

Improvements in the Design of the Cyclohexane Production Process Implementing Mass Exchange with a Counter Current Gas Permeation Membrane

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S Supporting Information

ABSTRACT: In this paper, we propose changes in the design of a cyclohexane production process, following a mass exchange design heuristic developed in a previous work (*Ind. Eng. Chem. Res.* **2011**, *50* (11), 6849–6859). In the study case considered, an optimal design was obtained which exhibits a significant 40.08% reduction in the power of the compressor that recycles unreacted reagents, and a respectable 3.59% reduction of the hydrogen consumption, resulting in an increase of the plant Net Annual Income of a 1.31%. These results highlight the importance of considering a mass exchange between the input and output streams from the reactor, at the time of synthesizing a new process.

INTRODUCTION

When designing a new process following the hierarchical procedure by Douglas,^{1,2} one advances in the design generating more detailed versions of the process with an increasing number of process blocks interconnected by process streams. The design procedure is guided by heuristics, which recommend among the options available at each stage of the design.

On the other hand, the technique for the synthesis of Mass Exchange Networks^{3–5} (MENs) dictates mass exchanging between process streams in a (as much as possible) counter-current arrangement. This technique needs, as input, the list of streams to be integrated, their flows, and inlet–outlet concentrations. Therefore, the mass integration methodology is currently being applied to existing processes, or in the final design stage of the process, once all streams have been generated. This actually restricts the integration to streams entering and exiting the process, because if internal streams were integrated this would change the input information to the MENs synthesis problem.

Previous works^{6–8} described in more detail the use of the MEN concept as a heuristic at an early stage (before defining all process streams) in the hierarchy of Douglas.^{1,2} The MENs heuristic dictates analyzing mass exchange between the reactor inlet and the outlet streams and was successfully applied to a process for the synthesis of biodiesel,⁶ the synthesis of benzene⁷ from toluene (HDA Process), and an Ammonia synthesis loop.⁸

This paper focuses on analyzing the new process alternatives generated in a cyclohexane synthesis loop, when including the concept of Mass Exchange Networks at an early stage of design. It resorts to novel counter-current mass exchanger equipment (a gas permeation membrane module) previously presented.⁷ This exchanger takes advantage of the concentration gradients between the process gaseous streams to perform hydrogen exchange, significantly reducing the cost of both the separation

and the recycle loop, as well as the amount of hydrogen feed, thus improving the overall performance of the process.

To model, simulate, and optimize the process, as well as to perform various estimations and analysis, we used different software: Aspen Plus V7.2, Aspen Custom Modeler V7.2, Aspen Energy Analyzer V7.2, and Aspen Process Economic Analyzer V7.2, among others.

Following, there is an overview of existing processes for the synthesis of cyclohexane and a brief description of the Hydrar process, selected to apply the mass exchange heuristic. Afterward we describe in detail the different cyclohexane process alternatives arrived at by using the heuristic of exchanging between the reactor inlet and outlet streams. Next, we analyze the economic impact of adopting the proposed new design, compared with the conventional process. Finally, the last section draws the conclusions of this work.

CYCLOHEXANE SYNTHESIS LOOP

Overview of Commercial Processes. Due to the economic importance of cyclohexane, several industrial processes have been developed.⁹ These processes differ from each other, mainly by

- The type of catalyst.
- The operating conditions at which the reaction is performed, i.e., liquid or gaseous phase.
- The reactor design, e.g., fixed or moving bed.
- The method used to dissipate the heat of formation, given that the reaction is highly exothermic.

This last point is of great importance and at which most processes differ.⁹ Over the years, many gas phase processes were developed, such as the Bexane process (D.S.M.

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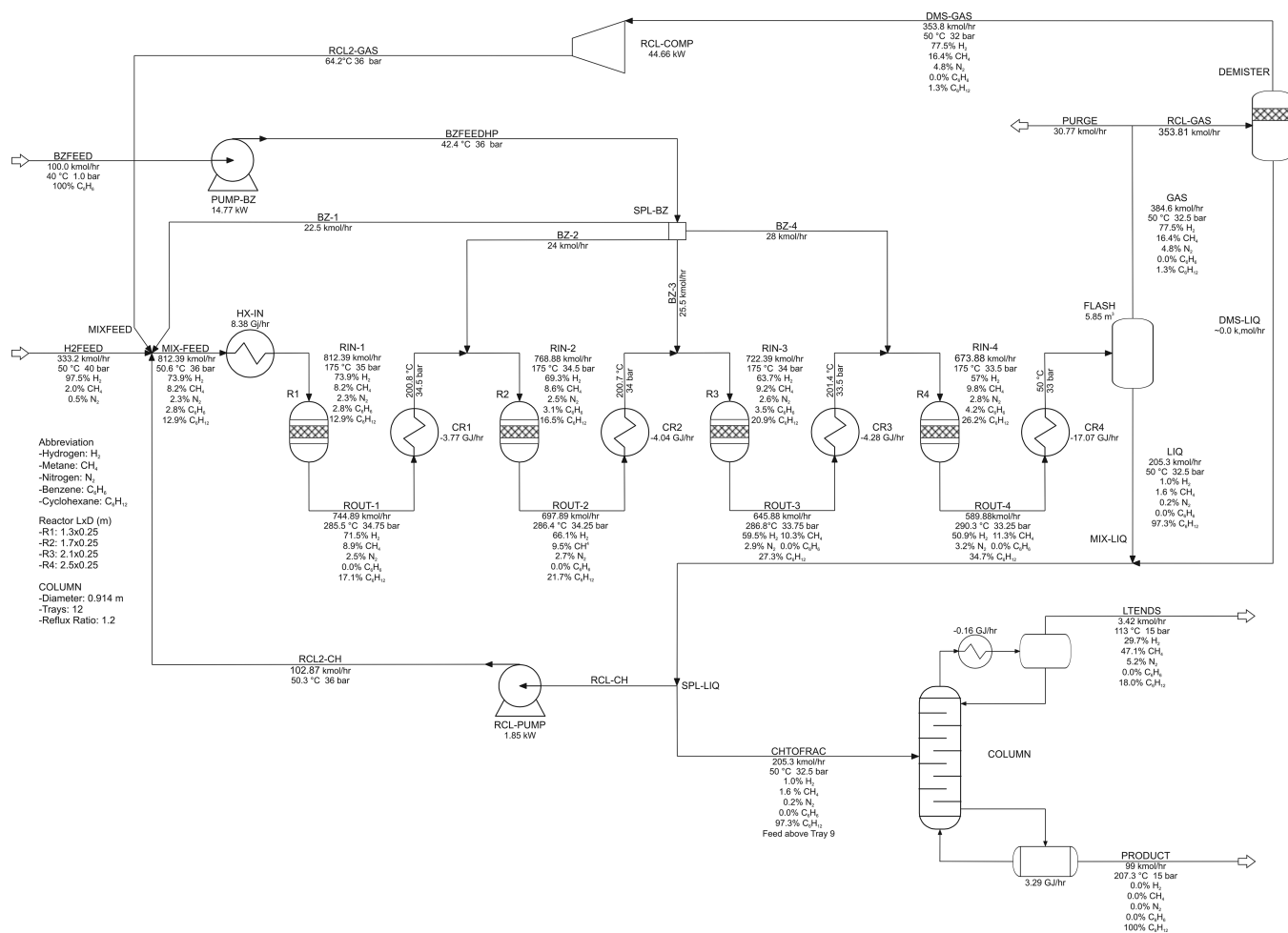


Figure 1. Flow sheet of the cyclohexane synthesis process.

Stamincarbone), Process HA-84 (Engelhard Industries & Sinclair Research Inc.), and the Hydrar Process (Universal Oil Products, U.O.P. now a Honeywell company). Liquid phase processes were also developed, such as the I.F.P. Process (Institut Français du Pétrole), the Arosat Process (Lummus), and The British Petroleum Process (The British Petroleum Company), among others.

The mentioned processes have in common that in order to accelerate the reaction and achieve a high conversion thereof (99.9%) they use hydrogen in excess, which after the reactor is separated from the reaction products and recycled to the reactor inlet with the addition of fresh reagents. This is the key feature that gives the mass exchange heuristic a good chance to be successfully applied.⁷ Out of all these existing processes, we are more interested in those whose reactants and products are in the gaseous state, because then we can resort to a previously proposed⁷ novel mass exchanger that uses the concentration difference as the driving force. To illustrate the application of the mass exchange heuristic we will use the Hydrar process, because it is the one that uses the greater hydrogen excess, that is, a large driving force to perform the mass exchange.

Brief Description of the Hydrar Process. In this process¹⁰ the hydrogenation of benzene to cyclohexane is performed in a series of adiabatic reactors under controlled conditions allowing the reaction to occur at as low as possible temperature. The reactants are drawn out from each reaction zone, cooled through steam generators, combined with more

benzene, and sent to the following reaction zone, where this sequence is repeated. There can be many numbers of reactors in series, although too many complicate the controllability of the process. Therefore, four reactors is usually the choice. In this process, the gaseous mixtures of benzene, cyclohexane, and hydrogen at a temperature between 163.33 and 204.44 °C and a pressure between 6.9 and 35 bar are fed to the adiabatic reaction zones where they contact the catalyst. The gases are removed from the reaction zones at a temperature between 260.00 and 315.55 °C, cooled to a temperature between 163.33 and 204.44 °C, and sent to the next reaction zone. The cyclohexane and hydrogen pass in series through all the reaction zones, while the benzene stream passes in parallel, with a fraction being derived to each reaction zone to be hydrogenated. It may be split in equal parts or in proportions such that the exit temperature of each reaction zone does not exceed a target value, usually not higher than 300 °C. In each of the reaction zones, the final conversion of benzene is sought to be complete to prevent further separation of benzene from cyclohexane downstream of the reaction.

The catalyst usually used is nickel compounded with kieselguhr, but any other hydrogenation catalyst may be used, such as nickel, platinum, palladium, iron, etc. supported on alumina, silica, kieselguhr, magnesia, zirconium oxide, or other inorganic or a combination thereof.

To achieve appropriate hydrogenation, hydrogen is in a mole fraction excess with respect to benzene from 4:1 to 50:1. In the

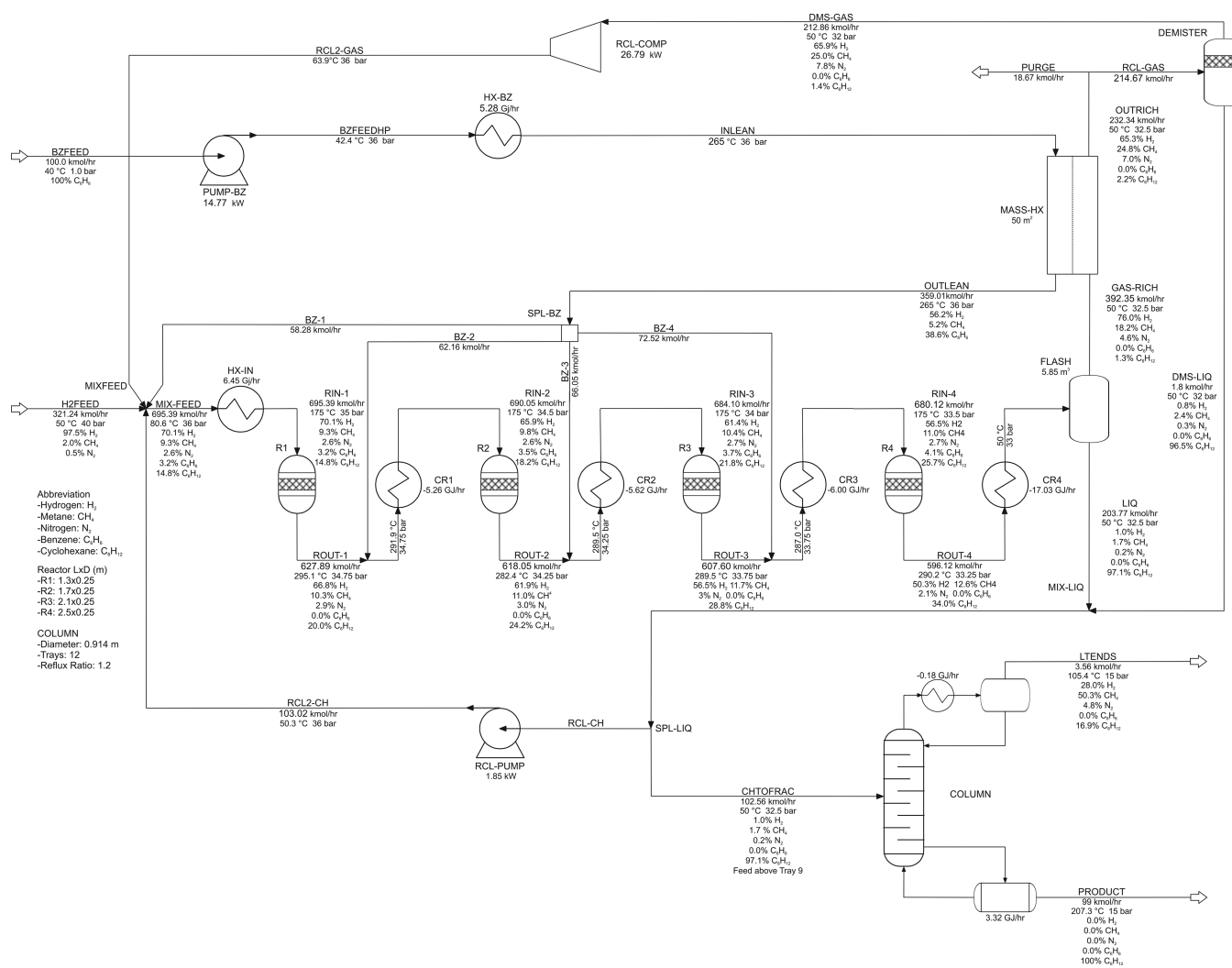


Figure 2. Process flow sheet with the inclusion of a mass exchanger.

reaction zones cyclohexane can be in a mole fraction with respect to benzene from 0.5:1 to 3.0:1 or more. Cyclohexane is recycled to act as a heat carrier.

We reproduced these process features for the production of 99 kmol/h of cyclohexane (an industry standard size) in Aspen Plus V7.2 using RV-SOAVE as the physical property model. We took the typical configuration of four reactors with Ni/SiO₂ catalyst. To model the reaction kinetics we referred to Keane and Patterson,¹¹ and we use a plug flow reactor model. Kinetic rate parameters are given in eq 1, where $\mathcal{R}1$ represents the reaction rates (expressed in units of kmol/s·m³); P_{H_2} , $P_{C_6H_6}$ are the partial pressures of hydrogen and benzene (given in Pa); R is the universal gas constant expressed in units of kcal/(mol·K), and T is the temperature (given in Kelvin). The activation energies are given in units of kcal/mol. The pre-exponential factor is expressed in units of kmol/(s·kg-cat·Pa^{1.5+0.2}).

$$\mathcal{R}1 = P_{H_2}^{1.5} P_{C_6H_6}^{0.2} \left[4.216 \times 10^{-7} \exp\left(\frac{-11.4}{RT}\right) \right] \quad (1)$$

The gas input to each of the reactors is at a temperature of 175 °C. The temperature of the gases exiting the reactors was maintained slightly below 300 °C by selecting a proper distribution of benzene feed. This was, in molar fractions of the fresh benzene feed, 0.225, 0.240, 0.255, and 0.280, from the first

to the last reactor, respectively. The pressure was set at 35.00 bar at the inlet of the first reactor and 33.50 bar at the inlet of the fourth reactor. For each reactor and heat recovery steam generator or heat exchanger present in the outputs of the reactors it was considered a conservative drop pressure of 0.25 bar. To maintain low concentrations of inert gases (methane and nitrogen) in the synthesis loop, a characteristic purge of 8% of the recycle stream was used. The molar fraction of hydrogen to benzene was kept at 4:1, while the fraction of benzene to cyclohexane was taken as 1:1. Figure 1 shows a flow sheet of this process while Table A1 (in Supporting Information) presents the properties of the main streams of this configuration. In the flow sheet the heat recovery steam generators and the heat exchangers are shown as heater or cooler.

Applying the mass exchange heuristic to this process (exchange hydrogen between the reactors inlet and outlet streams) strictly would lead to placing a mass exchanger between the benzene inlet stream BZFEED (which is free of hydrogen) after preheating and the stream exiting reactor R4. This last stream has a hydrogen mole fraction of 0.51 which gives a considerable driving force for exchange. However, as learned in a previous paper,⁷ if a gas–liquid separator immediately follows the reactor, the mass exchanger should be placed in the gaseous stream leaving the flash separator. This

gives a considerably greater driving force, increasing the hydrogen exchange per area of membrane used. Therefore, the mass exchanger (MASSHX) is placed in the gas stream (GAS) leaving the flash separator, where the hydrogen molar fraction is 0.78 as shown in Figure 2. Table A2 (in Supporting Information) presents the properties of the main streams of this configuration for a membrane area of 50 m². The module with the model of the mass exchanger equipment is described in a previous paper,⁷ and it is provided for this paper as Supporting Information for use only in Aspen Plus V7.2.

Different types of membranes could be used to exchange hydrogen between these streams. Among them we have the zeolite with structure MFI as ZSM-5 or with structure CHA as SAPO34. In this particular example, we use the ZSM-5 membranes because they have higher permeability than SAPO32. The literature¹² reports a ZSM-5 zeolite membrane which has a permeance for hydrogen of the order of 0.360 kmol/(m²·bar·h) with an ideal selectivity of pure gases with respect to methane of 7. While overall permeance does vary with pressure and temperature, here we use this reported pure gas permeance due to lack of experimental data for this specific application, as an approximation to the performance that can be expected if used in the cyclohexane process.

We performed a sensitivity analysis to notice that a membrane area over 500 m² does not significantly increase the amount of hydrogen transferred and tends to saturate the lean stream. Thus, we analyze the main effects on the process varying the membrane area in the range from 0 to 500 m².

The gas exchanger between the selected streams achieves a significant transfer of hydrogen as displayed in Figure 3 and

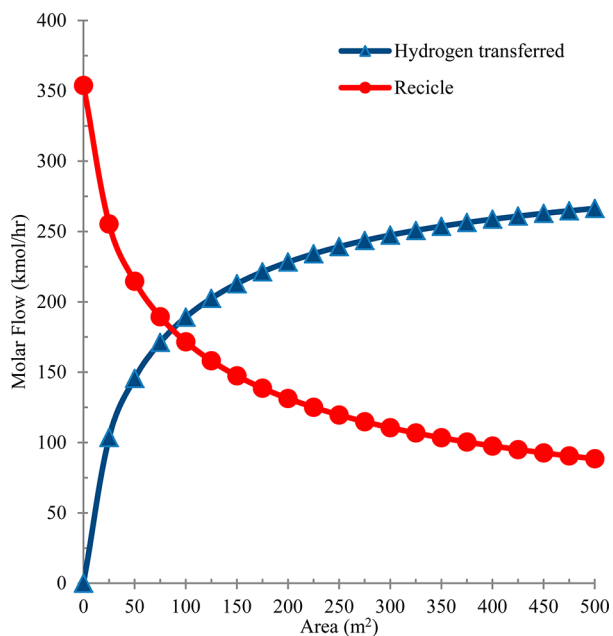


Figure 3. Hydrogen transferred in the membrane mass exchanger and flow rate of recycle stream as a function of membrane area.

tabulated in Table A3 (in Supporting Information). This exchange of hydrogen produced two significant changes in the process. One is that the hydrogen exchanged at the membrane unit is recycled directly to the reactor, so that the original recycle stream has a lower flow rate resulting in a recycle compressor with lower power and lower costs associated to it. Another significant change in the process is that as the purge

stream is taken after the hydrogen exchange, less hydrogen is lost in the purge, which results in a lower consumption thereof. Figure 3 also plots the molar flow rate of the recycle stream, showing that its reduction is significant. The respective values are tabulated in Table A3 (in Supporting Information).

Figure 4 plots the hydrogen stream feeding and purge stream exiting the process, data tabulated in Table A3 (in Supporting

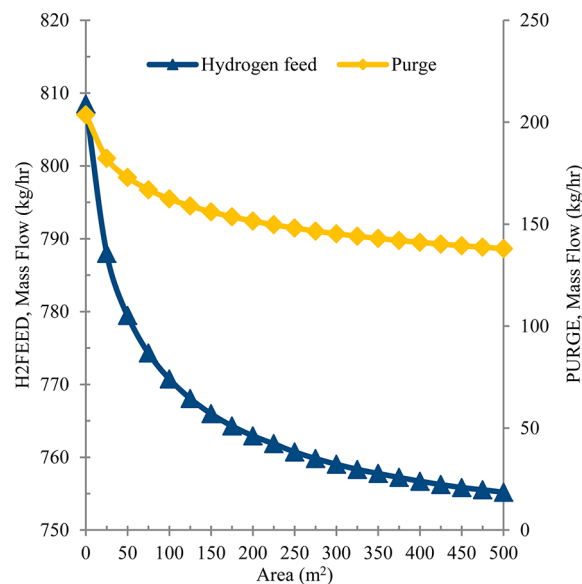


Figure 4. Hydrogen feed and purge stream as a function of membrane area.

Information). In this figure, it can be observed that, in the range of membrane area analyzed, the amount of hydrogen required by the process is reduced by 6.59%, and the purge does it in a 32.23%. The amount of benzene required and cyclohexane produced remain unchanged.

Although a detailed analysis of the changes in the heat exchangers network is beyond the scope of this work, we briefly analyzed the networks both for the traditional process and for the process with membrane. After changing the process structure to add HX-BZ, the amounts of heat to be exchanged and levels of temperature are not significantly altered. Using Aspen Energy Analyzer V7.2 we import from Aspen Plus V7.2 the data associated with heat integration. These data were used to do a quick assessment regarding to the heat exchange networks, using Aspen Energy Analyzer V7.2. So we obtained the composite curves for both the conventional and for the here proposed process (at the point of optimal mass exchange area), which are plotted in Figure 5.

From this figure, it can be seen that in both cases the composite curve of hot streams is safely above the composite curve of the cold streams, and it is possible to apply the heat exchange networks synthesis methodology to find a network that provides the energy required (at the appropriate temperatures) for the vaporization of the benzene. The curves differ mainly in the upper-right corner. Overall, the process with the membrane jeopardizes the heat integration (adding an important heating task at a high temperature level) but without altering the net energy surplus nature of the process. The streams exiting the reactors will now be used to heat and vaporize the benzene feed, instead of generating a medium pressure steam as in the original process, and part of the energy

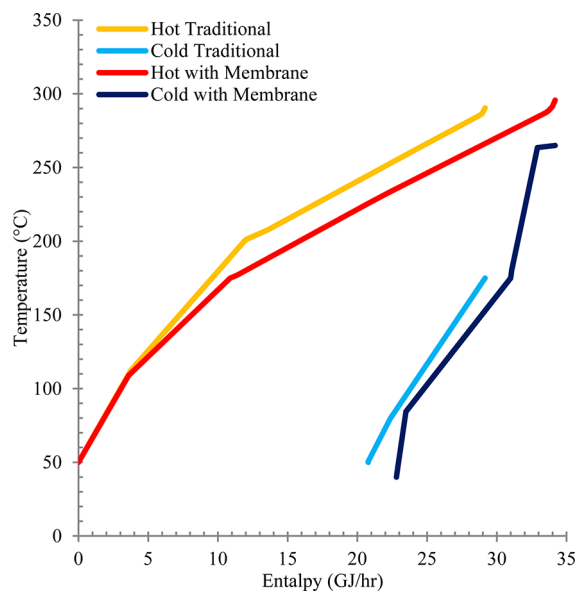


Figure 5. Composite curves for the conventional process and process with the inclusion of the mass exchanger.

supplied for this vaporization can be recovered by generating some extra low pressure steam.

Economic Analysis. The inclusion of a counter-current mass exchanger, besides considerably reducing the cost of the separation and recycle system, can change the requirement of reactants and the quality and quantity of the outlet streams of the overall process. Therefore, in order to assess the benefit of including the mass exchanger, we computed the Net Annual Income (NAI), measuring it as the difference between the Total Annual Income (TAI) from the sale of cyclohexane plus price of the purge streams and the Total Annualized Cost (TAC) of the main process units.

The TAC includes annualized equipment costs; some of these units do change their size when changing the area of the membrane exchanger, but others do not so they contribute to a fixed cost. Within this category are the reactors, the distillation column, the flash separator, the demister, and others. The cost of these items was determined quickly with Aspen Process Economic Analyzer V7.2 and amounts to \$1,097,800. Within the equipment with variable costs (dependent on the area of the mass exchanger), we have the compressor and the membrane unit itself. The TAC also includes costs associated with the variation of the heat exchange network. We briefly analyzed (without really finding the optimal heat exchange network) the costs of the networks for both the traditional process and for the process with membrane. For this we used all default values of Aspen Energy Analyzer V7.2 for the costs of equipment, services, and other parameters automatically provided. The analysis includes the cost of heating, the earnings due to steam generated, and an annualized cost of capital investment.

We consider a centrifugal compressor driven by an electric motor and find the installation cost using the correlations in Turton et al.¹³ We update the cost correlations using a Chemical Engineering Plant Cost Index (CEPCI) of 593.8 for May 2012. The power required by the compressor (brake horsepower) is determined with Aspen Plus V7.2, considering an isotropic efficiency of 0.72. For the cost of the ceramic zeolite membrane modules we adopted Babita et al.¹⁴ who

reported a cost of U.S. \$3000 per m². The TAC includes purchases of raw materials benzene and hydrogen, electricity, and all the equipment installation costs annualized using a Capital Charge Factor of 0.351.

To compute the energy consumed by the compressor, we consider an electrical to mechanical conversion efficiency of 0.9 and an electric energy cost of U.S. \$0.07 per kW hr. For the material streams, we take the following prices:¹⁵ hydrogen, U.S. \$0.5058/kg; benzene, U.S. \$1.266/kg; cyclohexane U.S. \$1.292/kg and purge U.S. \$0.010/kg.

In Figure 6 is a plot of the variations of the Total Annual Cost of the Process and Net Annual Income in the range of

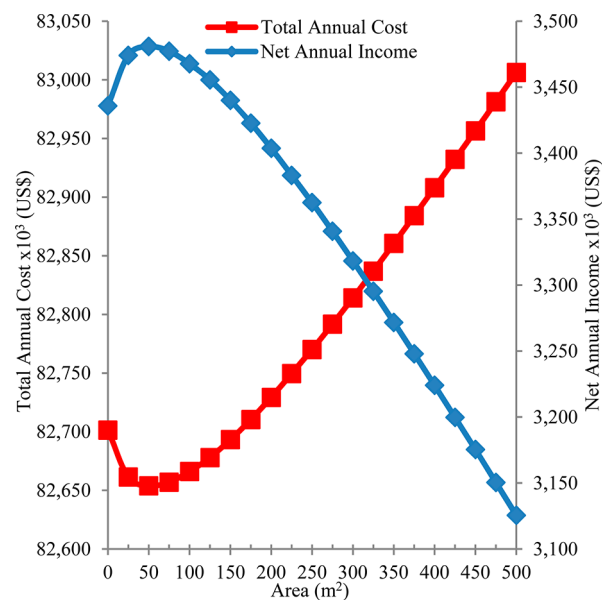


Figure 6. Total Annual Cost and Net Annual Income as a function of membrane area.

mass exchange area analyzed. In Table 1 these values are tabulated explicitly including those cost components that vary with the membrane area. The row with the maximum Net Annual Income is highlighted in bold.

When considering the TAC we note that it has a minimum at a membrane area of 50 m², where it reaches a small decrease of 0.06% because the TAC is strongly dominated by the purchase of raw materials and zeolite membranes are currently very expensive. But if we analyze the NAI we note that it reaches a maximum with a membrane area of 50 m², experiencing an increase of 1.31% which represents a value of U.S. \$45,036. Analyzing the recycle compressor we note that at the optimum membrane area a significant reduction in the compressor installed cost of a 40.08% is presented. For the process with the mass exchanger the TAC of the heat exchange networks is U.S. \$56,814/yr less profitable compared to the traditional process.

CONCLUSIONS

In the cyclohexane synthesis process analyzed in this paper, abidance to the mass exchange heuristic “If the reaction requires components which must be removed after the reaction and recycled, consider implementing a mass exchanger between the reactor outlet stream and some reactor inlet stream lacking these components” greatly reduced the cost of the separation and recycle system, as well as the amount of hydrogen needed, without changing the quantity and quality of the cyclohexane

Table 1. Cost and Their Components

membrane area (m ²)	Total Annual Income (U.S.\$)	cost of raw material (U.S.\$)	cost of electric energy (U.S.\$)	cost of the compressor (U.S.\$)	membrane unit cost (U.S.\$)	TAC of heat integration (income) (US\$)	Total Annual Cost (US\$)	Net Annual Income (US\$)
0	86,137,232	82,374,759	27,791	201,875	0	-157,307	82,701,428	3,435,803
25	86,135,509	82,291,753	19,924	145,075	75,000	-112,838	82,661,413	3,474,096
50	86,134,744	82,257,291	16,668	120,968	150,000	-100,493	82,653,903	3,480,840
75	86,134,244	82,236,468	14,644	105,814	225,000	-95,546	82,657,010	3,477,235
100	86,133,876	82,222,055	13,212	95,018	300,000	-93,057	82,666,190	3,467,686
125	86,133,585	82,211,196	12,125	86,786	375,000	-92,708	82,678,027	3,455,558
150	86,133,345	82,202,723	11,261	80,227	450,000	-92,082	82,693,339	3,440,006
175	86,133,143	82,195,930	10,553	74,841	525,000	-91,952	82,710,404	3,422,740
200	86,132,970	82,190,431	9,959	70,316	600,000	-91,700	82,729,299	3,403,671
225	86,132,820	82,186,079	9,453	66,449	675,000	-91,458	82,749,650	3,383,169
250	86,132,682	82,181,497	9,010	63,075	750,000	-91,103	82,770,121	3,362,561
275	86,132,560	82,177,823	8,623	60,117	825,000	-90,726	82,791,724	3,340,836
300	86,132,451	82,174,696	8,280	57,497	900,000	-90,231	82,814,153	3,318,297
325	86,132,350	82,171,782	7,972	55,149	975,000	-89,675	82,836,989	3,295,361
350	86,132,261	82,169,572	7,696	53,045	1,050,000	-89,209	82,860,556	3,271,704
375	86,132,177	82,167,360	7,446	51,132	1,125,000	-88,676	82,884,280	3,247,897
400	86,132,100	82,165,210	7,217	49,387	1,200,000	-88,226	82,908,063	3,224,037
425	86,132,029	82,163,436	7,007	47,793	1,275,000	-87,803	82,932,269	3,199,760
450	86,131,962	82,161,728	6,814	46,325	1,350,000	-87,389	82,956,591	3,175,371
475	86,131,901	82,160,458	6,637	44,976	1,425,000	-86,943	82,981,442	3,150,459
500	86,131,844	82,159,123	6,473	43,725	1,500,000	-86,458	83,006,313	3,125,531

produced. In order to properly analyze the overall economic impact we also considered the cost of process equipment whose size does not change with the inclusion of the mass exchanger, as well as the costs and benefits associated with raw materials and products. The Net Annual Income of the process presented a maximum increase of 1.31% with a membrane area of 50 m², while the amount of hydrogen consumed was reduced in a 3.59%. The power required by the recycle compressor showed a significant decrease of 40.08% representing a reduction of 40.08% of the compressor installed cost. These results are promising and could represent a new application of zeolite membranes in the industry. Currently zeolite membranes are very expensive, but in the future the cost of zeolite membranes is expected to decrease by a factor of at least 4¹⁶ and the NAI would rise to 3.66% (and also the cost of energy is expected to increase), making the process alternative with the mass exchanger more interesting. Although these membranes are under development and their use in industry is still small, we hope that this new application motivates its industrial development as countercurrent mass exchangers.

■ ASSOCIATED CONTENT

📄 Supporting Information

For more-interested readers, detailed Tables A1, A2, and A3 are available. Also available are the simulation files of the Hydrar Process (Cyclohexane-Hydrar.bkp) and of the Process with Membrane (Cyclohexane-Membrane.bkp). We provide a file (GPermM.msi) only for Aspen Plus V7.2, which has enclosed a simple custom model for the proposed gaseous mass exchanger equipment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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