# Membrane Retrofit Option for Paraffin/Olefin Separation - A Technoeconomic Evaluation

A. Motelica
O.S.L. Bruinsma
R. Kreiter
M.J. den Exter
J.F. Vente

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# Membrane Retrofit Option for Paraffin/Olefin Separation—A Technoeconomic Evaluation

Anatolie Motelica, Odolphus S. L. Bruinsma, Robert Kreiter, Marcel den Exter, and Jaap F. Vente*

ECN, Energy Research Centre of The Netherlands, Westerduinweg 3, P.O. Box 1, 1755 ZG Petten, The Netherlands

*Supporting Information*

**ABSTRACT:** The technical and economic feasibility of a hybrid separation process in which gas separation membranes are combined with conventional distillation are assessed for the separation of ethylene from ethane and of butadiene from a $C_4$-mixture. The potentials for increased energy efficiency and debottlenecking were determined in relation to the required membrane performances. The energy saving potential for the separation of ethylene from ethane is rather low owing to the required very high membrane selectivity. Energy savings can be expected when the membrane selectivity for ethylene is >60. However, the possibility to increase the column capacity in an existing plant by using a membrane is very high. This can become economically attractive if the membrane has a selectivity for ethylene of ≥10. In the case of butadiene separation, the energy savings can be as high as 30% depending on membrane selectivity and process configuration. This high value can be reached when the membrane selectivity for butadiene relative to saturated hydrocarbons equals 15. Again, an increase in the production capacity of butadiene can be achieved in an economic viable fashion.

## 1. INTRODUCTION

Olefins, such as ethylene, propylene, and butadiene, are among the most produced intermediates in the petrochemical industry. They are produced from a wide range of hydrocarbon feedstocks (ethane, propane, butane, naphtha, gas oil) via a cracking process (Figure 1). The last step in this process is the separation of olefins from other hydrocarbons, which is traditionally performed with distillation. As the physicochemical properties, such as volatility and boiling point, of the compounds are very similar, the purification becomes capital and energy intensive. For example, the top of an ethylene/ethane distillation column needs to be chilled to −30 °C which requires large amounts of refrigerant. The separation of butadiene from the $C_4$-fraction requires the aid of an additional solvent. This solvent has to be regenerated at the cost of additional high temperature steam. To overcome these separation disadvantages, different separation methods have been investigated and proposed in recent years. Suggested options are based on better heat integration of the overall process, or on novel separation systems such as heat integrated distillation columns[1] (HIDiC), dividing wall columns[2] (DWC), membrane separation,[3−6] adsorption−desorption systems[7−11] or on hybrid separation methods, for example, distillation combined with membrane separation.[12]

The focus of the current paper is the integration and combination of membrane-based gas separation with conventional distillation. The aim is to find the minimum required membrane performance, like selectivity and permeability, for an economically attractive process. In addition, options to debottleneck existing olefin/paraffin separation systems will be investigated. The increased energy efficiency, in comparison with the state of the art separation, will be taken as a figure of merit. The separation of ethylene from ethane and butadiene from a $C_4$-mixture are considered as the most representative separation cases. The case of propylene/propane separation is not considered due to mild temperatures (∼30 °C) at which this column is typically operated. At these temperatures usually no exergy is required. However, this does not mean that membrane integration in a propylene/propane splitter is not feasible. Kookos[13] has shown already that an annual cost reduction of 17% is possible. In addition, the conceptual findings published here for the ethylene/ethane separation case are also applicable for the separation of propylene/propane, as both cases have similar characteristics.

Several studies, available in the open literature, have shown that the combination of membranes with distillation in a $C_2$-splitter can lead to significantly reduced investment (∼67%) and operation (∼14%) costs.[16] In these studies, the transport mechanism through the membrane is facilitated by silver ions, and high membrane selectivities (up to 374) and reasonable permeance (up to $1.1 \times 10^{-7}$ mol·Pa$^{-1}$·m$^{-2}$·s$^{-1}$) have been reported.[17] These membrane performances are required to reach the impressive cost reductions. However, practical implementation of facilitated transport membranes is limited due to poor stability. Especially, the $Ag^+$ ions can react with impurities from the feed. For example, $H_2$ gas can reduce the $Ag^+$ ions and precipitate it as metallic silver and sulfuric and acetylenic compounds can react irreversible with $Ag^+$ and form solid precipitates. Especially the formation of silver acetylides is undesired as these compounds are shock-sensitive and may detonate.[18] These negative side effects of facilitated transport membranes require the development of membranes with selectivity based on a distinct separation mechanism that ensures the long time stability of the membrane. Caballero[19] proposes a programming approach to optimize and retrofit a

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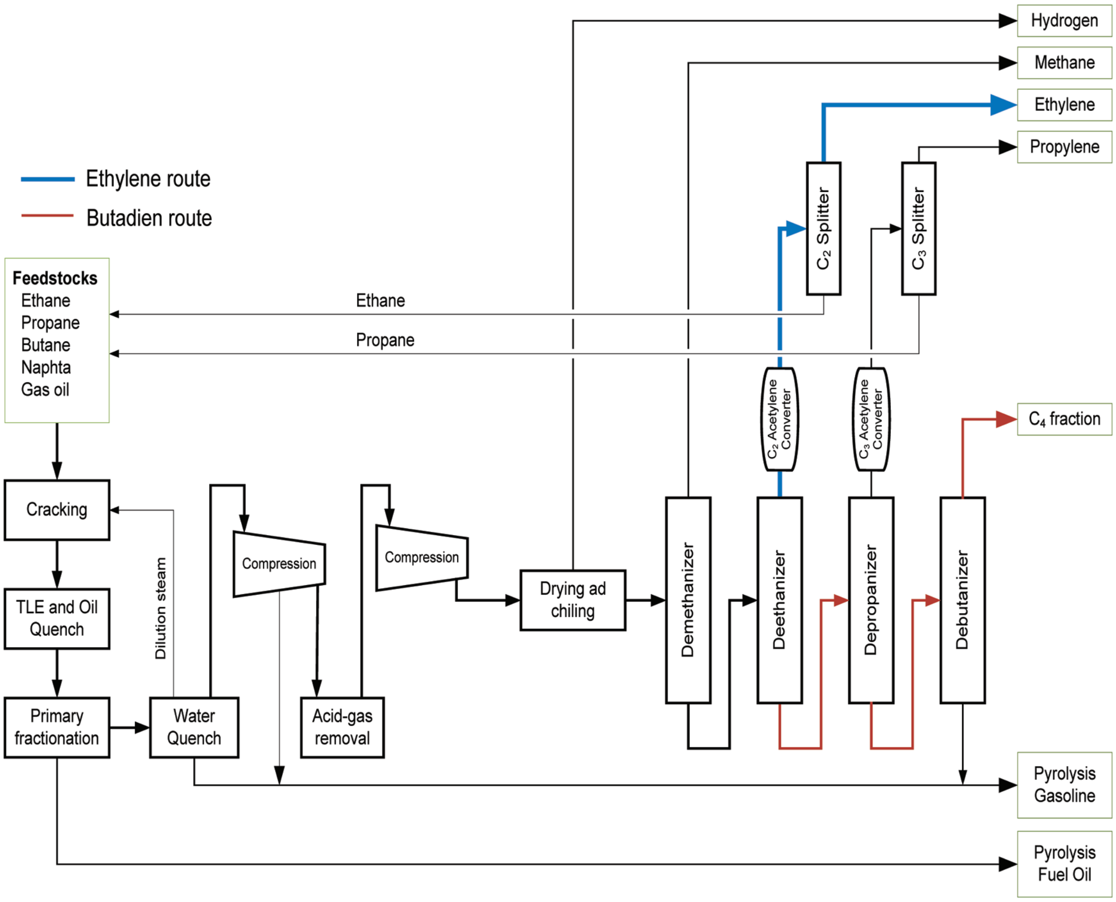

**Figure 1.** Simplified process flow diagram of an olefin plant with front-end demethanizer[14,15].

hybrid design for ethylene/ethane separation. They consider a membrane type based on a simple diffusion mechanism and a selectivity-permeance relationship for ethylene/ethane deducted by Fuertes and Menendez.[20] The conclusion was that a hybrid system can lead to an energy saving of up to 30% in the condenser and that this creates opportunities to retrofit an existing $C_2$-splitter. However, they did not take into account that a significant part of these savings has to be spent on the compressor in the permeate stream. An alternative approach can be found in the debottlenecking of an existing industrial $C_2$-splitter.[21,22] This aspect has been evaluated and is presented in this paper. In addition, we determined the required membrane selectivity, at fixed ethane permeance, for an economically attractive industrial hybrid process for debottlenecking purposes.

The same question arises for the separation of butadiene from the $C_4$-fraction with the aid of a membrane. For this process, the application of membranes is seldom discussed and presented in the open literature. Only a few isolated permeation measurements on polymeric membranes of butadiene and *n*-butane have been reported.[23,24] In addition, the butadiene extraction process has been continuously improved without considering the application of membranes.[25] Effective improvements were the utilization of a more selective solvent for the extraction of butadiene,[26] and/or more efficient heat integration within the process. *N*-methyl-2-pyrrolidone (NMP) was first proposed as a solvent in 1970 by Wagner,[27] and used commercially by BASF. A recent, technological breakthrough is the application of DWC, which is an alternative to the two conventional columns in series process. The reported benefits of DWC are savings of 20% in capital cost and 16% savings in energy cost.[2,25]

## 2. METHODOLOGY

Combinations of distillation and membranes leads to a large number of options due to many degrees of freedom related to the location where the retentate and/or the permeate stream are fed to the column, and/or the location where the feed stream to the membrane is extracted from the column. The optimal process layout of such systems has been studied extensively, and various design methods have been proposed.[13,28,29] In this work, we have used Aspen Plus simulation software to design the reference separation case. Further, we have employed a discrete optimization technique to find the optimal integration of the membrane and the base case process. With this method, basically the whole solution space has been explored to ensure that the global minimum was found. Several simulations and optimization steps of the integrated process were performed for different membrane selectivities. The relevant results of the simulations are presented in the following chapters. In the case of the separation of ethylene/ethane, the possibility of capacity increase was investigated. In the case of butadiene extraction, various hybrid process configurations have been analyzed to determine the effect of membrane selectivity on energy savings.

### 2.1. Membrane Modeling.

Many models are available that describe the transport through a gas separation membrane.[30−32] These models differ in degree of complexity at different scale. The most commonly used models for process flow sheeting are those based on a counter-current flow pattern, thus ensuring the highest driving force along the membrane and the lowest membrane surface area. For the sake of simplicity, we have described the membrane behavior with a semiperfect mixing model, which is sufficiently precise for the current assessment. In this model, the feed side composition is considered to be constant at the average of the feed and the retentate stream, while the permeate side of the membrane is assumed to be perfectly mixed. A schematic representation is presented in Figure 2. The simplicity and fair accuracy of this model makes it well suited for estimation purposes in process simulations and optimization. The estimated membrane surface area with this model is a maximum 10% higher than that calculated with a more rigorous model, for example, counter-current.

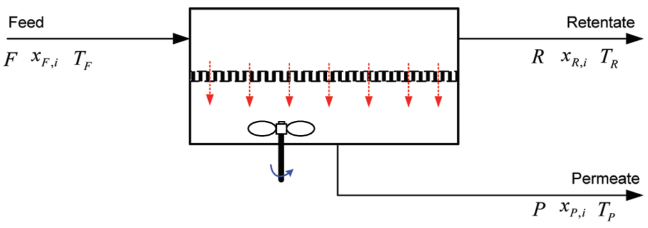

**Figure 2.** Schematic diagram of the semiperfect mixing model.

In the following transport equation trough, the membrane is given by relation 1 and the mass balances by relations 2−5.

$$Px_{P,i} = Q_i A_m (P_R x_{mR,i} - P_P x_{P,i}) \tag{1}$$

$$Fx_{F,i} = Rx_{R,i} + Px_{P,i} \tag{2}$$

$$x_{mR,i} = 0.5(x_{F,i} + x_{R,i}) \tag{3}$$

$$\sum_{i=1}^{nc} x_{R,i} = 1 \tag{4}$$

$$\sum_{i=1}^{nc} x_{P,i} = 1 \tag{5}$$

Throughout this paper, the membrane selectivity is defined as the ratio between the permeance of component *i* and the permeance of reference component *k*. For example, in the case of ethylene/ethane separation the reference component is ethane since the membrane is considered to be selective for ethylene.

$$\alpha_{i,k} = \frac{Q_i}{Q_k} \tag{6}$$

Further, the ratio between the retentate pressure ($P_R$) and the permeate pressure ($P_p$) was set to 4 for all cases. This factor has been selected to allow for the use of a one-stage compressor to recompress the permeate stream.

**2.2. Membranes for Ethylene/Ethane Separation.** One of the first experimental gas separation measurements on ethylene/ethane separation on various polyimide membrane was reported by Hayashi et al.[3] They have measured permeance values for ethylene between 2 × $10^{-9}$ and 1 × $10^{-8}$ mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ and selectivities between 4.5 (at 100 °C) and 6.9 (at 35 °C) on a membrane with thickness of ∼5.5 $\mu$m. At lower temperatures they have obtained higher selectivities, which is a good trend considering that the ethylene/ethane separation occurs at cryogenic temperatures. However, no experimental data of ethylene selectivity, at cryogenic temperatures, have been reported up to now. A few years later, Fuertes and Mendenez[20] made an extensive study on the optimization of carbon membranes for ethylene/ethane separation. Selectivities between 2 and 11, and permeances around $10^{-7}$ mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ were obtained. In addition, they have collected from literature various membrane data, and together with their results they represented the data in a Robeson plot. On the basis of this information they deduced an empirical trade-off relation between the ethylene/ethane selectivity and ethylene permeance. Recently, Xu et al.[33] published a slightly higher selectivity ∼12 (at 35 °C), in combination with a very low ethylene permeance of 8.4 × $10^{-11}$ mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ for a carbon molecular sieve hollow fiber membrane based on Matrimid.

Considering the existing membrane performance data for ethylene/ethane separation, we have assumed a membrane with typical ethylene permeance of 7.0 × $10^{-9}$ mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ and ethane permeance of 1.6 × $10^{-9}$ mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ ($\alpha_{C_2H_4,C_2H_6}$ = 4.4). Additional calculations are performed at higher ethylene permeance and fixed ethane permeance. The purpose is to find out the minimum required membrane selectivity that leads to an economically attractive hybrid process.

**2.3. Membranes for Butadiene Separation.** Okamoto et al.[23] published ideal selectivities ranging from 30 to 200 for the separation of 1,3-butadiene from *n*-butane, and 1,3-butadiene permeances ranging from $10^{-10}$ to $10^{-8}$ mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ depending on the membrane material at a membrane thickness of 5.5 $\mu$m. For mixed permeation tests, due to plasticization effects caused by 1,3-butadiene, the selectivity reduces with a factor between 3 and 6 when compared to ideal measured selectivity. In the current study, these later data were used as a starting point to generate the permeances of all, more than 15, components that are present in the $C_4$-fraction. For most of these compounds, no experimental permeation data are available in the open literature. Permeation values were estimated by grouping the components based on their Bunsen solubility in NMP (see Table 1). Subsequently, the same

**Table 1. Groups, Components and Permeances in Butadiene Separation**

| group | component | bunsen solubility in NMP,[27] $m^3_{gas}/m^3_{liq}$ | permeances, mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ | |
|---|---|---|---|---|
| saturated paraffins (SP) | n-butane | <10 | 4.96 × $10^{-9}$ | 4.96 × $10^{-9}$ |
| mono-olefins (MO) | *iso*-butylene<br>1-butene<br>*trans*-2-butene<br>*cis*-2-butene | 15−25 | 9.91 × $10^{-9}$ | 9.91 × $10^{-9}$ |
| di-olefins and acetylenes (DOA) | 1,3-butadiene<br>methyl acetylene<br>ethyl acetylene<br>vinyl acetylene | 41−226 | 7.43 × $10^{-8}$ | 5.95 × $10^{-7}$ |
| $\alpha_{DOA,SP}$ | | | 15 | 120 |
| $\alpha_{DOA,MO}$ | | | 7.5 | 60 |

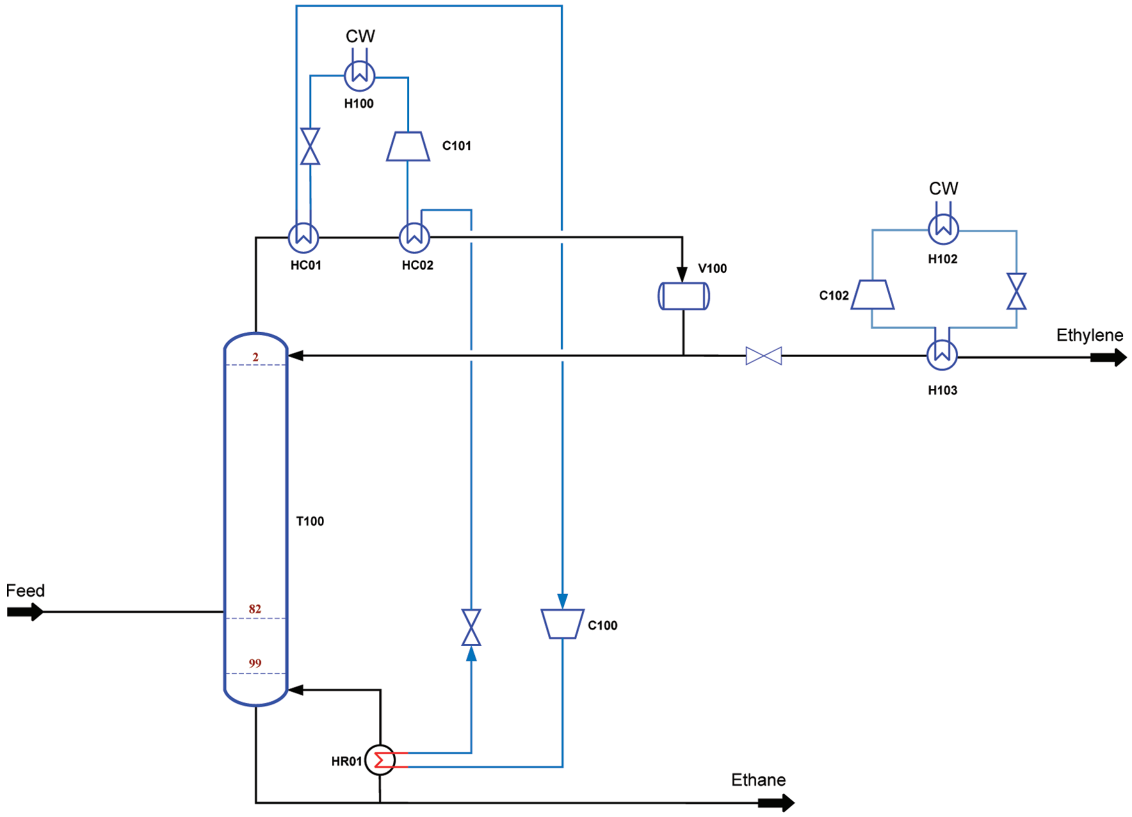

**Figure 3.** Ethylene fractionator—Base case.

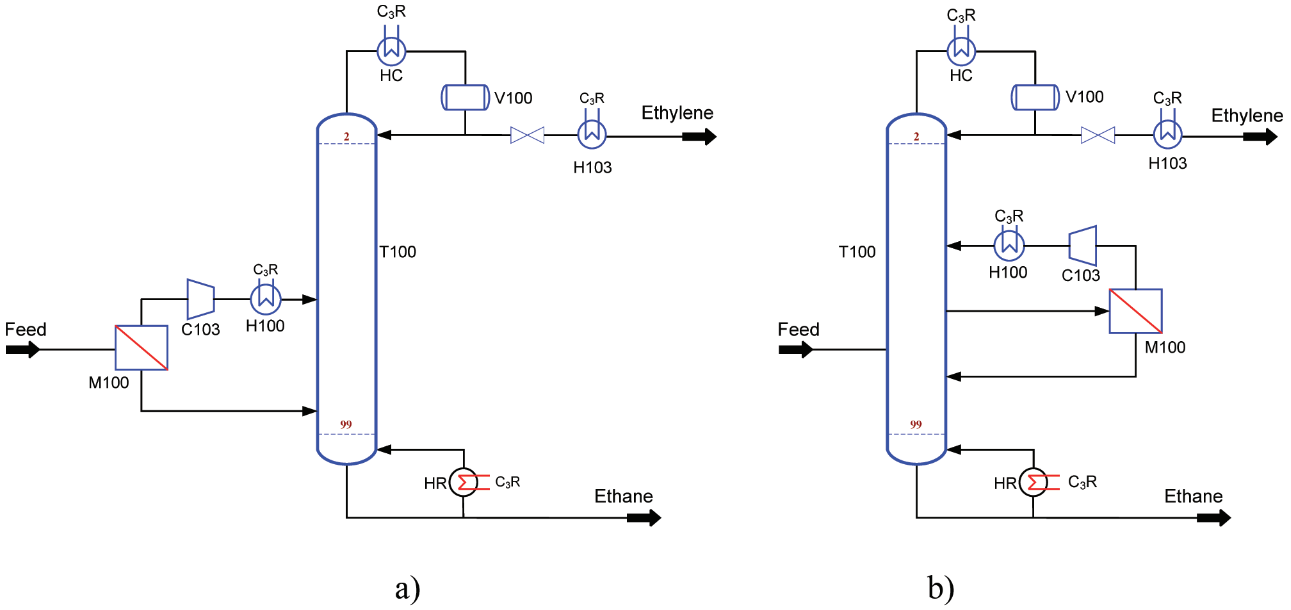

**Figure 4.** Hybrid configurations in ethylene/ethane separation: (a) membrane in upstream; (b) membrane in downstream.

permeance was assigned to each member of a specific group. For the group containing diolefins and acetylenes (DOA), which includes butadiene, a permeance of 7.43 × $10^{-8}$ mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ was estimated based on the measurements by Okamoto. Consequently, for the saturated paraffins (SP), including *n*-butane, a permeance of 4.96 × $10^{-8}$ mol·$Pa^{-1}$·$m^{-2}$·$s^{-1}$ is assumed, by considering a selectivity of $\alpha_{DOA,SP}$ = 15. This value is on the low side of the measured range by Okamoto. Apart from this low selectivity scenario, also a high selectivity case was investigated with $\alpha_{DOA,SP}$ = 120. No permeance data for the various mono-olefins were found, and we were forced to make an educated guess on the basis of selectivity ratios found in the current extractive-distillation process. We decided to relate the permeance of all mono-olefins to that of the permeance used for the saturated paraffins and to use a fixed selectivity of $\alpha_{MO,SP}$ = 2. The two sets of permeances, at which the evaluation will be performed are summarized in Table 1. The main task of the membrane is to

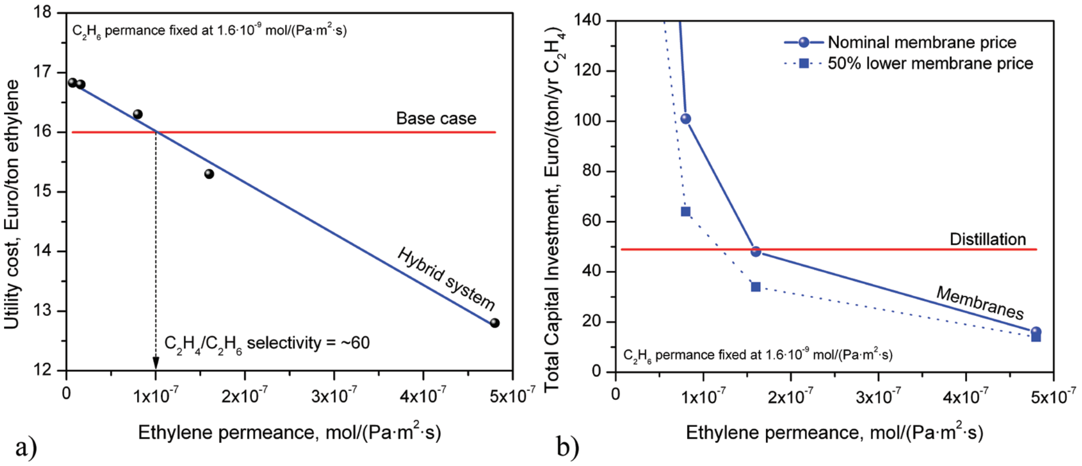

**Figure 5.** (a) Operation cost, only electricity and cooling water, and (b) total capital investment per capacity of ethylene produced vs ethylene permeance. The dots and squares indicate at which ethylene permeance the hybrid system was optimized.

allow butadiene to pass the membrane while rejecting, in first instance, the mono-olefins and then paraffins.

## 3. RESULTS AND DISCUSSION

**3.1. Ethylene/Ethane Separation.** The technology typically used to perform this separation, after acetylene hydrogenation in an olefin plant, is high-pressure fractionation (see Figure 1) rather than a direct heat-pump assisted method. The preferred process as described by Zimmerman and Walzl,[15] has been taken as the base case (Figure 3). The typical feed contains 85 wt % ethylene, and enters the distillation column at −18 °C and 20 bar. The column is designed to produce polymer grade ethylene (99.95 wt %) with an ethylene recovery of 99.9%. In our analyses, the column was operated at constant pressure of 20 bar on every tray. This leads to a temperature in the top equal to −29 °C, at which the vapors are condensed in the condenser. In the external refrigeration cycle, the propylene is compressed in two stages with intermediate cooling in H100 using water, and in the column reboiler using liquid ethane (see Figure 3). The compressors C100 and C101 act as indirect heat pumps, shifting thermal energy from the condenser to the reboiler. Before storage, the ethylene is expanded from 20 to 15 bar. The ethylene vapor formed during this expansion is condensed in a separate second refrigeration cycle that also uses propylene.

The design of the base case column leads to 100 sieve trays, with the first tray being the condenser and the last tray the reboiler. More trays do not lead to a significant decrease in condenser duty and operation costs. The optimum feed tray is no. 82. For an ethylene production capacity of 460 kt/yr, the column diameter is 3.65 m. The mass reflux ratio of the column is 4.23, and condenser and reboiler duties are 27.3 MW and 20.9 MW, respectively. The total compressor power needed for C100 and C101 in the refrigeration cycle is 11.7 MW, and in the second refrigeration cycle (C102) is 0.3 MW. These estimated values at base case conditions are consistent with those presented by Zimmerman and Walzl.

To reduce the energy consumption in the current fractionator, two basic hybrid process schemes were identified (Figure 4). For sake of simplicity, the refrigeration cycles shown in Figure 3 are not shown in these schemes. In the first process, the membrane is located upstream. The initial mixture is first fed to the membrane unit and both the permeate and the retentate are subsequently injected at different locations into the column. In the second option, the membrane is located downstream from the column and a side stream is taken from the column and fed to the membrane unit. Again the permeate and the retentate streams are returned to the column. The design challenge is to find the optimal locations to feed the permeate and retentate streams to the column and to extract the side draw for the second option. These locations will depend on component permeances and membrane selectivity. For example, for a highly selective membrane, the permeate stream may meet the imposed ethylene purity and can be directed to the ethylene storage vessel straight away, leading modified process schemes from that presented in Figure 4a. In general, the permeate stream can be injected to a location nearer to the top if it is purer, that is, if the membrane is more selective. Similarly, the optimal feed tray for the retentate stream will shift toward the bottom of the column if the ethane has a higher purity. As the membrane takes over part of the separation task and the column acts more as a polishing step for the product purity, the condenser duty and the reflux ratio will reduce. Consequently, energy efficiency of the overall process is expected to increase. Alternatively, this method can be used in debottlenecking an existing $C_2$-splitter. For example, Bernard et al.[22] describe the case of Nova Chemicals in Corunna (Canada) where they sought an increase in capacity with 25%. A solution to a similar problem has been proposed by Ronczy[21] by introducing a second distillation column to debottleneck the $C_2$-splitter.

To limit the optimization effort, for evaluation purposes, we are considering only the process presented in Figure 4a. This scheme is a specific case of the process shown in Figure 4b when the side draw location of the stream entering to the membrane is the same with the optimal feed location to the column. Because we have a high ethylene concentration in the feed, the most likely configuration in Figure 4a will be the optimal or near to optimal solution if the configuration in Figure 4b would be optimized (see rigorous optimization results of Kookos,[13] feed to column on tray 120 and side draw from tray 123; or Caballero et al.,[19] feed to column on tray 40 and side draw from tray 37).

The sensitivity analysis was performed by performing several optimizations with membranes having an ethylene permeance ranging from $7.0 \times 10^{-9}$ to $4.8 \times 10^{-7}$ mol·Pa$^{-1}$·m$^{-2}$·s$^{-1}$ and a constant ethane permeance of $1.6 \times 10^{-9}$ mol·Pa$^{-1}$·m$^{-2}$·s$^{-1}$. At

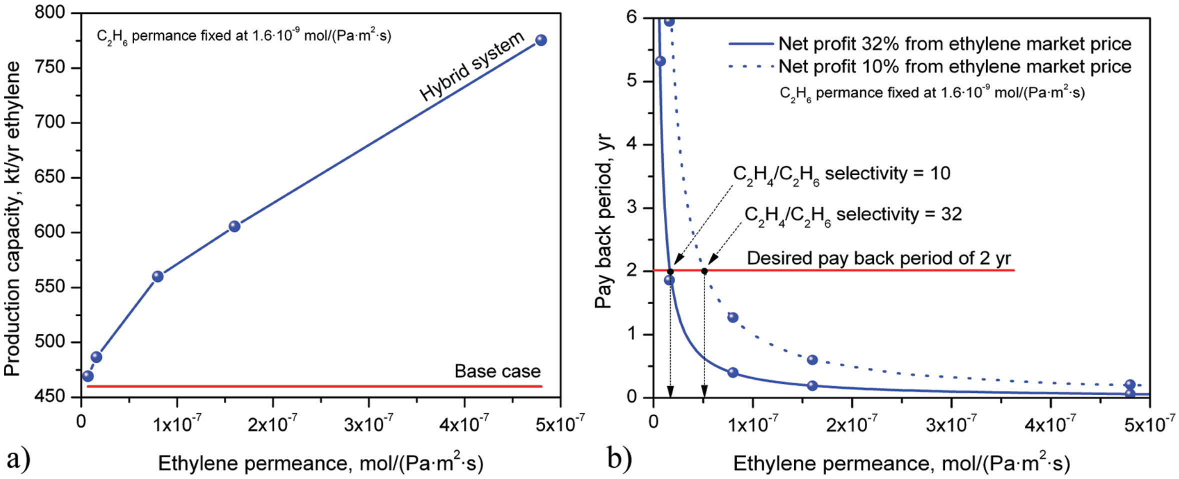

**Figure 6.** (a) Ethylene production capacity vs ethylene permeance for base case and the hybrid system. The difference in production capacity between hybrid system and base indicates the debottlenecking potential of a $C_2$-splitter by using the membranes; (b) Payback period of investment made in a membrane system to debottleneck a $C_2$-splitter vs ethylene permeance, shown at two different assumed net profits made from additional ethylene sales due to capacity increase. In both graphs the dots indicate at which ethylene permeance the hybrid system was optimized.

each optimization, the optimal membrane stage cut, retentate, and permeate feed tray was determined by employing a discrete optimization technique. This consists of performing consecutive simulations for every possible combination among all three decision variables by using the sensitivity tool in Aspen Plus. The continuous decision variable, the membrane stage cut, was meshed in several values within a reasonable range and discretization step. The feed locations of permeate and retentate streams were limited to be within a specific range of trays located in the vicinity of the tray that has a vapor composition close to the composition of the respective stream.

Optimization of the system shows that condenser duty decreases linearly with an increase of ethylene permeance (selectivity). However, to ensure that the permeate stream is at the same temperature and pressure as the vapor on the trays where it is fed, energy is required for C103 and H100, reducing the total efficiency gain. Figure 5a shows that the costs of the base case and the hybrid system are equal at an ethylene permeance of $\sim10^{-7}$ mol·Pa$^{-1}$·m$^{-2}$·s$^{-1}$. Under our current assumptions, this corresponds to a membrane selectivity of ∼60. Higher values result in a reduction of the operation cost with respect to the base case.

The total capital investment in the membrane system, including the one stage membrane module, compressor C103, and heat exchanger H100 is presented as a function of the ethylene permeance in Figure 5b. This graph shows that the relative investment in the membrane system used in hybrid configuration is cheaper than a new distillation column when the ethylene permeance $\geq 1.6 \times 10^{-7}$ mol·Pa$^{-1}$·m$^{-2}$·s$^{-1}$. If the membrane system is assumed to be 50% cheaper than the nominal value assumed in this work, which may be considered as a very conservative membrane price assumption, than the ethylene permeance can be $\geq 1.2 \times 10^{-7}$ mol·Pa$^{-1}$·m$^{-2}$·s$^{-1}$. If these conditions are met by the membrane it means that it is better to invest in a membrane hybrid system rather than using a second deethanizer to debottleneck the separation. As the hybrid system allows for a larger production capacity, the estimated capital investment of the membrane system is recalculated to extra production capacity when compared to the base case capacity. Figure 6a shows the dependence of capacity increase of a hybrid system on ethylene permeance (or selectivity). The capacity of an existing $C_2$-splitter can be almost doubled depending on membrane performance.

To assess the economic attractiveness of the investment in the membrane system for the required increase in the ethylene production capacity, the payback period (PBP) is selected as an indicator. This represents the time needed to recover the investment made in the membrane system only. The PBP is calculated by dividing the investment by the net income of the additional sales of ethylene. The required investment in the membrane system is estimated in the current study. The net income, however, is much harder to assess, as it depends on the market price of ethylene and other (by)products, and on the investment and operating costs of the entire plant (see Figure 1). As this is outside the scope of the current paper, we are using the calculation results presented in the book of Peters et al.[34] They report a net income on the sale of ethylene of 32% of the market price. To validate this very high value for a commodity product, we compared their evaluation of total capital investment (TCI) with that reported by the technology vendors (see Towler and Sinnott,[35] p 310) for a 500 kt/yr ethylene plant. The comparison is shown in Table 2. It can be concluded that the evaluation performed by Peters et al. is realistic.

**Table 2. Total Capital Investment in an Ethylene Plant**

| source of data | technology | TCI, mln USD | TCI, mln USD (in 2006) |
|---|---|---|---|
| Peters et al.[34] | ethane/propane cracking | 503.4 (in 2001 when CEPCI is 394.1) | 638.2 |
| Towler and Sinnott[35] | ethane/propane cracking | 660.7 (in 2006 when CEPCI is 499.6) | 660.7 |

At an ethylene market price of 795 €/ton, the net income under base case conditions is 254 €/ton of the ethylene. We assume that this value would be the same if a fractionator is equipped with a membrane system for capacity increase purposes (see Figure 6a). The additional capacity leads to a higher income that can be used to pay back the investment in the membrane system. The payback period can now be calculated by relation 7.

$$\mathrm{PBP} = \frac{\mathrm{TCI}}{\mathrm{NI}(\mathrm{PC}_{\mathrm{hs}} - \mathrm{PC}_{\mathrm{bc}})} \qquad (7)$$

Figure 6b shows the dependence between payback period and ethylene permeance for two situations. On the basis of this figure we can see that a membrane selectivity of 10 would be enough to recover the investment in 2 years. For the more conservative estimate of 10% net income, a selectivity of 32 would be necessary. Please note these values are estimated for a fixed ethane permeance meaning that the dependency between selectivity and permeance relationship has been ignored. In other words this means that these evaluations are valid for a membrane that meets the above-mentioned selectivity and has an ethane permeance around $1.6 \times 10^{-9}$ mol·Pa$^{-1}$·m$^{-2}$·s$^{-1}$.

**3.2. Butadiene/$C_4$-Fraction Separation.** Butadiene is predominantly produced from the "$C_4$-fraction" coming from the debutanizer as shown in Figure 1. Currently, the commercial technologies for butadiene recovery are based on extractive distillation. These technologies differ mainly in the applied solvent for the selective removal of butadiene from the mixture of hydrocarbons with the typical butadiene composition of 45 wt % presented. In this study, the BASF−NMP process was selected as the base case (Figure 7). In this process, the solvent is a mixture of NMP and 8.3 wt % water. Water increases the selectivity for butadiene.

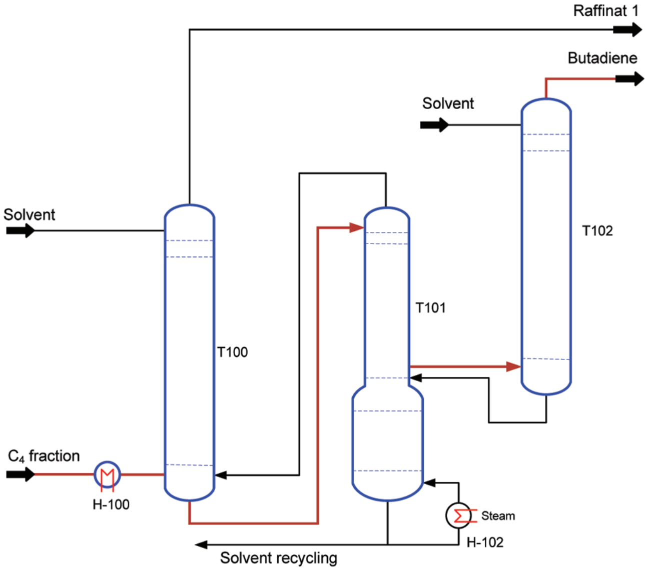

**Figure 7.** Simplified flow diagram of the BASF−NMP butadiene extraction process (the bold line shows the butadiene path in the process).

The liquid $C_4$-fraction at 4.5 bar is vaporized in H100 before it enters T100 at the bottom. The vaporized $C_4$-fraction contacts in counter-current the solvent that enters at the top of the column. The more soluble components, that is, butadiene and acetylenic impurities, leave the column at the bottom and are fed together with the NMP to T101, where the solvent is recovered from the valuable products. The less soluble compounds leave the column from the top. The composition of the top product from T101 is roughly the same as that of the fresh $C_4$-fraction and is recycled to the bottom of T100. This recycle stream is about 80% of the original feed. The main design specification of the T100 is to keep the butadiene concentration in Raffinate-1 below 0.2 wt %. This is reached at a NMP mass flow rate of almost 6 times that of the total bottom feed to the column. At higher solvent flow rates to T100, the butadiene loss via the top of T100 is smaller. Butadiene with a 97 wt % purity and at a recovery rate of 99.5% is withdrawn from T101 as a side stream. This side stream is contacted again with NMP in T102 to remove 99.5% of the vinyl acetylene, the last remaining impurity. The removal of vinylacetylene with a solvent is needed since it is a close boiling component with butadiene, and it will be difficult to remove it further via distillation. The vinyl acetylene recovery from the solvent is not represented in the simplified process flow sheet of Figure 7. First estimations indicate that the energy requirements for this separation step are much smaller than the separation of butadiene from NMP.

Considering the above design specifications and the feed composition of $C_4$ fraction, the calculated reboiler duty in T101 is 33.6 MW for a butadiene production capacity of 100 kt/yr. This value is equivalent with consumption of 4.2 tons of steam at ∼190 °C for every ton of butadiene produced.

One of the obvious measures to reduce the energy consumption is to reduce the amount of solvent required by the process. A major part of this solvent is evaporated in the reboiler to release the butadiene and other dissolved hydrocarbons. In addition, the high boiling temperature NMP (204 °C at 1 atm) requires the use of expensive high temperature steam. The results of the base case simulations show that 92% of the solvent is used in T100 and here the main reductions in solvent usage can be achieved. A first method to achieve this is by allowing a higher butadiene concentration in the top, followed by a membrane separation unit to prevent the unacceptable loss of butadiene (Figure 8a). A second option is to place a membrane unit upstream in the feed line to reduce the amount of butadiene entering column T100 (Figure 8b). Another way to reduce the feed flow to this column is by placing a membrane unit in the recycle from T101 to T100 (Figure 8c). The main difference is that in the process from Figure 8c the feed to T100 is already in the vapor phase, and therefore compression is needed to ensure the required driving force. The process shown in Figure 8d is a combination of processes b and c. The design specifications used to design the membrane unit for every case are as follows: for option A the feed and permeate pressure is 20 and 1 bar, respectively; butadiene concentration in the retentate stream is specified to be 0.2 wt %. For options B, C, and D the feed pressure to the membrane is specified at 20 bar and permeate pressure is equal to the pressure in the T101 column. In these options it is specified that the butadiene cut across the membrane is 0.5, where butadiene cut is the ratio of butadiene flow in permeate divided by the butadiene flow in the feed.

The results of the process simulations with the two different membrane selectivities from Table 1, are summarized and compared with the base case in Table 3. All membrane assisted processes result in a reduced primary energy demand, which is dependent on the membrane selectivity and on the process configuration. Process configuration A leads to the largest savings of ∼30% for the highly selective membrane case. For membranes with a low selectivity, configurations B or D are the most promising scheme with a savings potential of ∼23%. These results show that a highly selective membrane does not lead to a much higher energy savings potential. In addition, the membrane containing options, compared to the base case, lead to smaller column diameters and consequently to a lower capital expenditure for new plants. The reduced costs will be

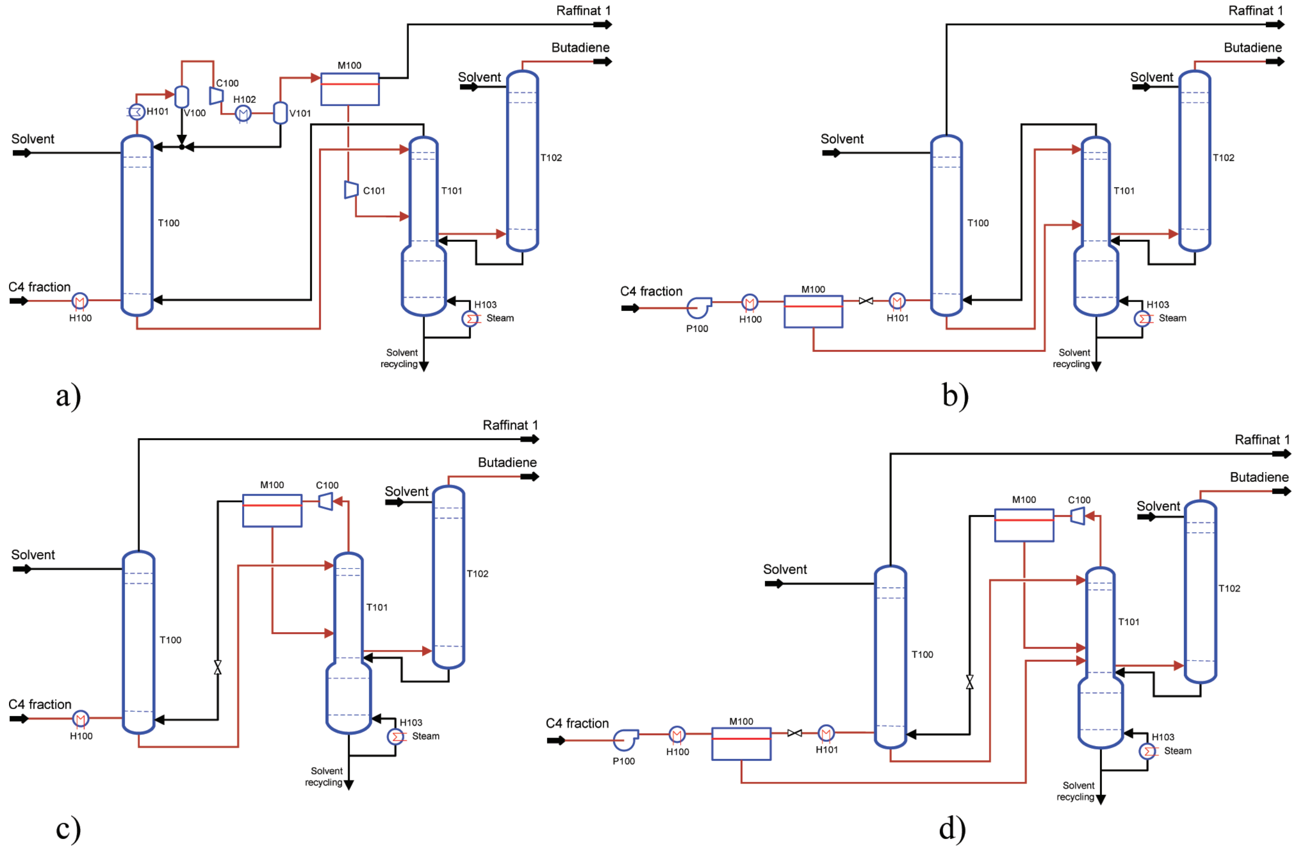

Figure 8. Hybrid membrane configurations for the butadiene extraction process (the brown line shows the butadiene path in the process).

**Table 3. Results of Simulation for Butadiene Extraction Process**[a]

| comparison criteria | base case | option A | | option B | | option C | | option D |
|---|---|---|---|---|---|---|---|---|
| $\alpha_{DOA,SP}$ | | 7.5 | 60 | 7.5 | 60 | 7.5 | 60 | 7.5 |
| | | | | Energy Use | | | | |
| steam (195 °C in reboiler of T101), [MW] | 33.58 | 30.72 | 22.09 | 26.02 | 24.84 | 28.98 | 28.40 | 24.70 |
| total electricity, [MW] | n.a. | 0.91 | 0.59 | 0.03 | 0.03 | 0.54 | 0.47 | 0.65 |
| total membrane area in M100, [$m^2$] | n.a. | 2728 | 322 | 1333 | 237 | 1159 | 224 | 2690 |
| specific primary energy, [GJ/ton butadiene] | 9.75 | 9.51 | 6.78 | 7.55 | 7.20 | 8.75 | 8.53 | 7.56 |

[a] n.a. = not applicable; T100, T101, and T102 have 45, 35, and 20 theoretical stages (incl. condenser and reboiler).

partly used for the membrane unit. For existing plants, integration of membranes within the process can be an attractive solution for butadiene capacity increase, similar as in the ethylene case. The simulation results also show that for a single plant with capacity of 100 kt/yr of butadiene, and under the current assumptions, the required membrane area will not exceed 3000 $m^2$.

## 4. CONCLUSIONS

In this work the technical and economic feasibility has been investigated of membrane application in ethylene/ethane separation and butadiene separation from the $C_4$-fraction in an olefin plant. The results reveal that the membrane combined with the existing separation process leads to reduction in energy consumption in both existing and new plants. In the case of ethylene/ethane separation the energy savings are possible if membrane selectivity for ethylene is > ~60. For this application the higher the selectivity the more energy can be saved. To reach ~20% increase in the energy efficiency a selectivity of ~275 is required. This value is over 20 times the highest value reported in the literature, and is unlikely to be met in the near future. However, an interesting application of membranes in ethylene/ethane separation is the debottlenecking of an existing column. In this case a membrane selectivity of ~10 is sufficient for an economically attractive process.

In contrast with the $C_2$-splitter, high selectivity is not required for the separation of butadiene from a $C_4$-mixture. The simulation results show that a membrane selectivity of 7.5 for the separation of butadiene from mono-olefins leads to ~23% reduction in energy consumption. The optimal location for the membrane is upstream of the first distillation column. When the membrane selectivity is increased to 60 the estimated energy savings are ~30%. This time, the most profitable process scheme is to locate the membrane downstream from the main wash. Similar as in ethylene/ethane separation, in butadiene separation, it is also possible to increase the production capacity of butadiene when membranes are used in combination with an existing process.

## APPENDIX

### Energy Type Transformation

For translation of secondary energy type (steam and electricity) to primary energy type (e.g., natural gas) the coefficient of 1.05 is used for steam and 2.33 for electricity.

### Utility Cost

The following cost of utilities are used to evaluate the operation costs: cooling water, 0.05 €/$m^3$ (or 1.19 €/GJ); electricity, 0.07 €/kWh (or 19.44 €/GJ); refrigeration at −20 °C, 5.68 €/GJ; refrigeration at −29 °C, 9.13 €/GJ; refrigeration at −39 °C, 13.50 €/GJ;

### Equipment Cost

The cost estimation of equipment is based on a module costing technique and relations published in ref 36. The Chemical Engineering Plant Cost Index of 580 is assumed. Columns are assumed to be equipped with sieve trays. All heat exchangers are assumed to be of fixed tube type. Centrifugal pumps and compressors have been applied. Carbon steel is considered as material of construction for all the above mentioned equipment. The installed cost of a membrane module has been assumed to be 1600 €/$m^2$, including all costs associated with membrane operation (e.g. replacement, maintenance, etc.).

### List of Symbols

$P$ = permeate flow rate out of the module, mol/s
$F$ = feed flow rate to the membrane module, mol/s
$R$ = retentate flow rate out of the module, mol/s
$A_m$ = membrane area, $m^2$
$Q_i$ = permeance of component $i$ trough the membrane (in a mixture), mol/(Pa·$m^2$·s)
$P_R$ = pressure on the retentate side of the membrane, Pa
$P_P$ = pressure on the permeate side of the membrane, Pa
$x_{mR,i}$ = average mole fraction of component $i$ on the retentate side, mol fr
$x_{F,i}$ = mole fraction of component $i$ in the feed, mol fr
$x_{R,i}$ = mole fraction of component $i$ in the retentate, mol fr
$x_{P,i}$ = mole fraction of component $i$ in the permeate, mol fr
$nc$ = number of components, $i = 1, 2, ..., nc$
NI = net income from ethylene sales, €/ton ethylene
$PC_{hs}$ = production capacity at hybrid system conditions, kt/yr
$PC_{bc}$ = production capacity at base case conditions, kt/yr
TCI = total capital investment in the membrane system, k€
CEPCI = chemical engineering plant cost index

## ASSOCIATED CONTENT

### Supporting Information

Composition of $C_4$ fraction used in the calculations and more extended results of simulation for the butadiene extraction process. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: vente@ecn.nl. Tel.:+31 244 56 4916.

### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Olujic, Z.; Sun, L.; De Rijke, A.; Jansens, P. J. Conceptual design of an internally heat integrated propylene-propane splitter. *Energy* **2006**, *31*, 3083.

(2) Bohner, G.; Klaus, K.; Pahl, M.; Kaibel, G., Method and device for obtaining 1,3 pure butadiene from 1,3 raw butadiene by distillation. US Pat. 2001, 7,132,038 B2.

(3) Hayashi, J.; Mizuta, H.; Yamamoto, M.; Kusakabe, K.; Morooka, S.; Suh, S. H. Separation of ethane/ethylene and propane/propylene systems with a carbonized BPDA-pp′ ODA polyimide membrane. *Ind. Eng. Chem. Res.* **1996**, *35*, 4176.

(4) Staudt-Bickel, C.; Koros, W. J. Olefin/paraffin gas separations with 6FDA-based polyimide membranes. *J. Membr. Sci.* **2000**, *170*, 205.

(5) Azhin, M.; Kaghazchi, T.; Rahmani, M. A review on olefin/paraffin separation using reversible chemical complexation technology. *J. Ind. Eng. Chem.* **2008**, *14*, 622.

(6) Bux, H.; Chmelik, C.; Krishna, R.; Caro, J. Ethene/ethane separation by the MOF membrane ZIF-8: Molecular correlation of permeation, adsorption, diffusion. *J. Membr. Sci.* **2011**, *369*, 284.

(7) Anson, A.; Wang, Y.; Lin, C. C. H.; Kuznicki, T. M.; Kuznicki, S. M. Adsorption of ethane and ethylene on modified ETS-10. *Chem. Eng. Sci.* **2008**, *63*, 4171.

(8) Gücüyener, C.; van den Bergh, J.; Gascon, J.; Kapteijn, F. Ethane/ethene separation turned on its head: Selective ethane adsorption on the metal−organic framework ZIF-7 through a gate-opening mechanism. *J. Am. Chem. Soc.* **2010**, *132*, 17704.

(9) Gücüyener, C.; van den Bergh, J.; Joaristi, A. M.; Magusin, P. C. M. M.; Hensen, E. J. M.; Gascon, J.; Kapteijn, F. Facile synthesis of the DD3R zeolite: Performance in the adsorptive separation of buta-1,3-diene and but-2-ene isomers. *J. Mater. Chem.* **2011**, *21*, 18386.

(10) Shi, M.; Lin, C. C. H.; Kuznicki, T. M.; Hashisho, Z.; Kuznicki, S. M. Separation of a binary mixture of ethylene and ethane by adsorption on Na-ETS-10. *Chem. Eng. Sci.* **2010**, *65*, 3494.

(11) Shi, M.; Avila, A. M.; Yang, F.; Kuznicki, T. M.; Kuznicki, S. M. High pressure adsorptive separation of ethylene and ethane on Na-ETS-10. *Chem. Eng. Sci.* **2011**, *66*, 2817.

(12) Moganti, S.; Noble, R. D.; Koval, C. A. Analysis of a membrane/distillation column hybrid process. *J. Membr. Sci.* **1994**, *93*, 31.

(13) Kookos, I. K. Optimal design of membrane/distillation column hybrid processes. *Ind. Eng. Chem. Res.* **2003**, *42*, 1731.

(14) White, W. C. Butadiene production process overview. *Chem.−Biol. Interact.* **2007**, *166*, 10.

(15) Zimmerman, H.; Walzl, R. Ethylene. *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; 13, 465, Wiley-VCH: Weinheim, Germany, 2009; Vol. 13, p 465.

(16) Benali, M.; Aydin, B. Ethane/ethylene and propane/propylene separation in hybrid membrane distillation systems: Optimization and economic analysis. *Sep. Purif. Technol.* **2010**, *73*, 377.

(17) Teramoto, M.; Shimizu, S.; Matsuyama, H.; Matsumiya, N. Ethylene/ethane separation and concentration by hollow fiber facilitated transport membrane module with permeation of silver nitrate solution. *Sep. Purif. Technol.* **2005**, *44*, 19.

(18) Safarik, D. J.; Eldridge, R. B. Olefin/paraffin separations by reactive absorption: A review. *Ind. Eng. Chem. Res.* **1998**, *37*, 2571.

(19) Caballero, J. A.; Grossmann, I. E.; Keyvani, M.; Lenz, E. S. Design of Hybrid Distillation-Vapor Membrane Separation Systems. *Ind. Eng. Chem. Res.* **2009**, *48*, 9151.

(20) Fuertes, A. B.; Menendez, I. Separation of hydrocarbon gas mixtures using phenolic resin-based carbon membranes. *Sep. Purif. Technol.* **2002**, *28*, 29.

(21) Ronczy, S. E., Secondary deethanizer to debottleneck an ethylene plant. US Patent, 2004, 0021379 A1.

(22) Bernard, A.; De Villiers, W.; Summers, D. R. Improve product ethylene separation. New high-capacity trays enable retrofitting existing splitter superfractionator to expand unit capacity and conserve energy. *Hydr. Proc.* **2009**, No. April, 61.

(23) Okamoto, K.; Noborio, K.; Jianqiang, H.; Tanaka, K.; Kita, H. Permeation and separation properties of polyimide membranes to 1,3-butadiene and *n*-butane. *J. Membr. Sci.* **1997**, *134*, 171.

(24) Shimazu, A.; Miyazaki, T.; Matsushita, T.; Maeda, M.; Ikeda, K. Relationships between chemical structures and solubility, diffusivity, and permselectivity of 1,3-butadiene and *n*-butane in 6FDA-based polyimides. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 2941.

(25) Bohner, G.; Klaus, K.; Pahl, M.; Kaibel, G., Method for recovering crude 1,3-butadiene by extractive distillation from a $C_4$ cut. US Pat. 2002, 7,226,527 B2.

(26) Tian, X.; Zhang, X.; Wei, L.; Zeng, S.; Huang, L.; Zhang, S. Multi-scale simulation of the 1,3-butadiene extraction separation process with an ionic liquid additive. *Green Chem.* **2010**, *12*, 1263.

(27) Wagner, U.; Weitz, H. M. BASF Process for Production of Pure Butadiene. *Ind. Eng. Chem. Res.* **1970**, *62*, 43.

(28) Pettersen, T.; Argo, A.; Noble, R. D.; Koval, C. A. Design of combined membrane and distillation processes. *Sep. Technol.* **1996**, *6*, 175.

(29) Stephan, W.; Noble, R. D.; Koval, C. A. Design methodology for a membrane/distillation column hybrid process. *J. Membr. Sci.* **1995**, *99*, 259.

(30) Fattah, K. A.; Hamam, S. M.; Al-Enezi, G. A.; Ettoueny, H. M.; Hughes, R. A nonideal model for analysis of gas separation permeators. *J. Membr. Sci.* **1992**, *65*, 247.

(31) Henis, J. M. S.; Tripodi, M. K. Composite hollow fiber membranes for gas separation: the resistance model approach. *J. Membr. Sci.* **1981**, *8*, 233.

(32) Marriott, J.; Sorensen, E.; Bogle, I. D. L. Detailed mathematical modelling of membrane modules. *Comput. Chem. Eng.* **2001**, *25*, 693.

(33) Xu, L.; Rungta, M.; Koros, W. J. Matrimid derived carbon molecular sieve hollow fiber membranes for ethylene/ethane separation. *J. Membr. Sci.* **2011**, *380*, 138.

(34) Peters, M. S.; Timmerhaus, K. D.; West, R. *Plant Design and Economics for Chemical Engineers*, 5th ed.; McGraw-Hill: New York, 2003.

(35) Towler, G.; Sinnott, R. K. *Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design*; Elsevier: London, 2008.

(36) Turton, R.; Bailie, C. R.; Whiting, B. W.; Shaeiwitz, A. J. *Analysis, Synthesis, and Design of Chemical Processes*, 3rd ed.; Prentice Hall: MA, 2008.