MODELING AND SIMULATION OF SEVERAL HYBRID DISTILLATION SYSTEMS FOR THE ETHANE/ ETHYLENE SEPARATION

A. A. AL-RABIAH, K. D. TIMMERHAUS, R. D. NOBLE
Dept. of Chemical Engineering, CB Box 424, University of Colorado, Boulder, CO 80309, USA

ABSTRACT

The separation of ethylene from ethane in a commercial process is quite expensive both in capital and operating costs. This study evaluates the feasibility of using facilitated transport membrane technology for improving the separation process. Simulation and optimization of various hybrid distillation/membrane configurations have been examined under different operating conditions of temperature and pressure. This analysis determines the best sequence that minimizes the energy consumption of the C_2 splitter while maximizing profitability of the ethylene plant. A number of hybrid system configurations provide significant cost savings. Several of these hybrid configurations are illustrated in this study.

1. INTRODUCTION

The low-temperature distillation process for the separation of ethylene from ethane has been the preferred technology for several decades. This process consumes about 40 percent of the refrigeration energy required in the ethylene plant. The ethylene/ethane splitter is commonly operated at high-pressure, utilizing closed-cycle propylene refrigeration which is incorporated with the refrigeration systems serving other parts of the plant. Therefore, any reduction in the refrigeration load will affect not only the economics in the propylene closed-cycle but also the entire ethylene plant.

Facilitated transport (FT) membrane technology is a less established separation technique. It has been demonstrated in the laboratory for the selective separation of ethylene from ethane. However, the economic effect of this technology when applied to a commercial system has not been analyzed and reported. The only attempts to date have been experimental studies. This study evaluates the economics of using this technology for the ethane/ ethylene separation.

The desired objectives for this ethylene separation process are to obtain a high purity ethylene product combined with a high percentage recovery of the ethylene. The conventional distillation technology can accomplish both objectives. However, the accompanying high-energy consumption of the refrigerant makes this technology costly.

Facilitated transport membrane technology also produces a high purity product, but with a lower percentage of recovery. This lower percentage of recovery dictates the use of a multi-stage system incorporating additional compressors with a high power requirement. The hybrid technology, on the other hand, incorporates the high purity product aspect of both technologies, maximizing the distillation column’s high percentage recovery while minimizing the overall energy consumption of the system, and thus provides the potential for significant economic advantages.

The reduction in the energy consumption of the C_2 splitter is economically more important to this part of the process than the cost of the distillation column itself, since reducing the cost of the distillation column will only have a marginal effect on the overall process. However, reducing the energy consumption at this stage directly affects many of the other unit operations in the process which will further reduce the overall fuel consumption of the plant.

In this study, various configurations of the membrane/distillation hybrid systems have been investigated. Among those configurations were those wherein the membrane was located at the top, at the bottom, in parallel, and in series with the distillation column. For each hybrid system, the optimum design is based on an economic comparison of the overall savings achieved in the total processing costs.

2. FACILITATED TRANSPORT PROCESS

2.1 Process Description

Separation of a low relative volatility mixture such as ethane/ethylene utilizing simple diffusion membrane systems is uneconomical because of the slow transfer rates and low selectivities in the separation (Hughes *et. al.*, 1986). However, using the facilitated transport (FT) scheme, membranes can make this process feasible. In such transport, the simple diffusional process is coupled with a chemical reactant that reversibly binds with one of the species to be separated, thereby increasing the net transport rate. In the separation of the ethane/ethylene mixture, silver ions reversibly bind to the double bond portion of ethylene and facilitate its transport across the membrane. Ethane, which does not contain a double bond, is unaffected by the silver ions. Fig. 1 illustrates the ethane-ethylene facilitated transport membrane system, in which the membrane consists of an aqueous solution of silver nitrate held by capillarity in the pores of a microporous membrane. Ethylene in the gas mixture, fed at high pressure, reacts with the silver ion to form a complex, which then diffuses freely across the membrane. When this complex reaches the opposite side of the membrane, the complex decomposes, releasing the ethylene into the permeate and permitting the aqueous solution to return to the membrane inlet.

2.2 Membrane Model

The membrane model is based on cross flow along the permeate side of the membrane and plug flow along the feed side of the membrane. Fig. 2 shows a schematic diagram of the cross flow membrane module. The cross flow model based on the model developed by Shindo *et al.* (1984). In their model, the local permeate-side composition is a function only of the local feed-side composition. Since the permeate composition changes along the membrane length, it is not affected by the composition at any other point along the membrane side but only by the local flux at that point. The assumptions used in developing the membrane model are summarized in Table 1.

3. BASE CASE DESIGN

The base case of the grass-roots plant used in this comparison is a state of-the-art design of the propane cracking process with a nominal capacity of 500,000 metric tons of ethylene. Fig. 3 shows a block flow diagram of this process. The base case employs a front-end deethanizer flow sequence with a front-end acetylene reactor. The refrigerants used in this base case are ethylene and

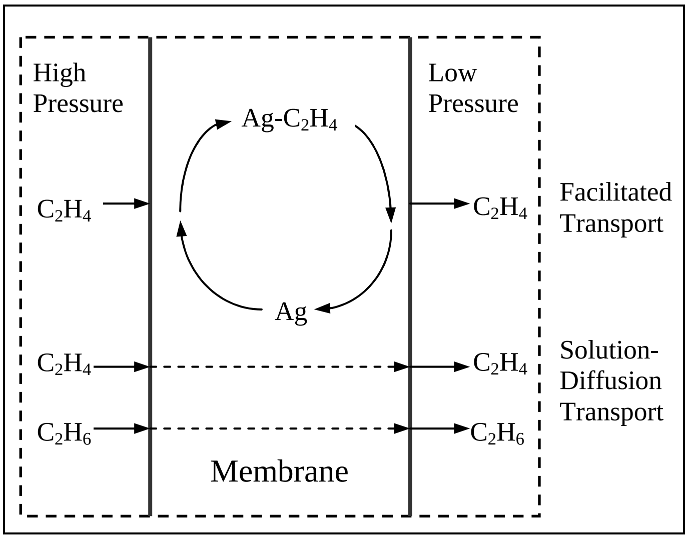

Figure 1: Mechanism for facilitated transport of ethylene by silver ion

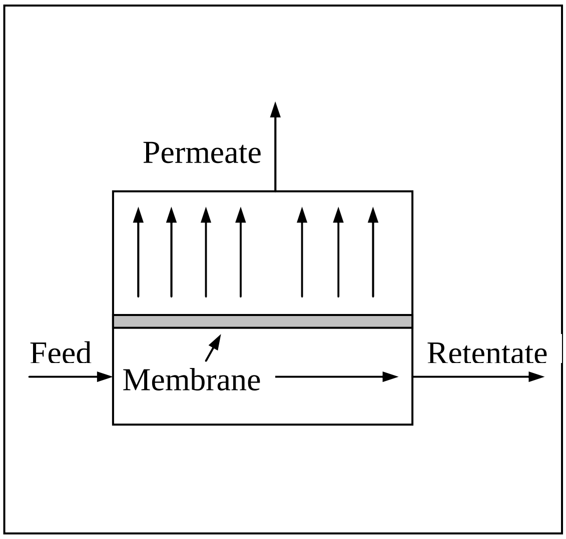

Figure 2: Schematic diagram of cross-flow membrane module

Table 1: Assumptions used in modeling of cross flow module with FT membrane

1- Cross-flow along the permeate side and plug-flow along the feed side of the membrane.
2- Negligible pressure drop along either side of the membrane.
3- Isothermal operation.
4- Instantaneous ethylene/silver reaction.
5- Equilibrium exists between product and reactant species at the membrane boundaries.
6- Steady state process.
7- The diffusivity and solubility coefficients of each species are independent of pressure.

propylene. A portion of the methane rich gas which is produced in the demethanization section is used as fuel. The principal products are polymer grade (99.9%) ethylene and polymer grade (99.6%) propylene. The feed to the C_2 splitter leaves the demethanizer bottoms at about – 4 °C and 3.45 MPa. This stream is flashed before it enters the C_2 splitter maintained at an average pressure of about 2 MPa (290 psia). Propylene refrigerant is used to condense the reflux stream. The overhead polymer grade ethylene is compressed before further processing. The ethane bottom stream from the C_2 splitter is recycled to the cracking furnaces. The 4.57 m (15.0 ft) diameter column requires about 111 trays and operates with a reflux ratio of about 2.75.

4. ETHANE/ ETHYLENE HYBRID DISTILLATION SYSTEM

Propylene is utilized as a refrigerant for the distillation process as well as for most of the hybrid system configurations. If this refrigeration requirement is changed, it will affect the propylene refrigeration system which affects both the steam and fuel consumption. Fig. 4 shows a block flow diagram of the elements that are directly connected with the distillation/ membrane hybrid system.

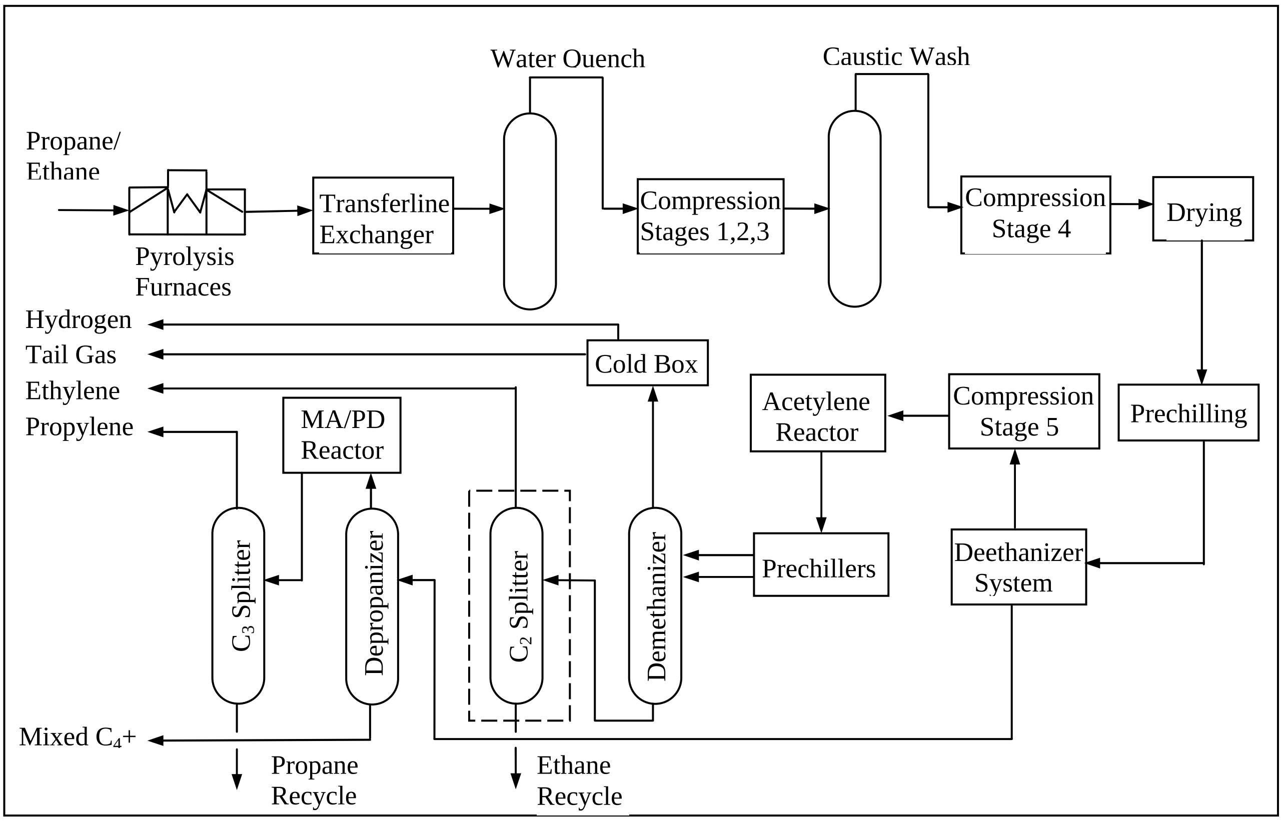

Figure 3: Ethylene front-end deethanization process

4.1 Hybrid Process Configurations

The distillation/membrane hybrid system may be represented by a large number of different schemes. The hybrid configurations may differ with regard to the location of the membrane relative to the distillation column. For example, the membrane can be located at the top of the distillation column. In this case, the membrane performs the final purification of the product. The permeate product is compressed and cooled to meet the specifications of the ethylene product. The retentate is recycled back to the distillation column at an appropriate location in the column. Another configuration is the bottom hybrid system. In this configuration, the membrane unit performs the final purification of the ethane recycle stream from the distillation column. The permeate as opposed to the retentate (as in the top configuration) is recycled and must be recompressed to the column pressure before returning to the distillation column. Operating conditions may be varied for each configuration in order to achieve optimum performance. Other possible configurations also have been investigated in this study.

4.2 Hybrid Process Considerations

The carrier inside the membrane is an aqueous solution of silver nitrate and this solution has different freezing points depending on the solute concentration. An increase in the solute concentration increases the freezing point depression. Since the temperature profile within the conventional distillation column decreases from –7 to –30 ^{o}C for an operating pressure of 2 MPa, an innovative design is required to effectively combine membrane and distillation technology. The 6 mol/L $AgNO_3$ has been used in the process simulation since this concentration does not freeze at the operating conditions of the ethane/ethylene separation. The facilitated transport membrane performance also is sensitive to some impurities such as acetylene and sulfur. Use of the front-end deethanization scheme assure that all acetylene produced in the pyrolysis furnaces is directly converted in the hydrogenation catalytic reactors. If sulfur contaminants are present, they can be removed by caustic scrubbers as in the conventional plant.

5. SIMULATION AND OPTIMIZATION RESULTS

Simulation studies are required to identify the optimal configuration which provides the greatest economic advantage. Such simulations are useful for determining the operational limits for each system. In the simulation process, parametric studies were conducted by varying the key parameters

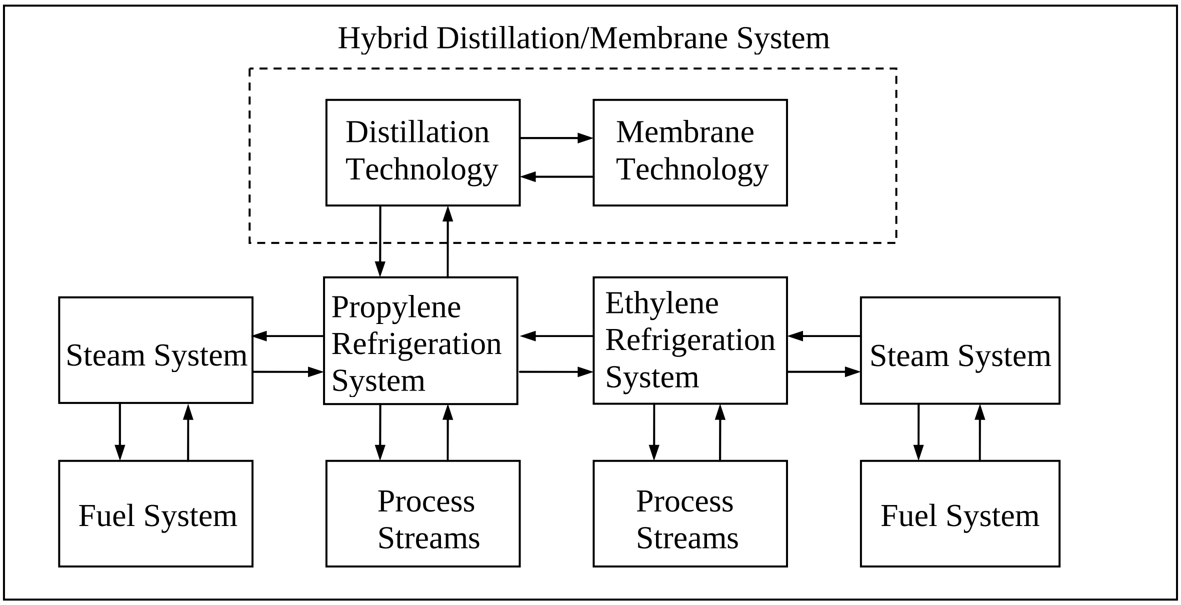

Figure 4: Hybrid system process integration

and observing the effects on the overall process. The membrane model used in this study was closely integrated with a rigorous distillation model utilizing SRK as the equation of state. In the simulator, the distillation hybrid system is linked to other parts of the plant. For the simulation and optimization of this process, two limiting permeate pressures of 15 psia and 50 psia have been selected. Following are two examples of the results.

5.1 Parallel Configuration Hybrid System

A parallel hybrid system configuration is illustrated in Fig. 5. The permeate and retentate streams leaving the membrane unit are recompressed and reenter the distillation column at appropriate stages where the stream composition matches the tray composition. The membrane system consists of the membrane unit, permeate compressor, retentate blower, and two heat exchangers. The permeate stream is recompressed to the column operating pressure and then cooled successively in two heat exchangers using cold water as coolant for the first heat exchanger and propylene refrigerant as coolant for the second heat exchanger. A blower is utilized to recompress the retentate to the operating pressure of the reentry stage. To optimize this hybrid system, the simulation was performed for a fixed condenser duty as well as for a fixed number of stages. For example, Fig. 6 shows the performance of the parallel configuration when the number of stages is fixed. The simulation studies were conducted for a permeate pressure of 15 psia and a carrier concentration of 6 *M* $AgNO_3$. The membrane feed flow rate and composition are optimized to obtain the minimal condenser duty for each membrane area specified. The reflux ratio decreases with both an increase in the membrane feed flow rate and an increase in the membrane feed composition. A smaller decrease in the reflux ratio is observed with an increase in membrane feed flow rate. The membrane stage cut also increases with an increase in the membrane feed flow rate. Consequently, the permeate flow rate increases, resulting in increased compressor and heat exchanger duties. An economic analysis shows that as the condenser duty is reduced by decreasing the reflux ratio, the capacity and required utilities of auxiliary equipment are increased.

5.2 Series Configuration Hybrid System

The series membrane/distillation process is shown in Fig. 7. The feed stream is flashed to about 2.62 MPa (380 psia) to obtain a refrigeration temperature of about -16 °C. The refrigeration associated with this feed stream is exchanged with other process streams to reduce the refrigeration load in other parts of the plant. The feed from the first membrane stage is concentrated by producing part of the recycled ethane as a retentate. This feed is then sent to the second membrane stage where the feed pressure is about 0.69 MPa (100 psia) and the ethylene mole fraction is about 0.915. The latter feed concentration is adequate for producing a high polymer grade product in the second stage. Only part of the ethylene product can be produced in the second membrane stage

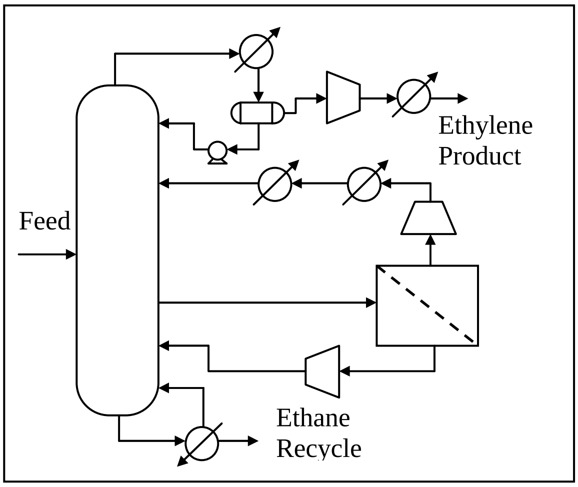

Figure 5: Parallel hybrid configuration

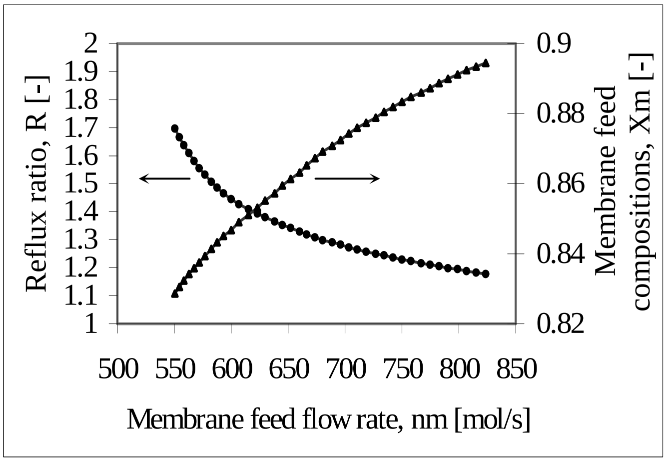

Figure 6: Parallel hybrid system performance

because membrane technology can not provide both a specified recovery and purity in just one stage. The retentate from the second stage is sent to a low-pressure distillation column. (Additional membrane stages do not improve the performance of the system). The latter provides the specified purity and recovery requirements but with a smaller than conventional column and condenser because of the reduced feed flow rate to the column. For this configuration, the distillation process utilizes ethylene instead of propylene refrigerant for the condenser resulting in an increase in compression duty of about 1,000 hp. On the other hand, a significant reduction in compression duty of about 14,600 hp was noted in the propylene refrigeration system. In addition, capital costs associated with such a system was reduced along with the steam requirements.

6. ECONOMICS

The economic performance of different hybrid systems was evaluated in this study. The conventional ethylene plant was compared with all other hybrid configurations that were investigated in this study. One of the criteria that was utilized for the economic comparison is the total processing cost. This processing cost includes all capital and operating expenses that are required to produce a polymer grade ethylene. The capital costs are the depreciated cost of all units associated with each process. Following are some results of the two previous examples that have been discussed.

6.1 Parallel Configuration:

The annual savings of the capital, utilities and processing costs for the parallel hybrid system are shown in Fig. 8. As the membrane product recovery increases, the fuel and cooling water savings increase. The permeate flow rate decreases with an increase in membrane product recovery. Therefore, the compression duty decreases which reduces the utility demand. The optimum hybrid system occurs with a membrane product recovery of 0.70. Under these conditions, maximum annual savings are around US$ 2.7 million. The membrane feed composition at this time is 0.853, which is close to the distillation feed stage where the pinch region is located. Fig. 8 shows that the annual savings decrease for a large product recovery. This indicates that the membrane performance is optimal for bulk separation where the feed composition is close to the column feed composition. As membrane feed composition increases, membrane performance decreases.

6.2 Series Configuration:

The optimum configuration occurs when the membrane is coupled with the distillation column in

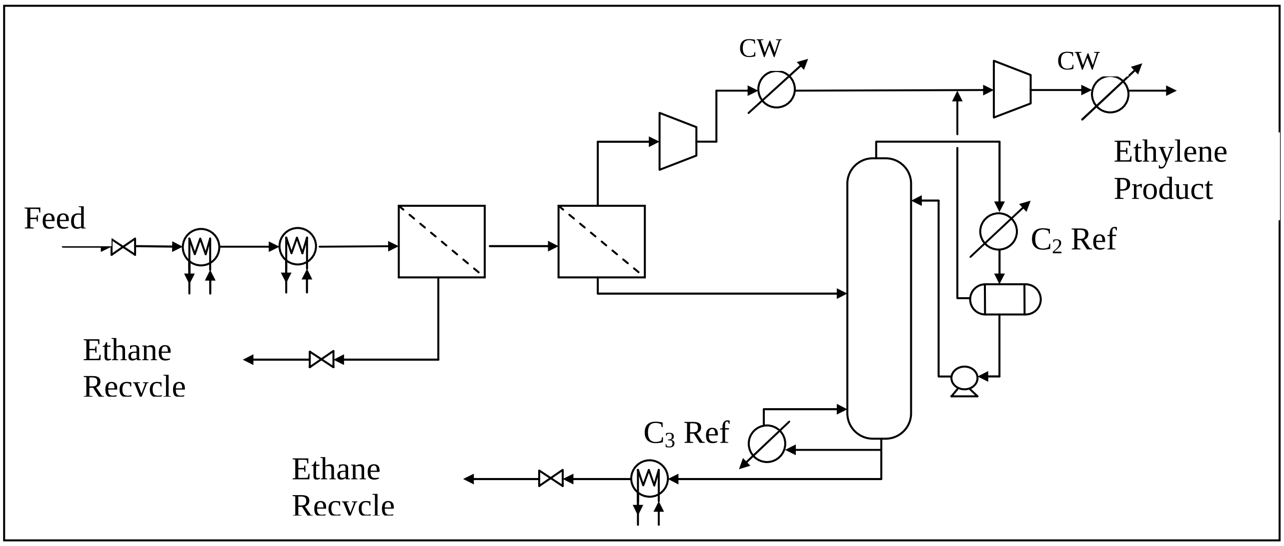

Figure 7: Hybrid membrane/ distillation series configuration

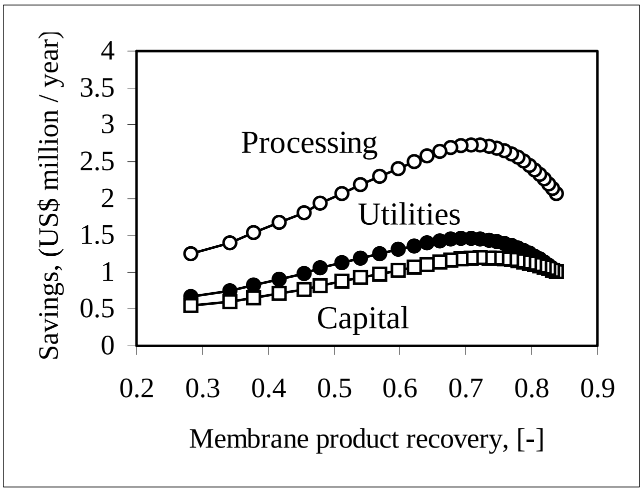

Figure 8: Economic performance of the parallel configuration hybrid system

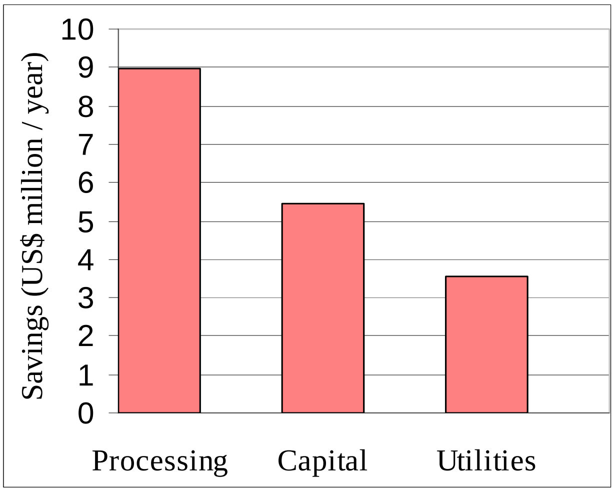

Figure 9: Economic performance of the series configuration hybrid system

a series configuration. Figure 9 shows for the series hybrid system an annual savings of about US$ 9 million. This configuration requires no propylene refrigerant. A small amount of ethylene refrigerant is used for the distillation column. The reboiler of the low pressure distillation column is utilized to cool other process streams that were conventionally cooled by propylene refrigerant. The recycled ethane also refrigerates other process streams.

7. CONCLUSIONS

The hybrid distillation/ membrane system utilizing facilitated transport technology is a promising alternative for the ethane/ethylene separation in the ethylene production process. This study shows that the reduction in refrigeration requirements is the key to successful hybrid system. The parallel configuration proved to be more economically advantageous than the top and bottom configurations. This study shows that the series hybrid configuration is the optimum design by providing the maximum processing savings.

REFERENCES

Hughes, R. D., Mahoney, J. A., Steigelmann, E. F., 1986, Olefin separation by facilitated transport membranes, *In*: Li, N. N., and Calo, J. M., *Recent Developments in Separation Science*, Vol. 9, CRC Press, Cleveland: p. 173-195.

Shindo, Y., Hakuta, T., Yoshitome, H., 1985, Calculation methods for multicomponent gas separation by permeation, *Sep. Sci. Tech.*, vol. 20, no. 5&6: p. 445-459.

MODELISATION ET SIMULATION DE PLUSIEURS SYSTEMES HYBRIDES DE DISTILLATION POUR LA SEPARATION ETHANE/ETHYLENE

RÉSUMÉ: La séparation de l'éthylène de l'éthane dans un procédé commercial est tres coûteuse à la fois en capitaux et en coûts d'opérations. Cette étude évalue la feasabilité de l'utilisation de la technologie de membrane de transport facilité en vue d'améliorer le processus de séparation. La simulation et l'optimisation de diverses configurations hybrides distillation/membrane ont été examinées dans des conditions variables de temperature et de pression. Cette analyse détermine la meilleure séquence à même de minimiser la consommation d'énergie de la colonne C2 tout en maximisant la rentabilité de l'usine d'éthylène. Nombre de configurations de systems hybrides conduisent à d'importantes économies. Plusieurs de ces configurations hybrides sont utilisées dans cette étude.