# Optimization of Hybrid Distillation-Hydrophilic and Organophilic Pervaporation Systems

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The hybrid distillation-pervaporation process is an efficient method for the removal or recovery of volatile organic compounds from their aqueous mixtures. The hybrid distillation-pervaporation process has not only shown its excellent performance in the purification of solvent mixtures but also proven to have a potential of saving energy. In this study, the hybrid distillation-pervaporation process is optimized for the treatment of low-alcohol waste solvents. Three combinations are examined: distillation with hydrophilic pervaporation, distillation with organophilic pervaporation and distillation with both pervaporation methods. The hybrid systems result in a better performance in term of energy-use compared to conventional distillation. It is observed that a combination of distillation and hydrophilic or/and organophilic pervaporation is suitable for the separation of ethanol-water mixtures and the most recommended is the third layout.
Keywords: hybrid distillation-pervaporation process, pervaporation, ethanol-water separation, azeotrope

## 1. Introduction

In fine chemical industries, specifically in the pharmaceutical industry, treatment of wastewater and industrial waste solvents is a principal requirement. Production procedures generate large amounts of liquid waste and industrial waste solvents which contain various organic substances such as alcohol, e.g. ethanol, methanol, isopropanol, butanol and isobutanol. The separation of various organic substances from industrial wastewater is an essential and demanding task for environmental protection. The distillation and pervaporation membranes are commonly used in wastewater treatment as well as water supply. It must be said that the components of organic solvent mixtures often form azeotropic mixtures, therefore it is difficult to separate them by conventional methods. The distillation technique often proves to be a good solution to wastewater separation, except in the case of a mixture with high-water content and low volatile component. The hybrid distillation-pervaporation process is one possible solution for the removal of small contaminants from liquid mixtures. The research in this specific direction is quite dynamic and many results have been presented in recent studies, i.e. separation of Volatile Organic Compounds (VOC) from wastewater using hybrid distillation and pervaporation membranes process (Sommer and Melin, 2004), separation of ethyl acetate-ethanol mixture (Parvez et al., 2012), ethyl acetate-ethanol-methanol (León and Fontalvo, 2018), acetone-butanol-ethanol (Tóth et al., 2019), isobutanol (Omidali et al., 2014), isopropanol (Van Hoof et al., 2004), (Hassankhan and Raisi, 2020), tetrahydrofuran (Koczka et al., 2007), ethanol (Haelssig et al., 2011), and methanol (Luis et al., 2014) from aqueous mixture. Naturally, this pervaporation and hybrid distillation-pervaporation process is favorably considered as an attractive technology for several separation processes.

In this study, the combination of the distillation and hydrophilic or/and organophilic membrane pervaporation is investigated. The hybrid distillation-pervaporation process is modelled and optimized by using the CHEMCAD process simulator to separate the ethanol-water mixture, which forms a homogeneous azeotrope with minimum boiling point.

## 2. Materials and methods

The ethanol-water mixture was subjected to a separation process targeting the ethanol and water content of the mixture, by a hybrid distillation-pervaporation system. "Steady-state" modelling was used. The modelling was performed using CHEMCAD, a hybrid package of intuitive chemical process simulation software. UNIQUAC thermodynamic model was applied for the modelling of distillation and pervaporation. The main goal of the modelling work was to optimize the characteristics of the distillation column for the given ethanol-water mixture (data can be seen in Tables 1): the number of theoretical plates of the distillation column, the ethanol and water purities and reflux radio.

### 2.1 Modelling schemes

The alcohol-water mixture separation procedures, hybrid distillation-hydrophilic pervaporation system and hybrid distillation-organophilic pervaporation system are shown in Figure 1a and Figure 1b, respectively. From hydrophilic systems, water can be obtained in principle as a permeate product and ethanol as a retentate product, and the opposite is true for organophilic systems.
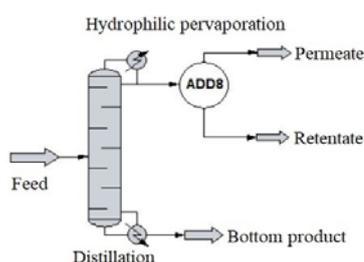


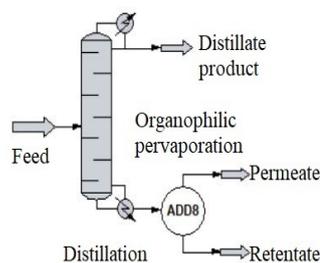Figure 1a: Flowsheet of hybrid distillation-hydrophilic pervaporation system

Figure 1b: Flowsheet of hybrid distillation-organophilic pervaporation system

### 2.2. Membrane characteristics, feed data

The model has used a pervaporation membrane of 80 m$^2$ for the separation, as a basic standard of industrial background. The number of theoretical plates of the distillation column was varied and optimized. The pervaporation membrane performance depends on the temperature and pressure at which the separation operates, and for this specific organophilic membrane type, they were set at 70 °C and 3 bar. In the case of the hydrophilic type, the feed conditions were 90 °C and 3 bar. The properties of the pervaporation membrane model ((Valentínyi et al., 2013), shown in Table 1, are in accordance with the experimental results which has been done by (Valentínyi et al., 2013) and (Haáz et al., 2019).

Table 1: Hydrophilic pervaporation membrane parameters (PERVAP ™ 1210 type membrane) (Valentínyi et al., 2013) and Organophilic pervaporation membrane parameters (PERVAP ™ 4060 type membrane) (Haáz et al., 2019) for ethanol-water mixture

| Pervaporation units | | PERVAP ™ 1210 | PERVAP ™ 4060 | Unit |
|---|---|---|---|---|
| Membrane surface | | 80 | 80 | m$^2$ |
| Section number | | 800 | 800 | - |
| Permeate pressure | | 0.008 | 0.008 | bar |
| Inlet pressure drop | | 0.1 | 0.1 | bar |
| Permeability | | $10^8$ | $10^8$ | kmol/m$^2$hbar |
| Transport coefficient | Water | 0.000202 | 0.026 | kmol/m$^2$h |
| | Ethanol | 0.0000193 | 0.077 | |
| Activity energy | Water | 77877 | 31363 | kJ/kmol |
| | Ethanol | 128572 | 33090 | |
| Parameter "B" | Water | 2.63 | -0.73 | - |
| | Ethanol | -8.68 | -0.04 | |

More specifically, the feed composition was investigated with 2 % by weight ethanol and 98 % by weight water at 20 $^{o}$C, 1 bar, and 1000 kg/h feed flow. The feed stream was entered into the middle of the distillation column. As a specific requirement, a minimum water content of 99.9% was targeted.

## 3. Results and discussion

### 3.1. Optimization of hybrid distillation-hydrophilic pervaporation system - D+HPV

The optimization of the hybrid distillation-hydrophilic pervaporation system was performed establishing the relationship between theoretical plate numbers and ethanol purities, distillation column's reboiler duties, and reflux ratios.

Figure 2 shows the relationship between the ethanol purities and theoretical plate numbers of the distillation column with ORIGIN program. As it can be seen, as the number of theoretical plate increases, the ethanol purity of the retentate product also increases. At first, the growth is more rapid, but it gradually becomes constant after a certain point. In Figure 2, the intersection of (11.45; 0.973) was found by plotting the equations. As the number of the theoretical plates approaches 12, the purity of the ethanol of the retentate product no longer increases significantly. Thus, it is not necessary to use a higher number of theoretical plates in this model.Similar analysis was performed between theoretical plate number and reflux ratio, as shown in Figure 3a. Figure 3b illustrates the relationship between the number of the theoretical plates and reboiler duties. Based on these figures, it can be said that in both cases, when the number of theoretical plates increases, the reflux ratio and the heat requirement decrease to a point and then become stabilized. In both cases, the reflux ratio and the heat requirement values do not change after 12 plates, so it can be stated that there is a correlation between the three indicators. By using 12 plates, one can achieve the most economical and efficient separation.
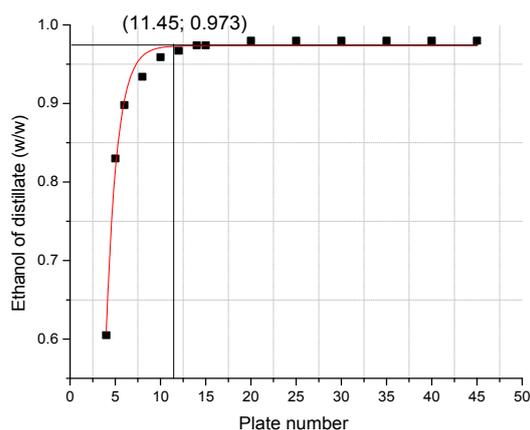


Figure 2: In D+HPV, Intersection of equations describing plate number and distillate ethanol purity curves
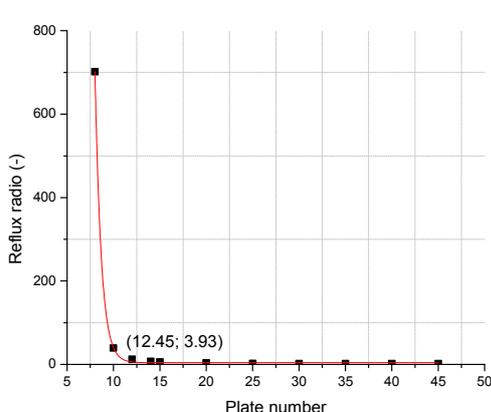


Figure 3a: In D+HPV system, Intersection of the reflux ratio-plate number relationship
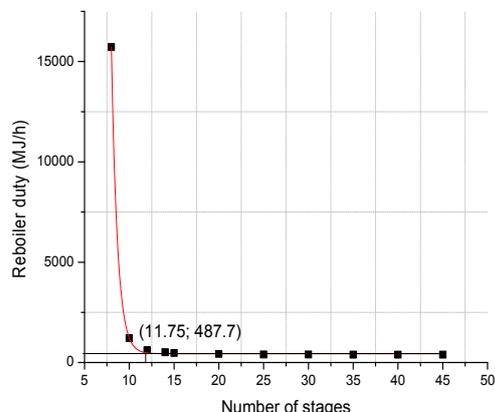
Figure 3b: In D+HPV system, Intersection of the Reboiler duty-plate number relationship

### 3.2. Optimization of hybrid distillation-organophilic pervaporation system - D+OPV

Similar investigation was performed for the relationship between theoretical plate numbers and ethanol purities (Figure 4), theoretical plate numbers and reflux ratios (Figure 5a), theoretical plate numbers and heat (Figure 5b) for the hybrid distillation-organophilic pervaporation system. Based on these figures, it can be seen that the theoretical number of plates increases, the ethanol purity of the distillate also increases, and the reflux ratio and reboiler duty decrease to a point and then become stable. Using the ORIGIN program, it's possible to define the point on the curve where it starts to stabilize. As a result, 20 is the optimized number of the theoretical plates, in order to achieve the most efficient separation.
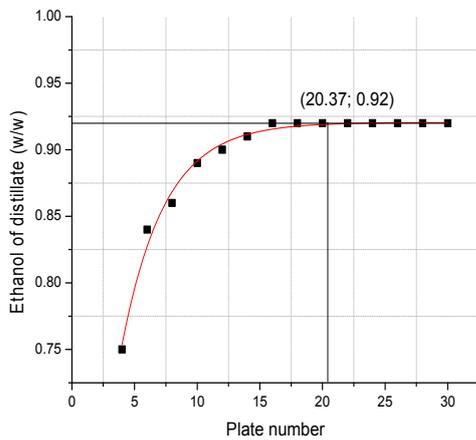


*Figure 4: In D+OPV, Intersection of equations describing plate number and distillate ethanol purity curves*
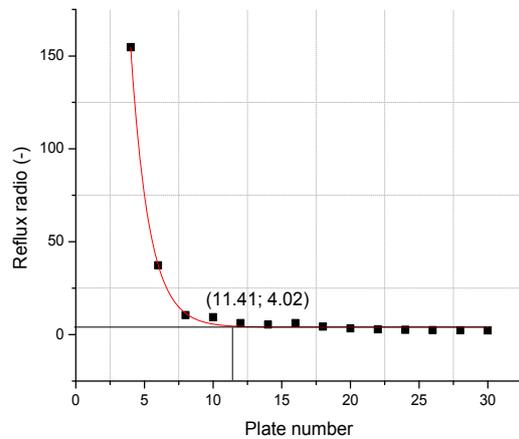


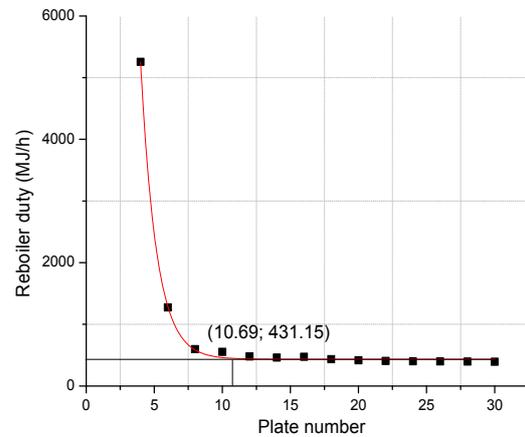*Figure 5a: In D+OPV system, Intersection of the reflux ratio plate number relationship*

*Figure 5b: In D+OPV system, Intersection of the Reboiler duty-plate number relationship*

### 3.3. Separation results at the optimum point

The results of D+HPV system (Figure 6), the D+OPV system (Figure 7) and the combination D+HPV+OPV systems (Figure 8) were examined at the optimum point. It can be seen, with the same feed composition flow (1000 kg/h, 98 % by weight water - 2 % ethanol and a membrane with an effective area of 80 m$^2$), the water received in the D+HPV process is qualitatively and quantitatively high (99.99 % water as a bottom product with a flow of 978.6 kg/h and 99.75 % water with a flow of 0.814 kg/h as a permeate). In this case, the amount of water leaving the D+OPV process is 921.299 kg/h as retentate (its composition is 99.93 % water) and 58.027 kg/h as permeate (its composition is 99.5 % water). The water's quality and quantity of retentate leaving from D+HPV+OPV process (940.566 kg/h, 99.99 % water) is not too different than D+HPV system. The highest ethanol purity is also obtained from the D+HPV system (20.586 kg/h, 96.7 % ethanol), the next is D+HPV+OPV system (20.688 kg/h, 96.2 % ethanol), and D+OPV system (20.675 kg/h, 92 % ethanol). The maximum of 99.75 % water can be obtained from D+HPV as permeate product.
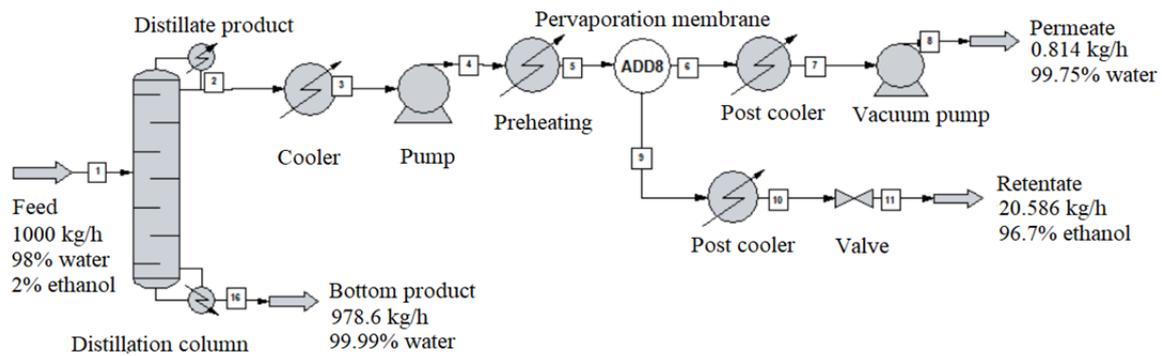
*Figure 6: The D+HPV system at the optimum point - 12 of theoretical plates*
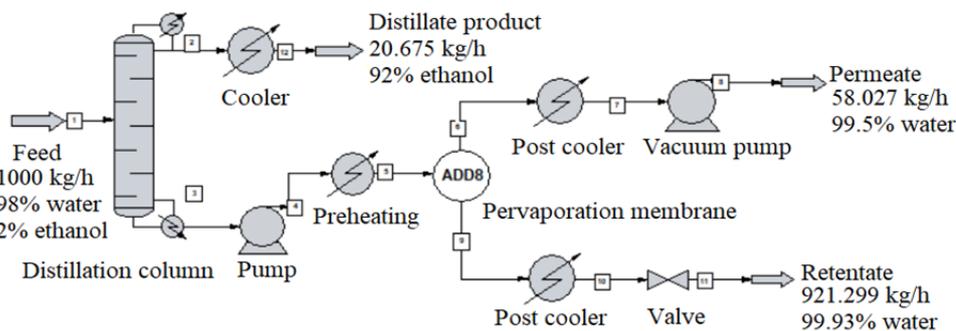


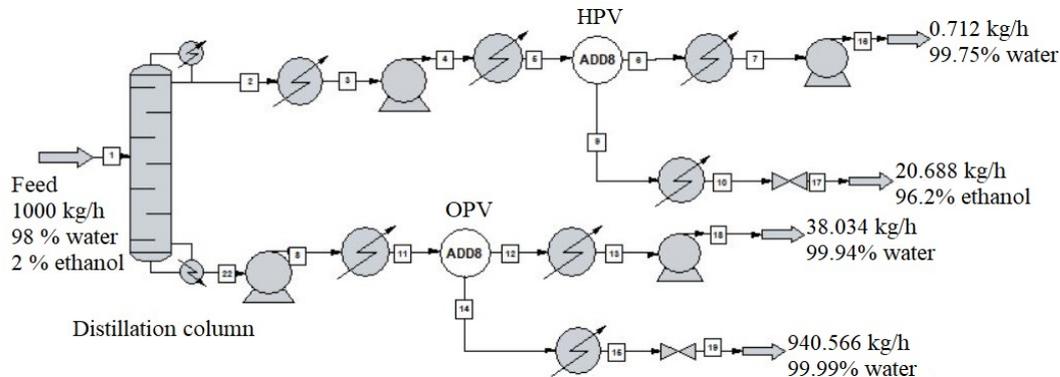*Figure 7: The D+OPV system at the optimum point - 20 of theoretical plates*



*Figure 8: The combination D+HPV+OPV system at the optimum point - 12 of theoretical plates*

Finally, the consumed heat energy in the three systems were analyzed. In the D+HPV system, the heat energy for separation of ethanol-water is 325.817 MJ/h while in the case of the D+OPV is -10.014 MJ/h and in the D+HPV+OPV is -6.527 MJ/h. If the amount of heat is positive (in D+HPV system), the heat energy is absorbed by the system, i.e. the heat is added to the system and a negative value (in D+OPV and D+HPV+OPV systems) indicates the release of heat. The D+HPV system used much more heat than the D+OPV and D+HPV+OPV. This can be explained by the fact that after the distillation, the system needs a cooler, pump, and preheating procedures, see Figure 6, to provide the optimal conditions for the flow which needs to enter the pervaporation membrane phase. Meanwhile, in the D+OPV and D+HPV+OPV systems, the flow is fed into the organophilic pervaporation membrane without the cooling phase, which results in the effective use of the heat from the bottom product. Therefore, the total absolute of the heat energy is, indeed, less than the D+HPV case.

## 4. Conclusion

The hydrophilic membrane performs better in both qualitative and quantitative aspects of ethanol-water mixture separation compared to the organophilic membrane, though it consumes more heat energy. From a hybrid hydrophilic membrane system, three products can be obtained: ethanol-rich retentate and water-rich distillation bottoms and permeate. Thus, it can be stated that, in addition to ethanol enrichment, almost pure water can be obtained as a final product. In the D+HPV system, nearly pure water in the bottom product is achieved in each run, so the required purification could be met. In the case of the retentate, ethanol with a purity of more than 96% by weight was obtained, i.e. it is possible to break the azeotropic point at the pressure of 1 bar. To summarize our work, it can be determined that the combination of D+HPV+OPV system obtained a better concentration of ethanol than the D+OPV system. Few differences can be detected in ethanol purity in the case of D+HPV and D+HPV+OPV layouts. However, D+HPV+OPV system requires the installation of additional pumps and heat exchangers, these do not bring significant extra expense due to their small size and capacity. It should be emphasized that the total heat requirement of the D+HPV+OPV system is lower, compared to the case of D+HPV system; therefore, the D+HPV+OPV arrangement is more favorable in terms of heat demand which results in more economical operation.

## References

Haáz, E., Valentínyi, N., Tarjáni, A.J., Fózer, D., André, A., Selim, A., Khaled, M., Fuad, R., Nagy, T., Deák, C., Mizsey, P., Tóth, A.J., 2019. Platform Molecule Removal from Aqueous Mixture with Organophilic Pervaporation: Experiments and Modelling. Periodica Polytechnica Chemical Engineering 63, 138-146.

Haelssig, J.B., Thibault, J., Tremblay, A.Y., 2011. Numerical investigation of Membrane Dephlegmation: A hybrid pervaporation–distillation process for ethanol recovery. Chemical Engineering and Processing: Process Intensification 50, 1226-1236.

Hassankhan, B., Raisi, A., 2020. Separation of isobutanol/water mixtures by hybrid distillation-pervaporation process: Modeling, simulation and economic comparison. Chemical Engineering and Processing - Process Intensification 155, 108071.

Koczka, K., Manczinger, J., Mizsey, P., Fonyo, Z., 2007. Novel hybrid separation processes based on pervaporation for THF recovery. Chemical Engineering and Processing: Process Intensification 46, 239-246.

León, J., Fontalvo, J., 2018. Basic Principles of a Hybrid Distillation and Pervaporation Unit in a Single Column: an Analytic Tool. Chemical Engineering Transactions 69, 565-570.

Luis, P., Amelio, A., Vreysen, S., Calabro, V., Van der Bruggen, B., 2014. Simulation and environmental evaluation of process design: Distillation vs. hybrid distillation–pervaporation for methanol/tetrahydrofuran separation. Applied Energy 113, 565-575.

Omidali, M., Raisi, A., Aroujalian, A., 2014. Separation and purification of isobutanol from dilute aqueous solutions by a hybrid hydrophobic/hydrophilic pervaporation process. Chemical Engineering and Processing: Process Intensification 77, 22-29.

Parvez, A.M., Luis, P., Ooms, T., Vreysen, S., Vandezande, P., Degrève, J., Van der Bruggen, B., 2012. Separation of ethyl acetate–isooctane mixtures by pervaporation and pervaporation-based hybrid methods. Chemical Engineering Journal 210, 252-262.

Sommer, S., Melin, T., 2004. Design and Optimization of Hybrid Separation Processes for the Dehydration of 2-Propanol and Other Organics. Industrial & Engineering Chemistry Research 43, 5248-5259.

Tóth, A.J., Szilágyi, B., Fózer, D., Do Thi, H.T., Selim, A.K.M., Haáz, E., 2019. Separation of acetone-butanol-ethanol (ABE) fermentation products by pervaporation, Circular Economy and Environmental Protection 3, 5-19.

Valentínyi, N., Cséfalvay, E., Mizsey, P., 2013. Modelling of pervaporation: Parameter estimation and model development. Chemical Engineering Research and Design 91, 174-183.

Van Hoof, V., Van den Abeele, L., Buekenhoudt, A., Dotremont, C., Leysen, R., 2004. Economic comparison between azeotropic distillation and different hybrid systems combining distillation with pervaporation for the dehydration of isopropanol. Separation and Purification Technology 37, 33-49.