The Use of Hybrid Membrane/Distillation System for the Ethane/Ethylene Separation in Olefin Plants

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ABSTRACT

Separation of ethylene from ethane in commercial processes is expensive both in capital and operating costs. This study has evaluated the feasibility of using facilitated transport membrane technology for improving the separation process. Simulation and optimization of various distillation/membrane hybrid configurations as well as stand-alone membrane cascade systems have been examined under different operating conditions of temperature and pressure. A detailed analysis has determined the optimum sequence that minimizes the energy consumption of the C_2 splitter while maximizing the profitability of the ethylene plant. This study has shown that the reduction in refrigeration requirement is the key to a successful hybrid system and that the series hybrid configuration is the optimum design, providing the maximum processing savings for a grass-roots ethylene plant. A retrofit design has also been investigated for an existing ethylene plant with the new membrane process. The parallel hybrid scheme, with a permeate pressure of about 50 psia, shows the ultimate design. For this parallel hybrid system, a net annual savings in processing cost of more than 0.86 million US dollars can be achieved to provide a payout period of about 19 months.

INTRODUCTION

The low-temperature distillation column for the separation of ethylene from ethane has been the preferred technology for several decades. However, this binary separation process consumes about 36 percent of the refrigeration energy required in the ethylene plant [1]. The C_2 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.

Facilitated transport membrane technology (FTMT) is a less established separation technique. It has been demonstrated in laboratories and pilot plants for the selective separation of olefins from alkanes. This technology has shown significantly high selectivity and flux rate of ethylene over ethane [2,3].

The desired objectives for any 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 of these objectives. However, the accompanying high-energy consumption of the refrigeration system makes the present distillation process costly. On the other hand, the FTMT is capable of producing a high-purity ethylene product, but with a lower percentage of recovery. The lower percentage of recovery dictates the use of a multi-stage system incorporating additional compressors.

The combination of membrane and distillation technologies to form a hybrid system is another design alternative for replacing the current distillation technology. The hybrid system incorporates the high-purity product aspect of both technologies as well as the high percentage recovery of the distillation process.

In the study reported here, various configurations of the membrane/distillation hybrid systems have been investigated for the ethane/ethylene separation. Among the many configurations studied were those wherein the membrane was located at the top, at the bottom, in parallel, and in series with the distillation column. Stand-alone

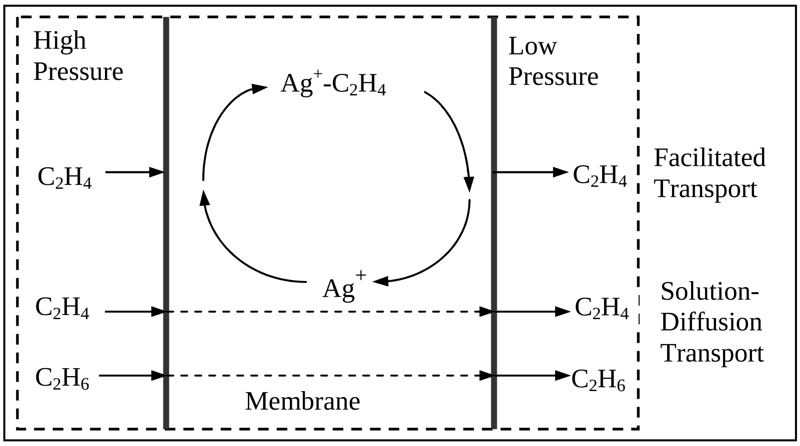

Figure 1: Mechanism for facilitated transport of ethylene by silver ions.

membrane cascade systems have also been evaluated and compared to other design alternatives. For each hybrid system, the optimum design is based on an economic comparison of the overall savings achieved in the total processing costs.

This study also evaluates the economic effect of using the FTMT process to retrofit the ethane/ethylene separation system in an existing ethylene plant. The FTMT process has been evaluated as a stand-alone membrane system as well as a hybrid distillation/membrane system. Economic comparison criteria, such as payout period, are presented in this study.

MEMBRANE PROCESS

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 selectivity in the separation [2]. However, using the facilitated transport 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. Figure 1 illustrates the ethane-ethylene facilitated transport membrane system, in which the membrane consists of silver nitrate solution held within the membrane by capillary action. Ethylene from the feed side at high pressure reacts with the silver ion to form a complex, which then diffuses across the membrane. The silver-ethylene complex decomposes when it reaches the product side of the membrane, releasing the ethylene into the permeate and permitting the silver solution to return to the membrane inlet. There is a need to provide a membrane system which can operate at a high pressure differential across the membrane without the need for a product side sweep as well as avoid stability problems caused by membrane drying. Valus et al. [4] solved this problem when they developed a novel technique in which the complex can be separated from the product gas in a flash drum and then recycled back through the membrane system.

Process 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. In this 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. The membrane properties used in the simulations are based on the experimental data of Teramoto *et al.* [5] and Hughes *et al.* [2]. The membrane properties that were reported are similar in both studies. For example, the diffusion coefficient of ethylene was reported by Teramoto et al. as 1.87×10^{-9} m^2/s. This value is similar to the one which was reported by Hughes *et al.* (1.85×10^{-9} m^2/s).

Table 1: Assumptions used in modeling of cross-flow model 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 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.

HYBRID SYSTEMS

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 wherein 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.

Propylene is utilized as a refrigerant for the conventional 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. Figure 2 shows a block flow diagram of the elements that are directly related with the hybrid system.

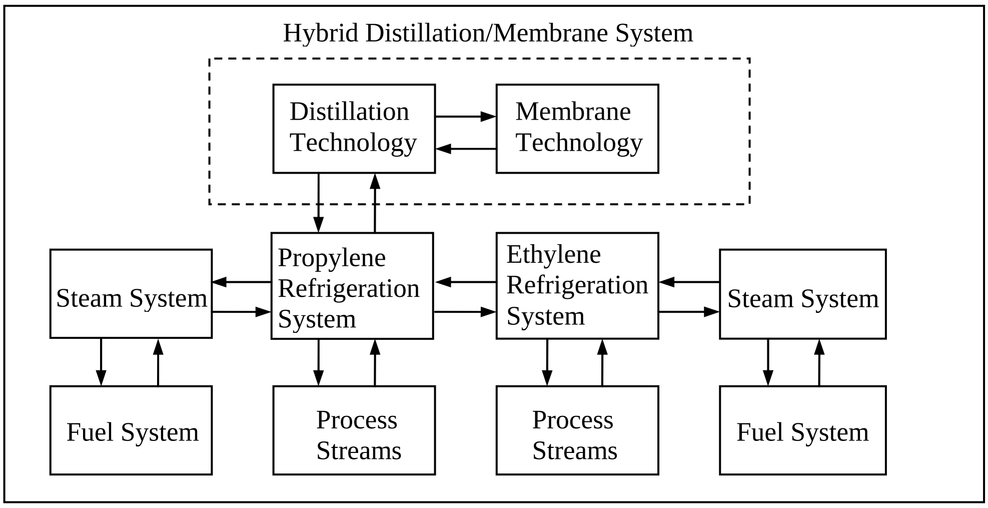

Figure 2: Process integration of the hybrid distillation/membrane system.

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 –29 ^oC 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 assures 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 ethylene plant.

SIMULATION 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 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 investigated. The simulation results for two configurations are summarized below.

Parallel Configuration Hybrid System

Figure 3 shows a simple flow diagram of the parallel configuration hybrid system (*PCHS*) for the separation of ethylene from ethane. In this configuration, the permeate and retentate streams leaving the membrane unit are recompressed and reenter the distillation column at the appropriate stages where the stream composition matches the tray composition. Figure 4 illustrates the performance of the parallel configuration when the number of stages is set equal to that used in the conventional ethane/ethylene splitter. The simulation studies shown in this figure were conducted for a permeate pressure (P_p) of 50 psia and a carrier concentration (C_{Ag}) of 6 mol/L $AgNO_3$. The membrane feed flow rate and composition are the two variables which link the membrane unit with the distillation column. These two variables 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. As the condenser duty is reduced by decreasing the column reflux ratio, the capacity and required utilities of the auxiliary equipment are increased. Figure 5 shows the membrane process performance of the previous example. It should be noted that the compression duty is greater when the permeate pressure is 15 psia rather than 50 psia.

Series Configuration Hybrid System

The series configuration hybrid system (*SCHS*) is illustrated in Figure 6. The feed stream is flashed to about 2.62 MPa (380 psia) to obtain a refrigeration temperature of about -16 ^oC. 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

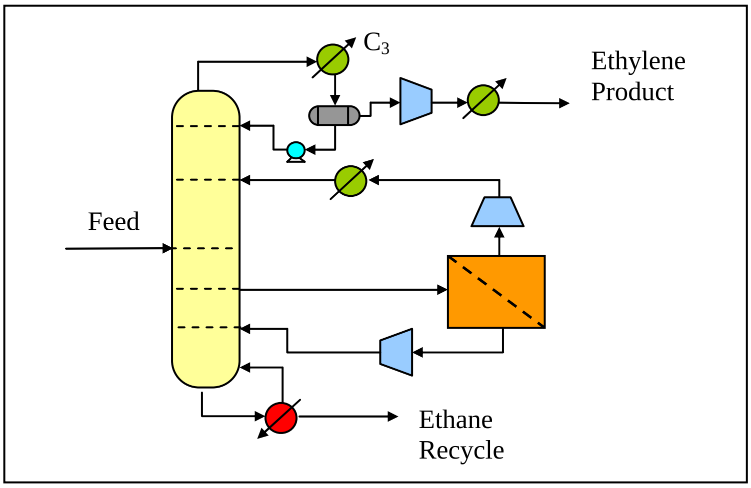

Figure 3: Parallel configuration hybrid system (*PCHS*) for the ethane/ethylene separation.

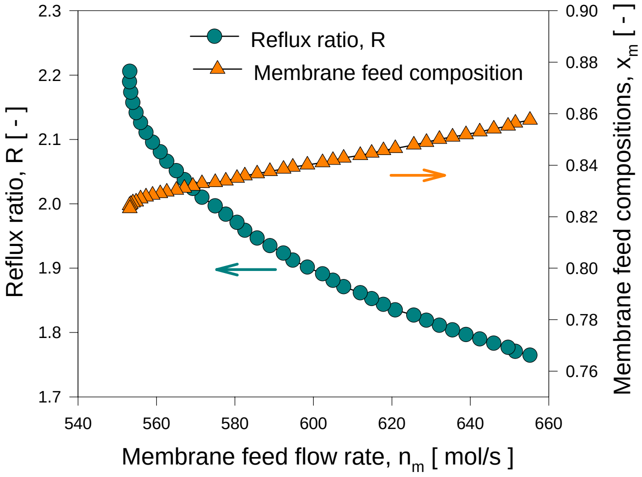

Figure 4: Performance of the parallel configuration hybrid system for the ethane/ethylene separation at a permeate pressure of 50 psia and carrier concentration of 6 mol/L.

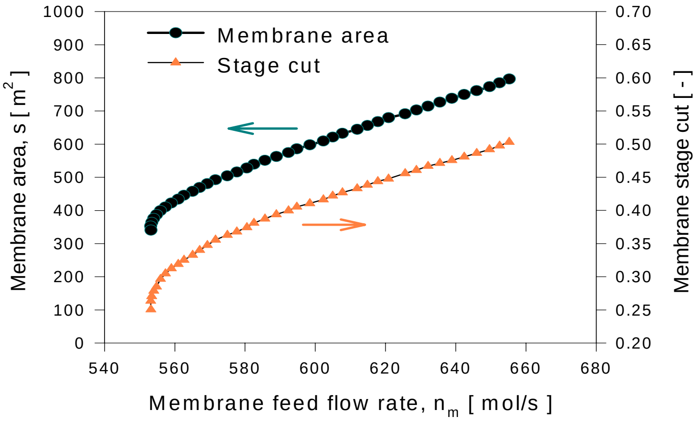

Figure 5: Membrane performance of the parallel configuration hybrid system for the ethane/ethylene separation at a permeate pressure of 50 psia and carrier concentration of 6 mol/L.

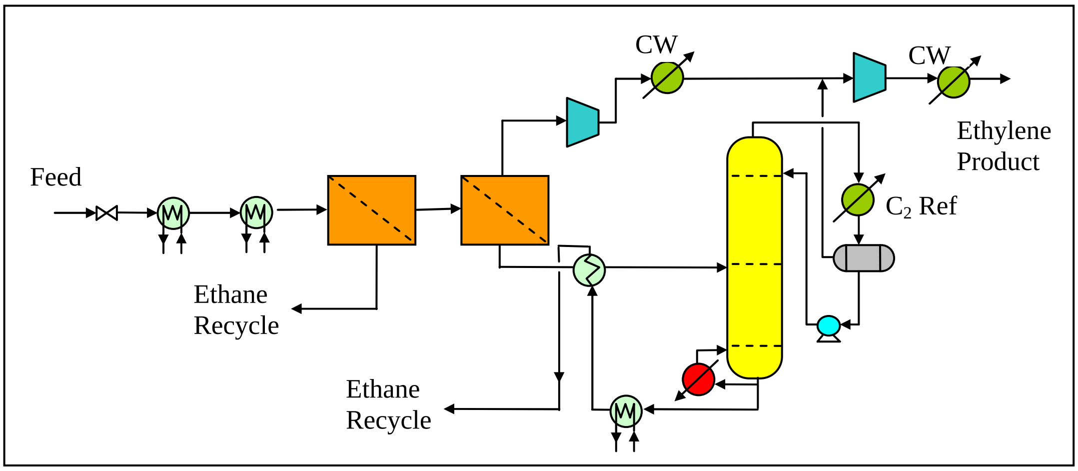

Figure 8: Series configuration hybrid system (*SCHS*) for the ethane/ethylene separation.

second stage. Only part of the ethylene product can be produced in the second membrane stage because membrane technology cannot 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, since 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 995 hp. The increase in ethylene product compression power is about 6,800 hp. On the other hand, a significant reduction in compression duty of about 11,000 hp was noted in the propylene refrigeration system. In addition, capital costs associated with the *SCHS* system were reduced along with the steam requirements.

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 a successful hybrid system. The parallel configuration proved to be more economically advantageous than the top and bottom configurations. However, this study shows that the series hybrid configuration is the optimum design by providing the maximum processing savings. In revamping an existing ethylene plant, the equipment for the refrigeration and steam systems (turbines, compressors, heat exchangers, …etc.) is not changed. Since a new plant would require smaller utilities equipment, the economic benefit of this new technology when implemented in an existing plant is less when compared to a new grass-roots plant. On the other hand, many parallel hybrid cases provide energy savings when compared with the conventional design in an existing ethylene plant. The ultimate parallel hybrid design provides a net annual savings of about 0.86 million US dollars and requires a payout period of 19 months. While the series configuration is the optimum hybrid design for a new grass-roots ethylene plant, such a scheme provides less economic advantages when applied to an existing plant.

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