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# A GENERALIZED METHODOLOGY FOR OPTIMAL CONFIGURATONS OF HYBRID DISTILLATION-PERVAPORATION PROCESSES

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## Abstract

The aim of this work is to illustrate the structural and parametric optimization of continuous hybrid distillation-pervaporation process with different configurations such as series, parallel, and series-parallel arrangement of pervaporation modules in the pervaporation network, and to propose a generalized methodology for difficult separations. A superstructure representation of hybrid process is considered and the process is modeled and optimized using an MINLP approach. The optimization strategy is to obtain the desired degree of either the retentate or the distillate purity without violating the composition constraints of products and heat exchange policy which minimizes the required membrane area by increasing the flux through the membrane. The structural and operating parameters such as number of trays required, feed tray location, reflux ratio, retentate recycle location, permeate recycle location, membrane feed location, number of pervaporation modules required, target composition (which is directly related to membrane area), and membrane selectivity are optimized for each configuration by minimizing the total annual cost (TAC) for the separation system. The optimization studies have been carried out with General Algebraic Modeling System software (GAMS/SBB/CONOPT) and the results of different configurations have been compared on the basis of TAC required for the separation. A total of three industrial case studies have been dealt with. The separation of isopropanol-water as an azeotropic mixture, propylene-propane as a close boiling mixture (system with a low relative volatility) and acetone-water as a tangent pinch mixture have been studied as representative examples.

**Keywords**: Hybrid process, optimization, MINLP, superstructure, pervaporation.

## 1. Introduction

Chemical industry is one of the largest consumers of energy, and distillation and related operations account for 95% of the total energy used for separations. However, many industrially important mixtures are difficult or impossible to separate by simple distillation due to various reasons such as low relative volatilities (< 1.5), presence of azeotropes, or presence of tangent pinches (Seader and Henley[1]). The pervaporation is a membrane process, where the components change their aggregate state from liquid to vapour while permeating (Bausa and Marquardt[2]). Its demand of energy is small when compared with distillation, and in many cases pervaporation can be an economical alternative. One of the applications is the separation of azeotropic mixtures, because the separation does not depend on the equilibrium between components but on the difference between the activities on the two sides of the membrane (Seader and Henley[1]). However, pervaporation is expensive because of relatively low permeate fluxes and usually low condensation temperatures, and generally in many cases pervaporation alone cannot supply products that are suitable for further processing or waste disposal (Gonzalez and Ortiz[3]). Therefore, hybrid processes of combined distillation and pervaporation are regarded as one means of overcoming these limitations. Hybrid distillation pervaporation processes have drawn attention of several authors in recent years, but only a few authors have focused their studies on the optimization aspects of hybrid processes with different approaches.

Kookos[4] carried out certain studies on optimal design of membrane/distillation column hybrid processes using the structural and parametric optimization procedures. The author described the superstructure model by assuming simplified steady state mathematical model where it was assumed that all streams taken from or returned to the distillation column were vapour streams. The methodology is therefore not suitable for other membrane processes such as pervaporation process or for dynamic systems such as batch processes. Daviou *et al.*[5] carried out the studies on optimal design of hybrid distillation pervaporation systems for the separation of EtOH/ETBE mixtures using rigorous models for both the distillation column and pervaporation membranes. Here, only series arrangement of membrane modules in the pervaporation network of hybrid process is considred. They did not mention anything about parallel or series/parallel arrangement of membrane modules and the authors considered only the parametric optimization of hybrid process and nothing is mentioned about the structural optimization of hybrid process. Barakat and Sorensen[6] carried out the studies on simultaneous optimal synthesis, design, and operation of batch and continuous hybrid separation processes. The authors considred only parallel arranegement of membrane modules in the membrane network of hybrid process, and did not cosider the series or series-parallel arrangement of membrane modules in the membrane network of hybrid process. Therefore, the superstructure poposed by the authors cannot be applied for the azeotropic separations, where generally series arrangement of membrane modules is required. The objective of this work therefore is to carry out the structural and parametric optimization of distillation pervaporation hybrid process for different configurations with series, parallel, and series-parallel arrangement of pervaporation modules in the membrane network of hybrid process and to propose a generalized methodology for the separation of azeotropes, close boiling mixtures, and tangent pinch mixtures.

## 2. Superstructure of Hybrid Process

Superstructure of hybrid process can be obtained by combining the superstructures of distillation column and pervaporation network. In this work, two different types of superstructures are considered for separation of azeotropes, close boiling mixtures, and tangent pinch mixtures. Figures 1 and 2 depict the superstructures of the hybrid process.

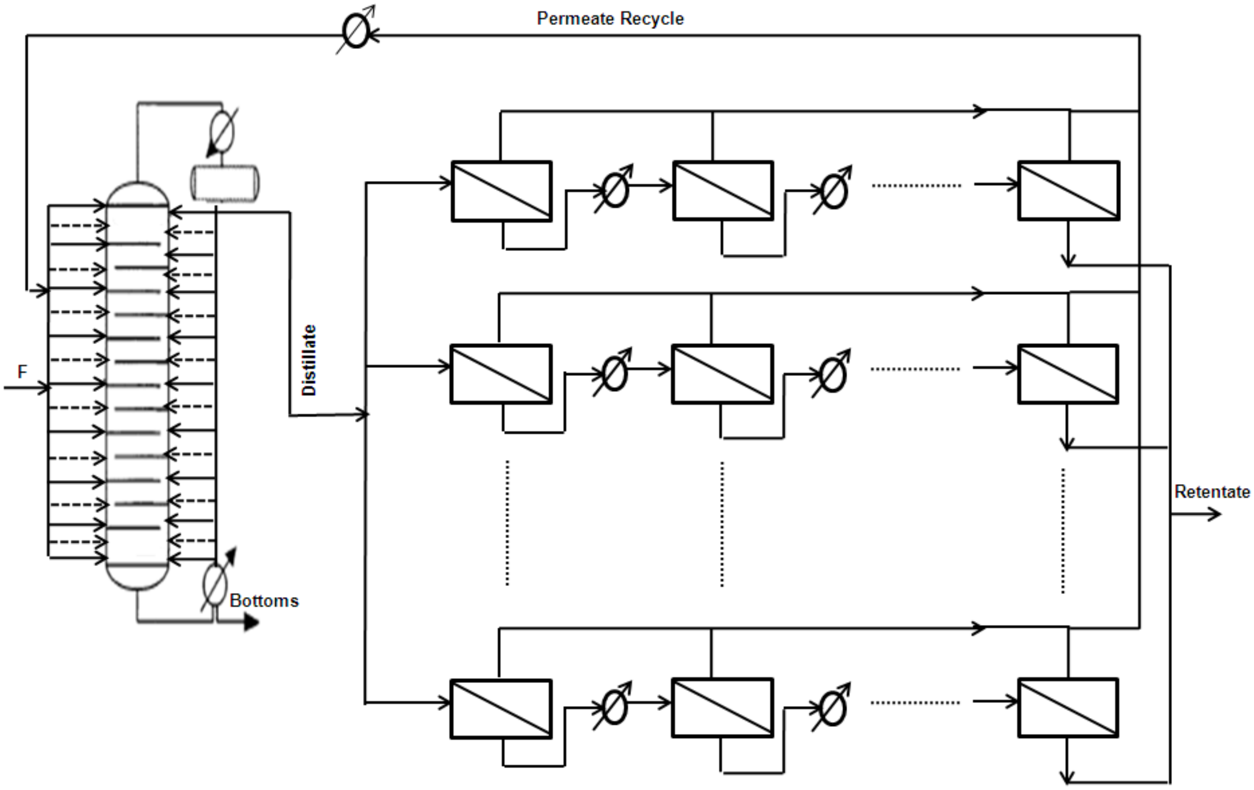

**Figure 1.** Suprestructure representation of hybrid process-I

According to the superstructure of Figure 1, separation is carried out in the distillation column up to certain concentration, i.e., up to critical concentration region, and then the distillate coming from the column is purified using pervaporation network. For example, in case of azeotropic separations, purification is carried out in the distillation column until azeotropic composition is achieved and then breaking of azeotrope is carried out in the pervaporation network. The tray model for this superstructure consists of four extra potential streams in addition to original vapour/liquid streams.

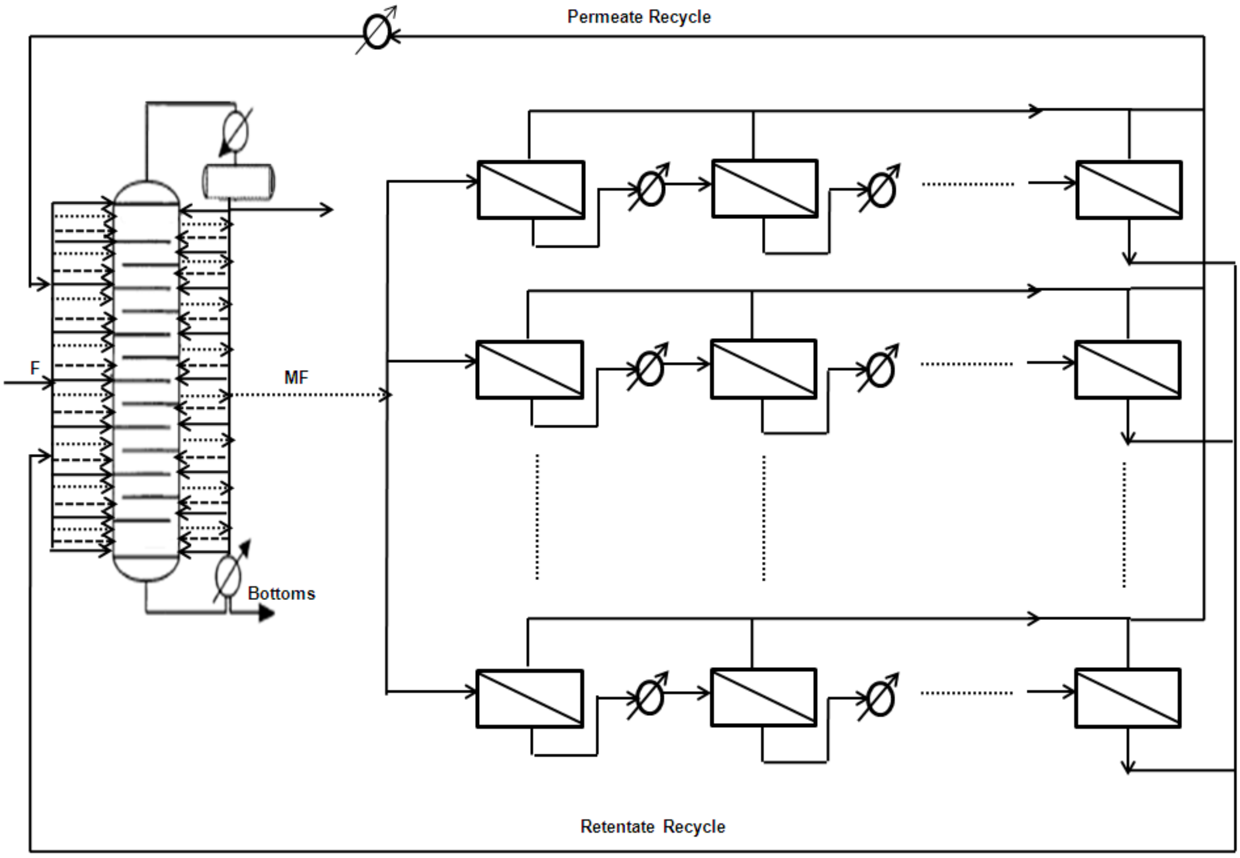

**Figure 2.** Superstructure representation of Hybrid process-II

According to the superstructure given in Figure 2, the final products of required purity can be obtained from the distillation column only, but this is not the case of superstructure shown in Figure 1, where the final purity of the required product can be obtained from the pervaporation network only. In this type of arrangement, the membrane feed stream is the side stream from the distillation column and both the retentate and the permeate coming from the pervaporation network are recycled back to distillation column for further purification. This superstructure is more complex compared to that of superstructure given in Figure 1. This configuration is more useful for the separation of close boiling mixtures. The tray model for this configuration consists of six extra potential streams in addition to the original vapour/liquid streams.

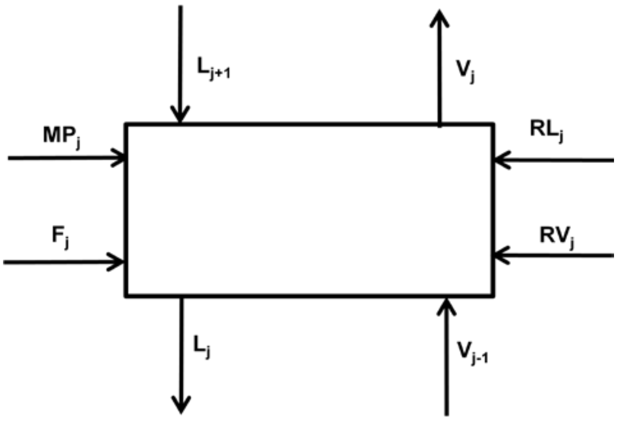

**Figure 3.** Tray model for Superstructure-I

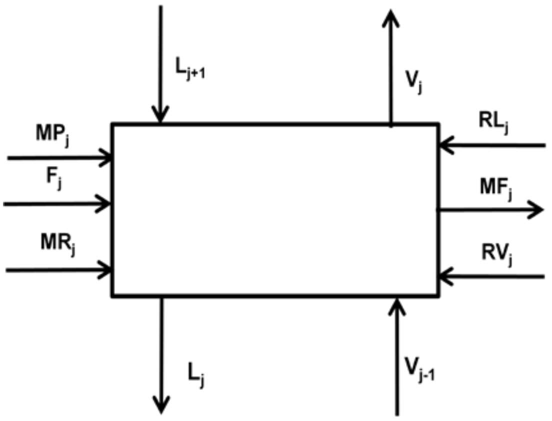

**Figure 4.** Tray model for Superstructure-II

Here, $RL_j$ is the refluxed liquid entering on tray j, $RV_j$ is the reboiled vapour entering on tray j, $MP_j$ and $MR_j$ are the permeate and retentate streams entering on tray j of the column. L and V (with proper suffix) represent the liquid and vapour streams entering/leaving the tray j of column.

## 3. Optimization problem formulation

The objective of the problem is to minimize the TAC required for the separation, subjected to all model equations of distillation and pervaporation processes, purity constraints, bounds on design and operating variables such as number of trays, mole fraction, temperature etc. The optimization problem formulated is as given below:

*Objective function* Minimize $TAC = rC_{TCI} + C_{OP}$ (1)

Subject to: *Model equations* $f(X) = 0$ (2)

*Purity constraints* $x_i \ge x_i^{\max}, i \in 1, 2....NC, x_i \in X$ (3)

*Design variable bounds* $x_d^{\min} \le x_d \le x_d^{\max}, x_d \in X$ (4)

*Operating variable bounds* $x_o^{\min} \le x_o \le x_o^{\max}, x_o \in X$ (5)

*Logical Constraints* $\sum_j x_j = x^{\max}, x_j - x^{\max} a_j \le 0, \sum_j a_j = 1.0, x \in X$ (6)

Here $C_{TCI}$ is the total capital investment and $C_{OP}$ is the operating cost and $r$ is rate of return on investment. Logical constraints are the binary variable constraints for determining the optimum tray location and optimum number of pervaporation modules. Here $a_j$ is the binary variable which can take the value of either 0 or 1. The mathematical formulation is a mixed integer nonlinear programming (MINLP) problem, where the binary variables are integers and remaining all equations are in non linear algebraic form. GAMS interface to SBB/CONOPT solver was used for solving this MINLP problem.

## 4. Case Studies

### *4.1 Separation of isopropanol-water (Azeotropic separation)*

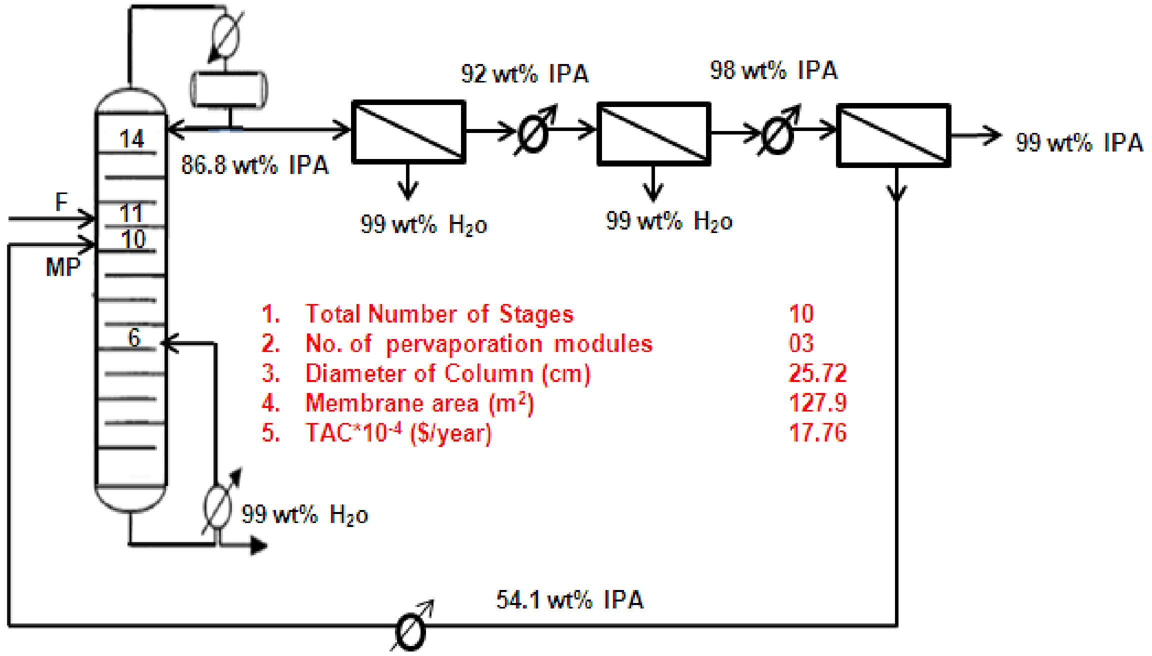

**Figure 5.** Optimized configuration of Hybrid process for isopropanol-water separation

Optimized configuration of hybrid process for the separation of IPA-water system is given in Figure 5. Separation of IPA-water into pure IPA by ordinary distillation is difficult, because of formation of azeotrope at a pressure of 1 bar with a composition of 87 wt % of IPA and 13 wt % of water and with a boiling point of $80^0$ C. The aim of this case study is to separate 10 kg mol/hr of saturated liquid mixture having 23.1mol % IPA and 76.9 mol % water into a product having 99 wt% IPA using hybrid distillation pervaporation process by minimizing TAC required for the separation. The optimization studies were carried out for different configurations and it is found that the configuration with series arrangement of pervaporation modules is more economical when compared with the configuration of parallel or series-parallel arrangement of membrane modules.

In case of parallel arrangement, since there are no intermediate heat exchangers, the driving force decreases in such a way that the separation is no longer possible, after certain concentration. So the final compositions of the product obtained at the retentate are poorer in IPA. On the other hand, IPA purity of 99 wt % can be achieved by the parallel configuration, but at the same time, the temperature of retentate goes to infeasible level. So use of parallel arrangement of membrane modules is not feasible for obtaining required purity in the case of azeotropic separations. In case of series/parallel arrangement total membrane area required is same as that of series arrangement of membrane modules even though the membrane area per unit module is decreasing and the number of modules required is increasing. As a result, investment cost is more for obtaining the same amount of purity. Comparison of results with different configurations is given in Figure 6.

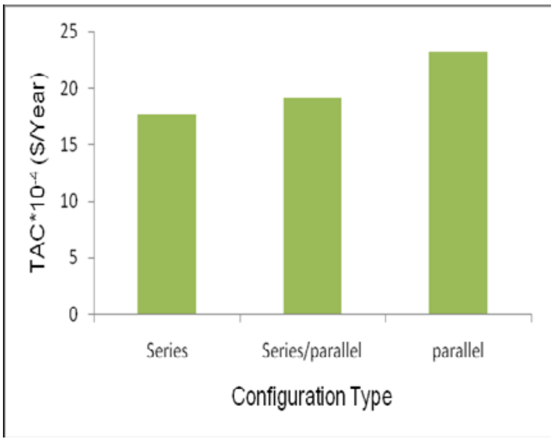

**Figure 6**. Comparison of TAC for different configurations

*4.2 Separation of propylene-propane mixture (close boiling mixture)*

Propylene-Propane form a close boiling mixture, which is difficult to separate by ordinary distillation process. Optimization studies were carried out with SRK model and the results showed that the configuration with parallel arrangement of membrane modules is more economical when compared with configurations of series or series/parallel arrangement of membrane modules. This is because the membrane which is taking the side stream from the distillation column is able to do the separation in the critical concentration region, if we provide sufficient amount of membrane area, without violation of the constraint on the outlet temperature of the retentate. The impure products from the membrane can be recycled to the column, so that the final purification can be obtained from the distillation column. If the load on the membrane is high, and if we are unable to provide the required membrane area with a single module, then splitting of the feed and doing separations with some parallel sections works well, and the results showed that this is more economical when compared with the series-parallel arrangement. But this is not the case with azeotropic separations, because in the case of azeotropic separations the final purity of required component can be obtained from the membrane modules only. So we should provide sufficient amount of membrane area and the number of modules, which must satisfy the constraints on the temperature to treat the azeotropic composition coming from the distillation column. Figure 7 shows the optimized configuration of hybrid process for this case study. Optimized results showed that, optimum membrane area is 724.77 $m^2$; optimum

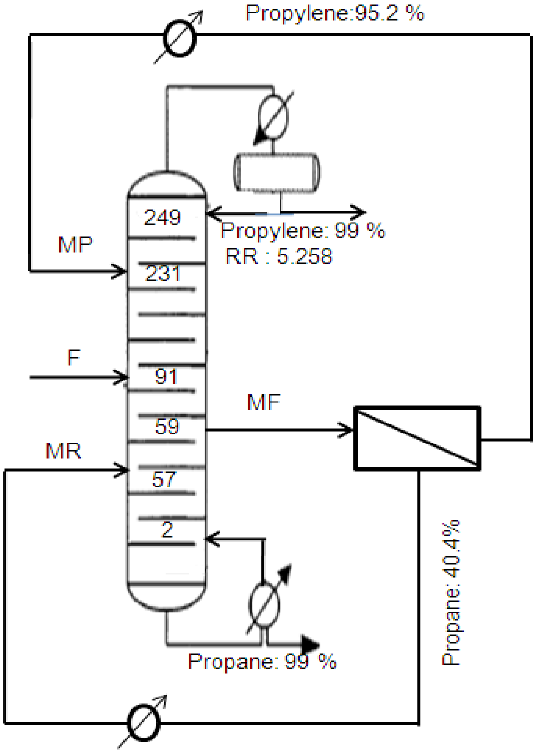

**Figure 7.** Optimized configuration of hybrid process for propylene/propane separation

number of trays required is 250 and the diameter of the column is about 3.766 m. The TAC required for the separation of propane/propylene is 5.0810 M$/year.

### *4.3 Separation of acetone-water mixture (Tangent pinch mixture)*

Acetone-water mixture forms, a tangent pinch, so separation of this mixture into pure products is difficult by ordinary distillation. Optimization studies were carried out for diffrernt configurations and the results showed that hybrid process with parallel arrangement of memebrane modules is more economical when compared with series or series/parallel arrangement of membrane modules. In case of acetone/water separation process the duty of the membrane module is to do the separation from 93.4 mol % of acetone to 97.0 mol % of acetone, which is the critical concentration region. Since the critical concentration region is very small, when compared with the IPA/water azeotropic separation critical region, which is in the range of 86 wt% of IPA to 99 wt% IPA, only one membrane module is sufficient to get the required purity of the products. If the load on the membrane module is high, and we are unable to provide sufficient membrane area for a single module within the limits of temperature constraints, then more number of modules arranged in parallel work well. But in the case of azeotropic separations, where the critical concentration region is large, one membrane module is unable to give the products of required purity. So in order to get the required purity, membrane modules should be arranged in series. Optimized configuration of hybrid process is given in Figure 8

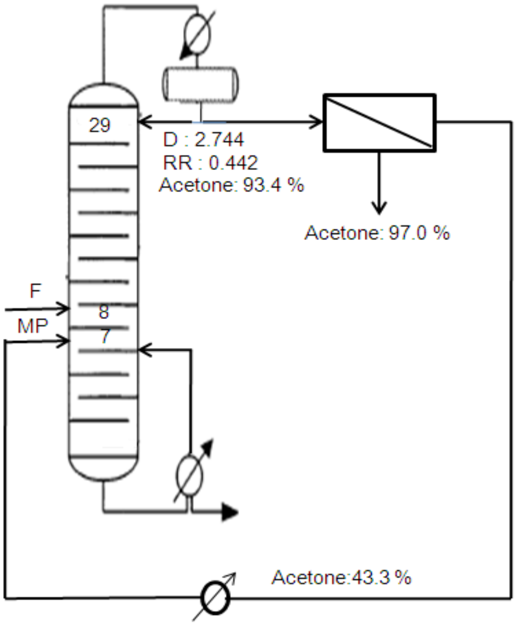

**Figure 8**: Optimized configuration of hybrid process for acetone/water separation

## 5. Conclusions

The structural and parametric optimization of continuous hybrid distillation-pervaporation process has been considered with different arrangement of membrane modules in the hybrid process such as series, parallel, and series-parallel, for separation of azeotropes, low relative volatility mixtures, and tangent pinch mixtures. The separation of isopropanol-water mixture (azeotropic separation) showed that the configuration with series arrangement of membrane modules is more economical when compared with the configurations of parallel or series/parallel arrangements. For propylene-propane separation (close boiling) and acetone-water separation (tangent pinch) the study showed that the configuration with parallel arrangement of membrane modules is more economical when compared with the configurations of series or series-parallel arrangement of membrane modules.

## References

1. J.D. Seader and E.J. Henley, *Separation Process Principles*, John Wiley & Sons, New York (1998).
2. J. Bausa and W. Marquardt, *Ind. Eng. Chem. Res.* 39(2000) 1658-1672.
3. B. Gonzalez and I. Ortiz, *J. Chem. Techn. Biotechn.*, 77(2001) 29-42.
4. I.K. Kookos, *Ind. Eng. Chem. Res.*, 42(2003) 1731-1738
5. M.C. Daviou, P.M. Hoch, and A.M. Eliceche, *Presented at Mercosur Cong. on Chem.Engg.* (2005).
6. M.M.T. Barakat and E. Sorensen, *Chem. Eng. Res. Des.*, 86(2008) 279-298.