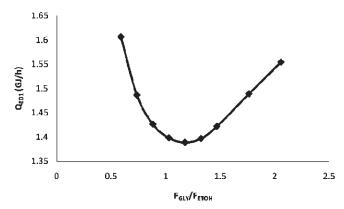


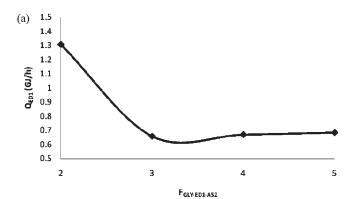
Figure 11. Effect of glycerol/ethanol molar feed ratio on energy consumption of the extractive distillation column for AS-1.

consumption of the extractive distillation column. According to Figure 7a, in order to reduce the energy requirements of the column, the glycerol stream must be located in a stage close to the top of the column. From Figure 7b, it can be seen that the ethanol feed stream must be located in a stage close to the bottoms of the column. The positions of feed streams allow better contact between the ethanol stream and the entrainer, enhancing the separation. The effect of the glycerol/ethanol molar feed ratio on the energy requirements is shown in Figure 8. The mol flow of glycerol required to perform the separation is relatively low, but enough to achieve the desired ethanol purity, which has been fixed as a design specification. For lower flow rate ratios than those shown in Figure 8 (about 0.4), the design specification for ethanol is not achieved. Once the analysis of the extractive distillation column has been carried out, a third column is used to purify the glycerol. This column has been designed to obtain a molar purity of 99% for the glycerol in the bottoms of the column. The main design characteristics of the columns involved in the CS-1 purification scheme are shown in Table 1.

The results for the AS-1 purification sequence are as follows. Since the separation in the extractive distillation column depends on the separation taking place in the liquid—liquid extraction column, the analysis of energy requirements will take into account the variables in the liquid-liquid extraction column and the extractive distillation column. The impact of the number of stages in the liquid-liquid extraction column on the energy requirements of the extractive distillation column has been found to be almost insignificant. The impact of the molar feed ratio for n-dodecane and ethanol/water feed to the liquid—liquid extraction column on the heat duty is presented in Figure 9. It can be seen that a low flow rate for n-dodecane is required to perform the prepurification of ethanol from the ethanol/water mixture with a low heat duty in the extractive distillation column. For molar ratios lower than 0.19, ethanol purity has not been achieved. Once the main degrees of freedom for the liquidliquid extraction column have been analyzed, the study focuses on those corresponding to the extractive distillation column. The number of stages in the extractive distillation column has an insignificant impact on the energy consumption. Figure 10 shows the effect of the location of the feed streams on energy requirements. It can be seen that, to reach a low heat duty for the extractive distillation column, the glycerol stream must be located in a stage close to the top of the column and the ethanol stream must be located in a stage close to the bottom of the column. These results are similar to those obtained for the extractive distillation

Table 2. Design Characteristics of Columns in the AS-1 Sequence

	E-1	ED-1	D-1	D-2
number of stages	20	20	10	12
feed stage	20	18	6	7
entrainer feed stage	1	3		
feed molar flow (kmol/h)	45.36	15.44	29.14	28.03
entrainer molar flow (kmol/h)	9.98	18.14		
top stage flow (kmol/h)	39.90	4.44	1.11	9.80
bottoms stage flow (kmol/h)	15.44	29.14	28.03	18.23
temperature, top (K)	302.89	351.47	366.65	489.04
temperature, bottoms (K)	300.15	481.43	524.95	559.53
design pressure (kPa)	101.35	101.35	101.35	101.35
reflux ratio		4.4556	0.9551	1.4898
heat duty (GJ/h)		1.39	0.51	1.12



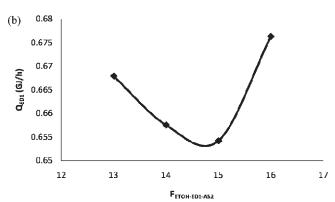


Figure 12. Effect of locations of feed streams on energy consumption of the extractive distillation column for AS-2: (a) glycerol feed stream, (b) ethanol feed stream.

column in the CS-1. The effect of the glycerol/ethanol molar feed ratio is shown in Figure 11. A molar ratio between 1 and 1.3 is required to obtain lower energy consumption for the extractive distillation column. For molar ratios lower than 0.5, it has been not possible to obtain the desired ethanol purity. Once the required parameters for the liquid—liquid extraction column and the extractive distillation column have been found, the conventional distillation columns are designed to purify the *n*-dodecane and the glycerol. These columns are designed to obtain a molar purity of 99% for both entrainers. The main design characteristics of the columns involved in the AS-1 purification scheme are shown in Table 2.

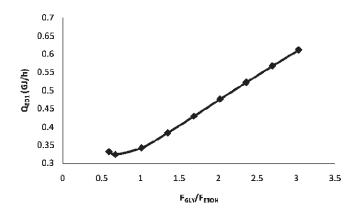


Figure 13. Effect of glycerol/ethanol molar feed ratio on energy consumption of the extractive distillation column for AS-1.

Table 3. Design Characteristics of Columns in the AS-2 Sequence

	E-1	D-1	ED-1	D-2
number of stages	20	16	18	15
feed stage	20	13	15	7
entrainer feed stage	1		3	
feed molar flow (kmol/h)	45.36	15.44	5.39	4.60
entrainer molar flow (kmol/h)	9.98		3.63	
top stage flow (kmol/h)	39.90	5.39	4.42	0.9349
bottoms stage flow (kmol/h)	15.44	10.05	4.60	3.6654
temperature, top (K)	302.94	351.44	351.47	309.67
temperature, bottoms (K)	300.09	475.17	447.40	555.88
design pressure (kPa)	101.35	101.35	101.35	101.35
reflux ratio		0.023	1.4498	1.9999
heat duty (GJ/h)		0.99	0.32	0.22

Table 4. Total Energy Requirements for the Analyzed Sequences

	$Q_{\mathrm{T}}\left(\mathrm{GJ/h}\right)$	$\%_{\rm savings}$
CS-1	2.19	0
AS-1	3.02	-37.15
AS-2	1.54	30.03

We will now consider the results for the AS-2 sequence. The design for the liquid-liquid extraction column has been considered to be the same as that obtained for the AS-1 sequence, since said design has proven to be appropriate to perform the separation with the lowest energy consumption for the extractive distillation column. Once the liquid-liquid extraction occurs, a conventional distillation column is used to purify the *n*-dodecane to a purity of 99 mol %. The distillate stream enters the extractive distillation column. Since the molar flow entering the column is different from the molar flow of the AS-1 sequence, the degrees of freedom for this column must be analyzed. As observed for the other cases, the influence of the number of stages on the extractive distillation column's energy requirements is quite small. The effect of feed stream locations on energy requirements for the extractive distillation column is shown in Figure 12. As expected, the glycerol stream must be located on the top stages of the

Table 5. Cost Analysis Results (USD \times 10³/year)

	equipment	utilities	TAC
CS-1	58.14	611.31	669.44
AS-1	75.96	719.55	795.51
AS-2	62.95	291.64	354.59

Table 6. Emissions of Carbon Dioxide

	CO ₂ emissions (kg/h)
CS-1	214.1
AS-1	293.6
AS-2	149.8

column, and the ethanol feed stream must be located near to the bottoms of the column. For molar ratios lower than 0.5, ethanol purity has not been achieved. Figure 13 shows variation in energy requirements with the glycerol/ethanol molar feed ratio. It can be seen from this figure that the glycerol molar flow required to perform the separation with a low heat duty is relatively low, with a glycerol/ethanol ratio of around 0.8. Once the ethanol has been purified, the glycerol is recovered with a purity of 99 mol % in a conventional distillation column. Design characteristics of the columns in the AS-2 purification scheme are shown in Table 3.

The total energy requirements for all the analyzed processes are presented in Table 4, together with the energy savings taking the CS-1 separation scheme as a basis. It can be seen that, when the two entrainers enter the extractive distillation column (AS-1), the total energy requirements in the process are higher than those of the conventional separation sequence. On the other hand, if the *n*-dodecane is separated from the ethanol/water mixture before entering the extractive distillation column, energy savings of around 30% over the CS-1 are obtained. Thus, in terms of energy consumption, the best alternative is the AS-2 sequence, first preconcentrating the ethanol by liquid—liquid extraction, next separating the *n*-dodecane, then purifying the ethanol in an extractive distillation column, and finally recovering the glycerol used as entrainer in the extractive distillation system.

Total annual costs have been calculated for the three analyzed sequences. Table 5 presents the results of these calculations. Even considering that the AS-2 sequence requires four pieces of equipment and the CS-1 sequence requires only three, according to Table 5 the total annual cost for the AS-2 sequence is approximately half of the total annual cost for the CS-1 sequence. The AS-1 sequence proves to be more expensive than the CS-1 because of its high steam requirements. Finally, in Table 6 the results of the emissions analysis are shown. Given the low energy duty required for the AS-2 sequence compared with the other sequences, this sequence has also the lower CO₂ emissions among the analyzed systems, thus having the potential of a low environmental impact in terms of thermal energy distribution. Thus, it can be stated that, in terms of energy consumption, costs, and CO₂ emissions, the AS-2 sequence is the most promising scheme among the systems under study.

4. CONCLUSIONS

Alternatives have been proposed for the purification of a typical mixture of ethanol—water obtained from fermentation of biomass. These new schemes involve the use of *n*-dodecane as entrainer in a liquid—liquid extraction system to preconcentrate

the ethanol from the ethanol—water mixture, followed by extractive distillation with glycerol as entrainer. This method is expected to require less energy to perform the separation than the traditional distillation-extractive distillation sequence, since the liquid-liquid extraction column requires no energy input. According to the results, among the alternatives under analysis, the most promising is the system involving preconcentration of ethanol in a liquid—liquid extraction column using *n*-dodecane as entrainer, followed by separation of the *n*-dodecane from the mixture containing ethanol and the remaining water, and finally purification of the ethanol, using extractive distillation with glycerol as entrainer. This process requires less energy than the traditional separation sequence and has lower carbon dioxide emissions. The alternative process requires more equipment than the traditional one; even so, the estimated costs are lower for the proposed scheme because of its lower energy requirements. The other proposed separation method resulted in higher energy consumption, CO₂ emissions and costs, because a higher molar flow is processed in the extractive distillation column.

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■ REFERENCES

- (1) Balat, M.; Balat, H.; Öz, C. Progress in Bioethanol Processing. *Prog. Energy Combust. Sci.* **2008**, 34, 551.
- (2) John, R. P.; Anisha, G. S.; Nampoothiri, K. M.; Pandey, A. Micro and Macroalgal Biomass: A Renewable Source for Bioethanol. *Bioresour. Technol.* **2011**, *102*, 186.
- (3) Petrou, C. E.; Pappis, P. C. Biofuels: A Survey on Pros and Cons. *Energy Fuel* **2009**, 23, 1055.
- (4) Bergeron, P. Environmental Impacts of Bioethanol. In *Handbook on Bioethanol: Production and Utilization*; Wyman, C. E., Ed.; CRC Press: Boca Raton, FL, 1996; pp 89–103.
- (5) Chiaramonti, D. Bioethanol: Role and Production Technologies. In *Improvement of Crop Plants for Industrial End Uses*; Ranalli, P., Ed.; Springer: New York, 2007; pp 209–251.
- (6) Eggeman, T.; Atiyeh, C. The Role for Biofuels. Chem. Eng. Prog. 2010, 106, 36.
- (7) Aggarwal, N. K.; Nigam, P.; Singhm, D.; Yadav, B. S. Process Optimization for the Production of Sugar for the Bioethanol Industry from Sorghum, a Nonconventional Source of Starch. *World J. Microbiol. Biotechnol.* **2001**, *17*, 411.
- (8) Champagne, P. Bioethanol from Agricultural Waste Residues. Environ. Prog. 2008, 27, 51.
- (9) Elnashaie, S.; Garhyan, P. Bioethanol Production—Solving the Efficiency Bottleneck. *Chem. Eng.* **2004**, 30.
- (10) Dias, M. O. S.; Ensinas, A. V.; Nebra, S. A.; Maciel Filho, R.; Rossell, C. E. V.; Maciel, M. R. W. Production of Bioethanol and other Bio-Based Materials from Sugarcane Bagasse: Integration to Conventional Bioethanol Production Process. *Chem. Eng. Res. Des.* **2009**, 87, 1206.
- (11) Garcia-Herreros, P.; Gomez, J. M.; Gil, I. D.; Rodriguez, G. Optimization of the Design and Operation of an Extractive Distillation System for the Production of Fuel Grade Ethanol Using Glycerol as Entrainer. *Ind. Eng. Chem. Res.* **2011**, *50*, 3977.

- (12) Chavez-Islas, L. M.; Vasquez-Medrano, R.; Flores-Tlacuahuac, A. Optimal Synthesis of a High Purity Bioethanol Distillation Column Using Ionic Liquids. *Ind. Eng. Chem. Res.* **2011**, *50*, 5175.
- (13) Vane, L.M. A Review of Pervaporation for Product Recovery from Biomass Fermentation Processes. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 603.
- (14) Luyben, W. L. Control of a Column/Pervaporation Process for Separating the Ethanol/Water Azeotrope. *Ind. Eng. Chem. Res.* **2009**, 48, 3484.
- (15) Arifeen, N.; Wang, R.; Kookos, I. K.; Webb, C.; Koutinas, A. A. Process Design and Optimization of Novel Wheat-Based Continuous Bioethanol Production System. *Biotechnol. Prog.* **2007**, *23*, 1394.
- (16) Bhownath, R. The Use of *n*-Dodecane as a Solvent in the Extraction of Light Alcohols from Water. Master of Sciences in Engineering Thesis, University of Kwa-Zulu Natal, Durban, South Africa, 2008.
- (17) Kummar, S.; Singh, S. P.; Mishra, I. M.; Adhikari, D. K. Recent Advances in Production of Bioethanol from Lignocellulosic Biomass. *Chem. Eng. Technol.* **2009**, 32, 517.
- (18) Turton, R.; Bailie, R. C.; Whiting, W. B.; Shaeiwitz, J. A. Analysis, Synthesis, and Design of Chemical Processes; Prentice Hall: New York, 1998.
- (19) Smith, R. Chemical Process Design and Integration; Wiley: Chichester, UK, 2005.
- (20) Gadalla, M. A.; Olujic, Z.; Jansens, P. J.; Jobson, M.; Smith, R. Reducing CO₂ Emissions and Energy Consumption of Heat-Integrated Distillation Systems. *Environ. Sci. Technol.* **2005**, *39*, 6860.