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# Hydrogen recovery from the purge stream of a cyclohexane production process using a mass exchange heuristic

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## ABSTRACT

In this paper, we propose a novel hydrogen recovery structure in a cyclohexane production process, arrived at by following a mass exchange heuristic developed in previous works [1,2].

In the cyclohexane production process considered, we explore the effect of process design variables and find the optimal design for a mass exchange between the purge stream and the feed of benzene to the process. We compare our results with a conventional process design lacking hydrogen recovery from the purge, and with a process design which implements a conventional membrane recovery system at the optimum setup of the decision variables. The process with recovery through mass exchange here proposed obtained a respectable 7.12% reduction of hydrogen consumption, resulting in an increase of the plant Net Annual Income of a 4.24% respect to the conventional process design without recovery. These figures are similar to the ones that result from implementing a process design with a conventional membrane recovery system. These results highlight the importance of considering a mass exchange between the process feed and purge stream as an alternative design of the recovery system.

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## Introduction

The design of a new process following the hierarchical procedure by Douglas [3,4] 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, e.g. definition of the input–output structure of the flow sheet, definition of the recycle and separations structure, etc.

The technique for the synthesis of Mass Exchange Networks (MENs) [5–7] dictates mass exchanging between process streams in a counter-current arrangement, as much as possible. This technique needs as input, the list of streams to be integrated, their flows and inlet–outlet concentrations. Therefore, the mass integration methodology is naturally being applied to existing processes, or in the final stage of a new process design once all streams have been generated.

In previous works [1,2,8,9], we proposed and described in detail the use of the concept of Mass Exchange Network as a

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mass exchange heuristic at two levels of Douglas [3,4] hierarchical process design procedure. We considered applying the mass exchange heuristic to a process that involves a reaction between two or more gas-phase reactants, performed at medium or high pressure, which react to form a product and eventually byproducts. Usually, some of the reactant is fed in excess to either expedite or complete the reaction, so that this reactant is found in abundance in the reactor outlet stream, together with the product and some byproduct or any inert component fed together with the other reactants. The reactant added in excess, after separation from the reactor product, is recycled to the reactor inlet, and a purge is extracted from the recycle to prevent accumulation of inert components and/or byproducts.

We proposed to use the mass exchange heuristic at the higher level of the hierarchical design procedure of Douglas [3,4] (after defining the reaction, when deciding the structure of the recycle and separation system). At this level, we can exchange mass between the stream exiting the reactor (rich in a reactant) and a reactor inlet stream (without or with a poor concentration in the same reactant). The reactant in the stream leaving the reactor is at a high partial pressure, while in the stream that feeds the reactor, this reactant has a null or low partial pressure. Thus, we have a considerable gradient of partial pressure to transfer this reactant, even if the stream entering the reactor was already pressurized. The driving force for mass exchange in gas permeation membranes is always the difference in partial pressure of the component of interest across the membrane, but this driving force is provided by the concentration gradient rather than by the trans membrane total pressure. At this level, the heuristic can be stated as “after the reaction is defined, tray integrating streams entering and exiting the reactor (or after a flash separation in our case) to recover the valuable reactant”.

The purge stream is also rich in the reactant added in excess, so we can apply the mass exchange heuristic also at the last design refinement step of the hierarchical design procedure, leading to exchange reactant between the purge stream rich in it, and a reactor inlet stream lean in the same component. At this level, the heuristic can be stated as “once all process streams have been generated, tray to integrate streams entering to the reactor and purge streams exiting the process, to recover the valuable reactant”.

In the process design literature there exist several modified hierarchical procedures to extend the original by Douglas [3,4] to new applications, for example the paper by Douglas [10] to waste minimization, Rossiter and Douglas [11,12] to handle solids operations, Steffens et al. [13] to biotechnology separations, or by Konda et al. [14] to include process control. It is our goal to do the same to include countercurrent mass exchange into the design procedure. However we still lack enough casuistic to support a general new hierarchical procedure.

We successfully applied the mass exchange heuristics to a process for the synthesis of Biodiesel [8], the synthesis of Benzene from Toluene (HDA Process) [1,2], a Cyclohexane production process [15] (in this case at the higher hierarchy level), and an Ammonia synthesis loop [9], resorting to a novel counter-current mass exchanger equipment (a gas permeation membrane module) previously presented [1].

This paper focuses on analyzing the new recycle alternatives generated in a cyclohexane synthesis process, when applying the mass exchange heuristic at the end of the hierarchical design procedure, which leads to integrating streams entering and exiting the process [7]. To model, simulate and optimize the process, as well as to perform various analysis, we resorted to the following software: Aspen Plus V8.2, Aspen Custom Modeler V7.2, Aspen Energy Analyzer V7.2 and Aspen Process Economic Analyzer V7.2.

Following, there is a brief description of the Cyclohexane synthesis process Hydrar. Afterwards we assess different recovery systems: the conventional recovery system design using a gas permeation membrane along with diverse recovery system alternatives arrived at by using the mass exchange heuristic. Next, we analyze the economic impact of adopting the proposed new design and compared it with both conventional process designs, with and without recovery system. Finally, the last section draws the conclusions of this work.

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## Cyclohexane synthesis process

### Overview

To illustrate the application of the mass exchange heuristic at the end of the hierarchical design procedure, we will use the Hydrar Process (Universal Oil Products, U.O.P. now a Honeywell company). In this process [16] the hydrogenation of benzene to cyclohexane is performed in a series of adiabatic reactors under controlled conditions allowing the reaction to occur at a temperature, as low as possible. The reactants are drawn out from each reaction zone, cooled through steam generators, combined with more benzene and sent into the following reaction zone, where this sequence is repeated. There can be many 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 (with their impurities) at a temperature between 163.33 °C and 204.44 °C and a pressure between 6.9 bar and 35 bar are fed to the adiabatic reaction zones where they contact the catalyst. The gases are removed from the reactors at temperatures between 260.00 °C and 315.55 °C, cooled down to temperatures between 163.33 °C 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 reaction exit stream contains cyclohexane, hydrogen and their impurities or inert gases (normally methane and nitrogen from make-up hydrogen). Most of the hydrogen and impurities are separated from the cyclohexane using a partial condenser, followed by a flash that separates the light gases, which are recycled after purging some of this stream, to prevent the accumulation of impurities in the process.

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 respect to benzene from 4:1 to 50:1. In the 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 V8.2 using RK-SOAVE as physical property model [17]. We took the typical configuration of four reactors with Ni/SiO<sub>2</sub> catalyst. To model the reaction kinetics we referred to Keane and Patterson [18], and we used a plug flow reactor model. These authors use the power law, where the energy of activation is 11.4 kcal/mol and the pre-exponential factor is  $4.216 \times 10^{-7}$  kmol/s · kg – cat · Pa<sup>1.2+0.2</sup>. This reaction kinetics is expressed in the equation below.

$$r = P_H^{1.2} P_B^{0.2} \left[ 4.216 \times 10^{-7} \exp\left(\frac{11.4}{RT}\right) \right]$$

The gas inputs to each of the reactors are 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 generators or heat exchangers at the output of the reactors we considered a conservative pressure drop 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 1:1. Fig. 1 shows the flow sheet of this process. In the flow sheet the heat recovery steam generators and the heat exchangers are labeled as heaters or coolers.

### Purge recovery using conventional membrane recovery system

We may add a conventional membrane recovery system to the former process, to recover the hydrogen available in the purge stream. This recovery system is shown in Fig. 2. The purge stream is fed to a membrane module, whose retentate stream is sent to the burner and the permeate recycled to the process through a secondary compressor where it is compressed up to

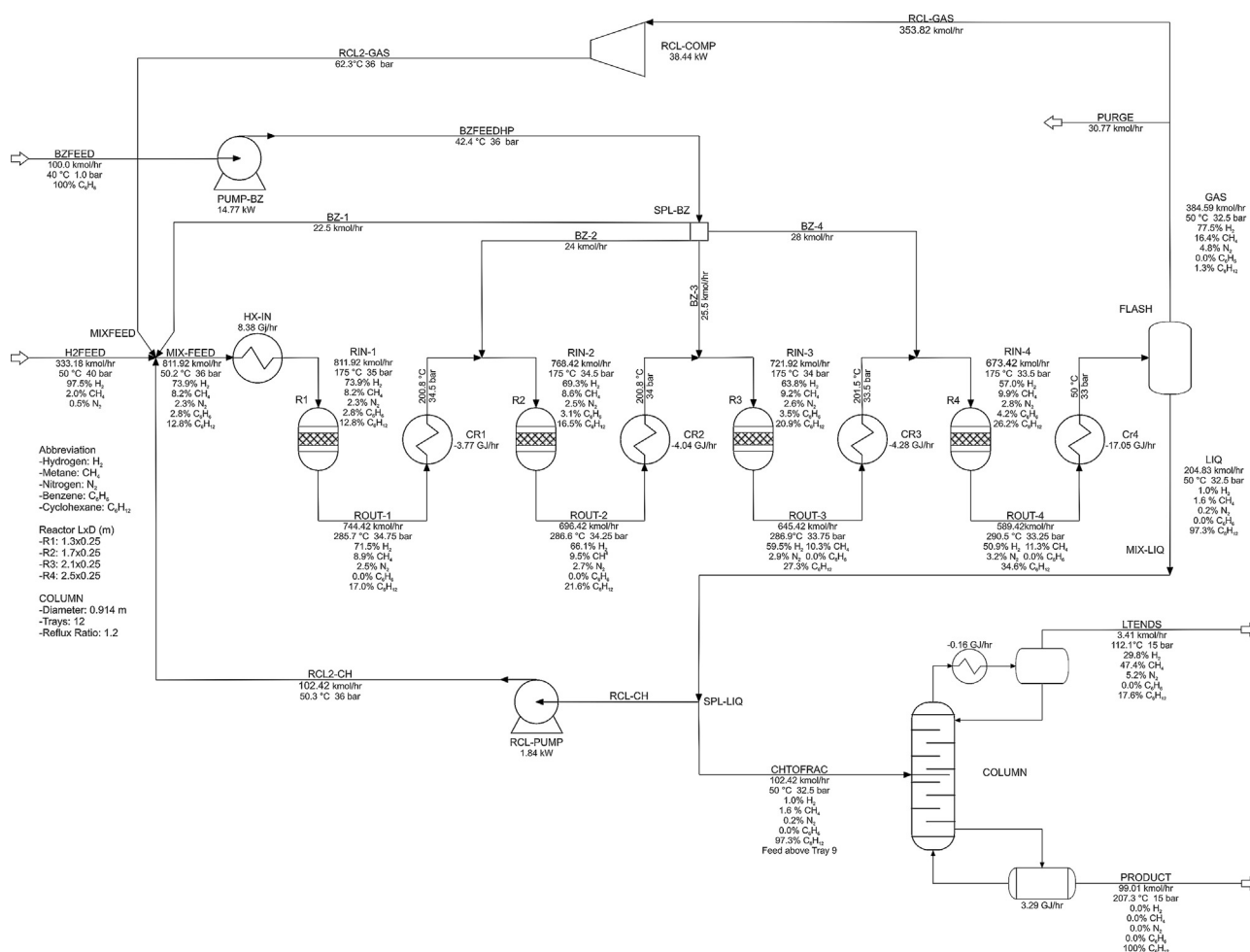


Fig. 1 – Flow sheet of the cyclohexane synthesis process.

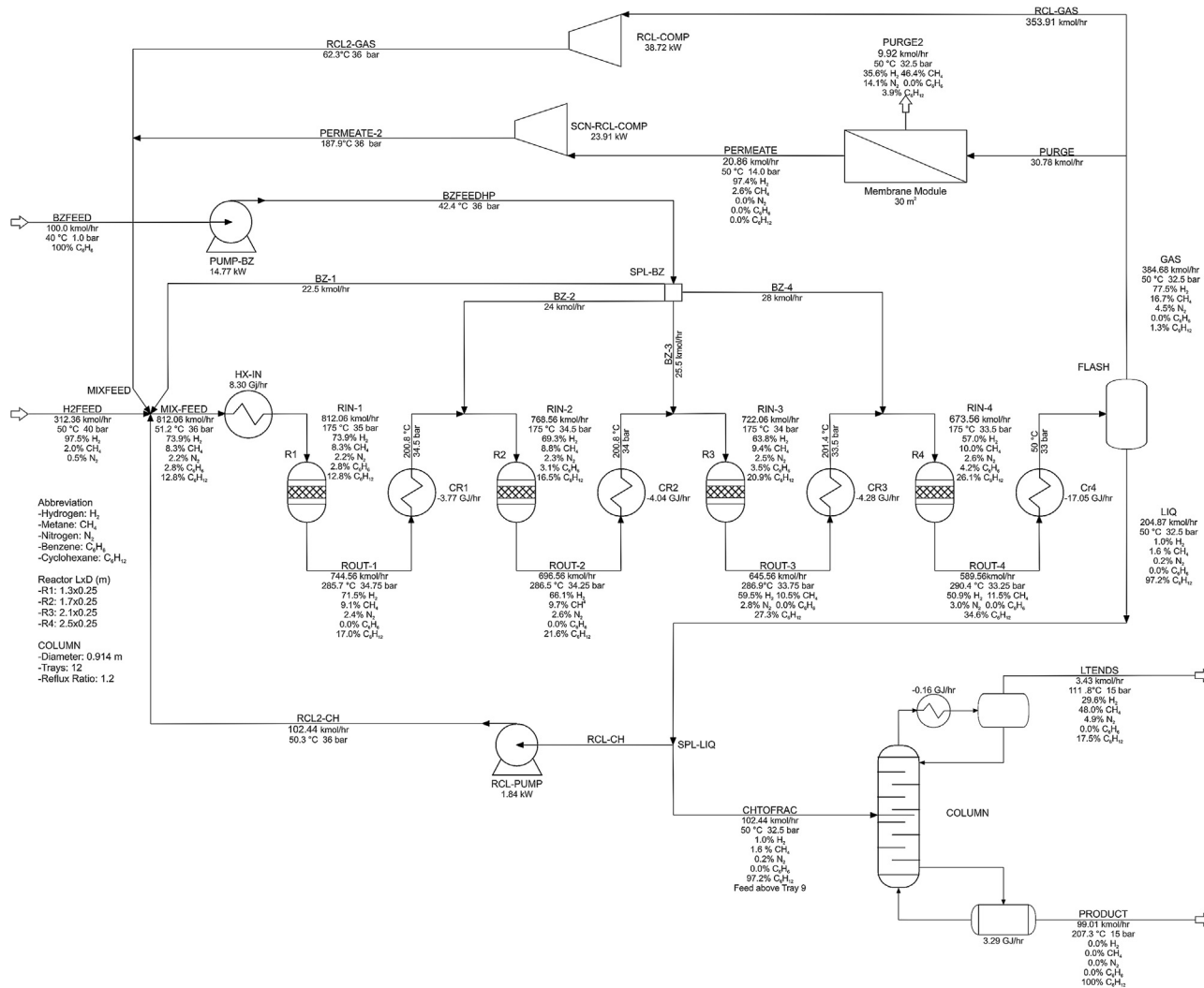


Fig. 2 – Process flow sheet with a conventional recovery system.

the feed pressure. After compression, this stream is mixed with the reactor feeds and the recycles streams. This recovery system does not change the operating conditions of the process, and reduces the amount required of fresh hydrogen feed. To optimize this reduction of hydrogen feed, we may consider varying the fraction of the purge stream, and take it after the recycle compressor to provide a larger driving force for the transfer of hydrogen. In addition, the membrane area and the pressure of permeate stream can be optimized too.

We explored these possible configurations and scanned variables, to find that the optimal design is with the purge stream taken before the compressor and at a ratio of 0.08 of the recycle stream. For this conventional recovery system we considered a polymer type membrane [19] with a permeability of  $0.201 \text{ kmol/m}^2 \cdot \text{bar} \cdot \text{hr}$  and a selectivity of 110 for hydrogen with respect to methane. At the optimal condition the membrane area is  $30 \text{ m}^2$ , operating at 32.5 bar upstream and 14 bar downstream of the membrane. With this configuration we were able to reduce the consumption of hydrogen by  $20.827 \text{ kmol/h}$  (6.25% of the  $333.183 \text{ kmol/h}$ ). The permeate stream is  $20.86 \text{ kmol/h}$  and requires a power of 23.91 kW for the secondary recycle compressor (considering an isentropic

efficiency of 0.72). The purge stream RETENTATE is smaller by  $20.85 \text{ kmol/h}$  than the purge stream prior to incorporating the membrane module and its principal component is methane. This stream is usually disposed as fuel in furnaces or boilers due to its high energy value.

#### Purge recovery using mass exchange heuristic at the end of the hierarchical design procedure

Applying the mass exchange heuristic at the end of the hierarchical design procedure, leads to integrating streams entering and exiting of the process. For the cyclohexane process considered, this leads to placing a mass exchanger between the benzene inlet stream BZFEED (which is free of hydrogen) after preheating, and the purge stream (PURGE) of the process, as shown in Fig. 3. This last stream has a hydrogen mole fraction of 0.775 and a pressure of 32.5 bar, which gives a considerable driving force for exchange of the hydrogen. Another possible alternative is to take the purge stream after the recycle compressor to provide a greater driving force, even though this requires extra compression costs. Furthermore, the purge fraction can be varied. A larger

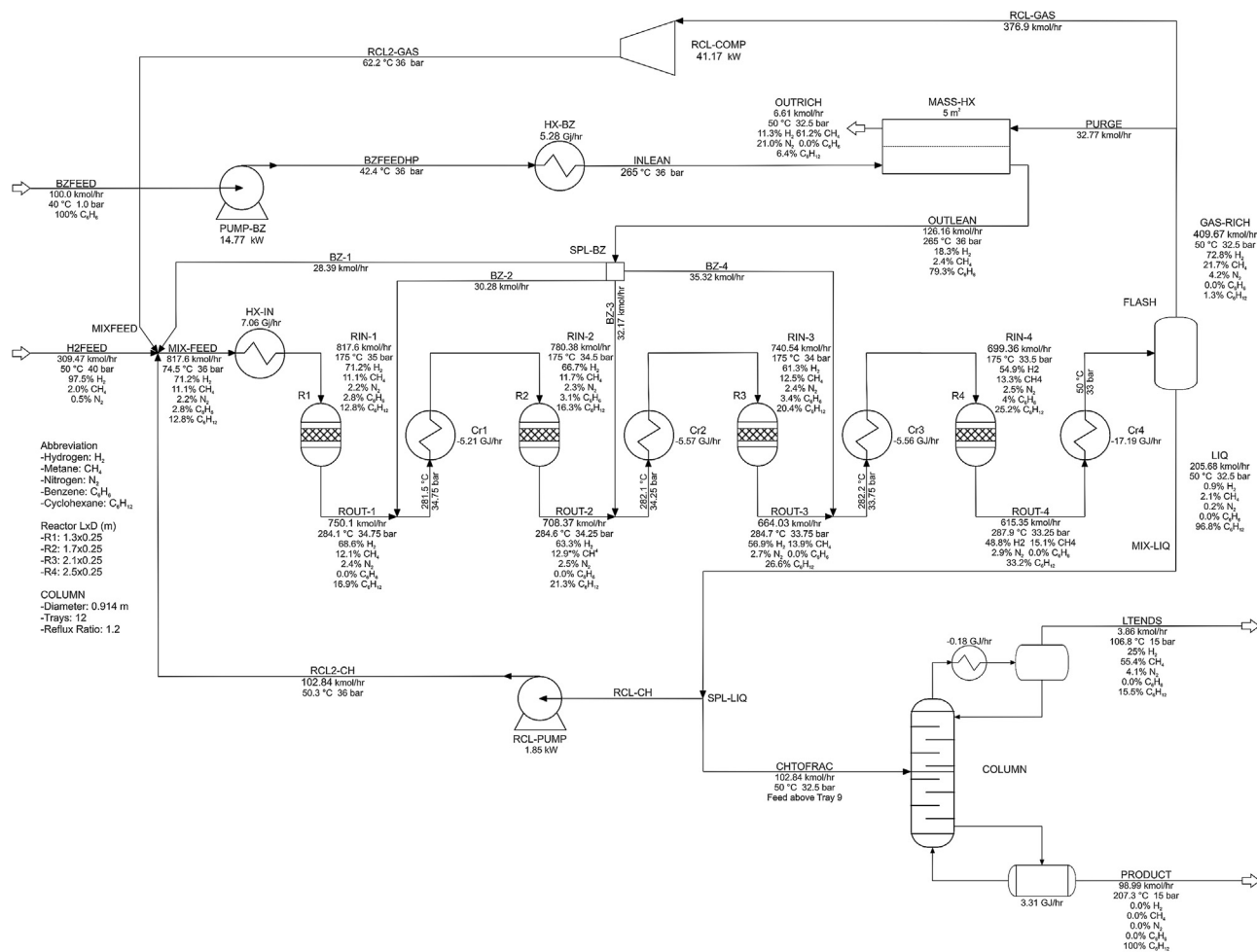


Fig. 3 – Process flow sheet with the inclusion of a mass exchanger.

purge fraction requires more hydrogen feed, reduces the costs associated to the recycle stream compressor and increases the hydrogen available in the purge stream to exchange.

Different types of membranes could be used to exchange hydrogen between the selected streams at these process conditions. Among them are the zeolite with structure MFI as ZSM-5, or with structure CHA as SAPO34. In the present work we assessed both types of membranes, which despite having very different features, may prove to be competitive in a future scenario. The ZSM-5 membrane selected [20] has a permeance for hydrogen of the order of  $1 \times 10^{-6}$  mol/m<sup>2</sup>·Pa·s with an ideal selectivity of pure gases with respect to methane of 7. The SAPO32 membrane selected [21] has a permeance for hydrogen of  $3.9 \times 10^{-8}$  mol/m<sup>2</sup>·Pa·s with an ideal selectivity of pure gases with respect to methane of 32. Table 1 summarizes the characteristic of the zeolites membranes and the polymeric membranes.

By recovering part of the hydrogen from the purge stream, less hydrogen is needed as feed to the process. Thus, to maintain the original reaction conditions without appreciable modifications, we controlled the input stream of hydrogen. Besides hydrogen, the equipment also exchanges methane, as the selectivity of the available membranes is relatively low.

We tested the performance of a hydrogen mass exchanger for both alternatives of taking the purge stream before and after the recycle compressor, while the purge fraction was varied in the range from 0.08 to 0.40 of the recycle stream. Also, we considered the implementation of the mass exchanger in a membrane area range from 0 to 100 m<sup>2</sup> for the ZSM-5 membrane, and from 0 to 1000 m<sup>2</sup> for the SAPO-34 membrane. Above these upper bounds the driving force for hydrogen exchange is minimal and furthermore, the driving force for methane exchange remains high, favoring this undesirable exchange. Figs. 4 and 5 show the amounts of hydrogen and methane transferred in the area ranges and purge ratios analyzed for the two types of membranes, when the purge stream is taken before the recycle compressor.

Table 1 – Characteristic of the membranes.

Membrane type	Hydrogen permeance (mol/m <sup>2</sup> ·Pa·s)	Ideal selectivity respect to methane
Polymeric	$5.583 \times 10^{-7}$	110
ZSM-5	$1 \times 10^{-6}$	7
SAPO-34	$3.9 \times 10^{-8}$	32

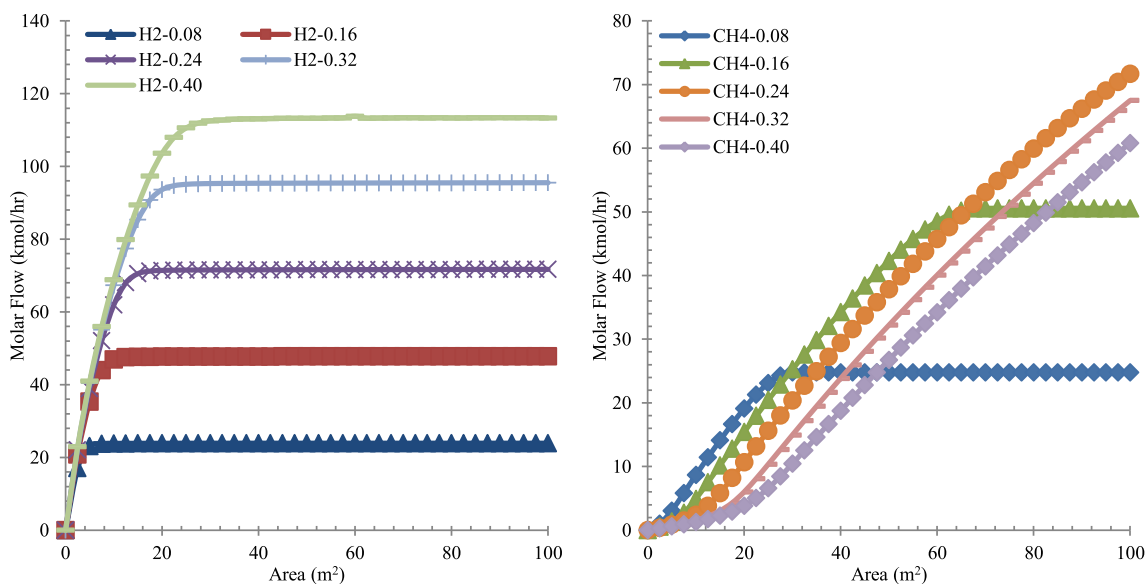


Fig. 4 – Hydrogen and Methane exchanged for Zeolite ZSM-5.

When the purge stream is taken after the recycle compressor, these figures are only slightly different.

For the alternative with the ZSM-5 membrane (which has high permeance and low selectivity) it can be seen that at a very small exchange area almost all the hydrogen available in the purge stream is transferred. When the purge fraction increases, there is also more methane in the purge stream, but its molar fraction decreased. Fig. 4 shows that for a purge fraction of 0.08 almost all the methane is transferred with a relatively low exchange area (an undesired effect because the purge main purpose is to reduce the methane of the recycle). For purge fractions over 0.16, only part of the methane from the purge stream is transferred. It is important to note that neither hydrogen nor methane can be transferred entirely. They are only transferred while the driving force (partial pressure difference across the membrane) is still significant.

For the alternative with the SAPO-34 membrane (which has lower permeance and relatively higher selectivity) it can be seen in Fig. 5 that hydrogen transference requires larger exchange area than with ZSM-5 membranes. Furthermore, note that in the transfer of methane the equilibrium is never reached.

Figs. 6 and 7 display hydrogen fed to the process and the cyclohexane stream produced. For the alternative with the ZSM-5 membrane, the hydrogen feed stream presents a reduction of 29.69% when the purge fraction is of 0.08, and a reduction of 27.34% when the purge fraction is of 0.40. The amount of hydrogen fed is the same for all purge fractions at large enough areas. The cyclohexane produced falls slowly at low exchange areas, and faster at larger exchange areas. This behavior is caused by the undesired accumulation of methane in the synthesis loop at large exchange areas (almost all

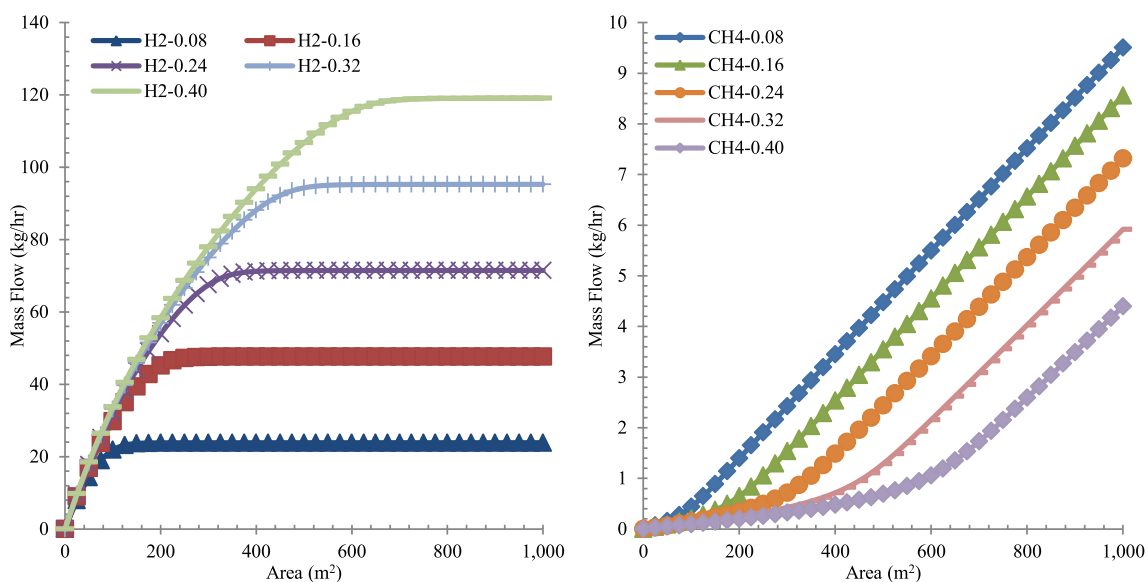


Fig. 5 – Hydrogen and Methane exchanged for Zeolite SAPO-34.

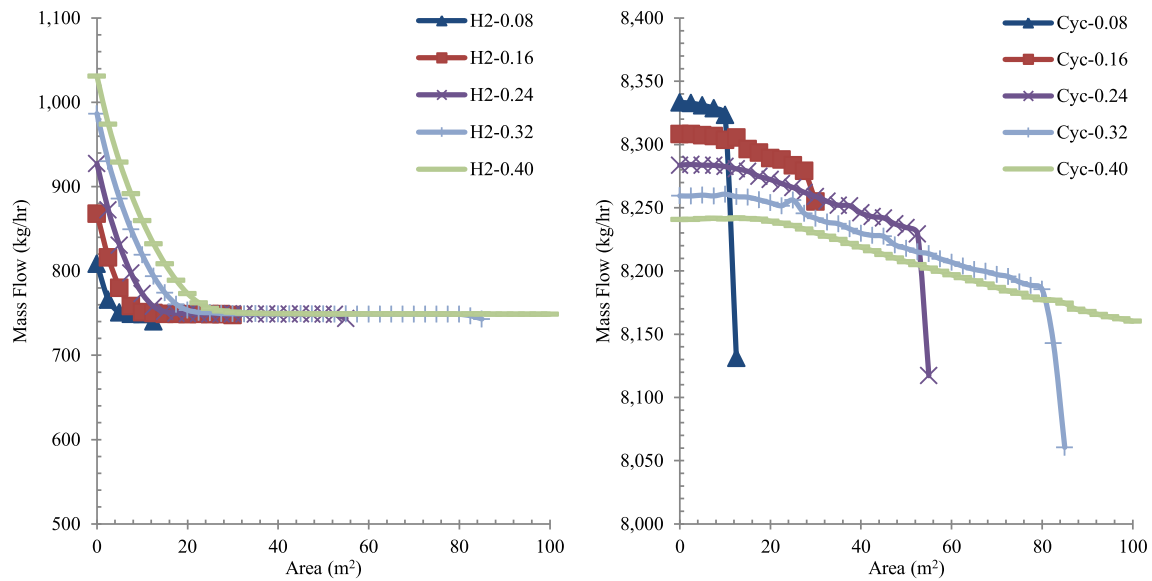


Fig. 6 – Hydrogen feed and cyclohexane produced (ZSM-5).

methane purged is permeated across the membrane due to the low selectivity of the membrane). This accumulation causes that not all the benzene is converted in the reactors (its feed flow rate is being kept constant as a design parameter).

For the alternative with the SAPO-34 membrane the hydrogen exchange is similar as with the ZSM-5 membrane, but the same amounts are reached with larger exchange areas. The cyclohexane product stream undergoes no major variation because methane does not accumulate in the synthesis loop.

Although a detailed analysis of the changes in the process Heat Exchanger Network (HEN) is beyond the scope of this paper, we briefly discuss their variations. Using Aspen Energy Analyzer V7.3 we imported from Aspen Plus V8.3 the data associated with the heat exchanger network.

The Hydrar process mixes the recycled cyclohexane, the recycled gaseous stream, the fresh hydrogen and the benzene fraction which goes to the first reactor. This mixture is not completely in the gaseous state (as it is needed in the reactor) therefore, it is vaporized and heated up to the recommendable reaction temperature 175 °C. In this conventional process flow sheet, before mixing these streams we have a liquid stream of recycled cyclohexane (RCL2-CH) at 50.3 °C, the fraction of liquid benzene feed (BZ-1) at 42.4 °C, the stream of fresh hydrogen (H<sub>2</sub>FEED) at 50 °C and the recycled gaseous stream (RCL2-GAS) at 62.3 °C. After mixing them we have a temperature of 50.2 °C and a vapor fraction of 0.85 (almost all the benzene and cyclohexane are in the liquid phase). This stream needs the addition of 8.38 GJ/h to reach a temperature of 175 °C and a vapor fraction of 1. This energy can be supplied by

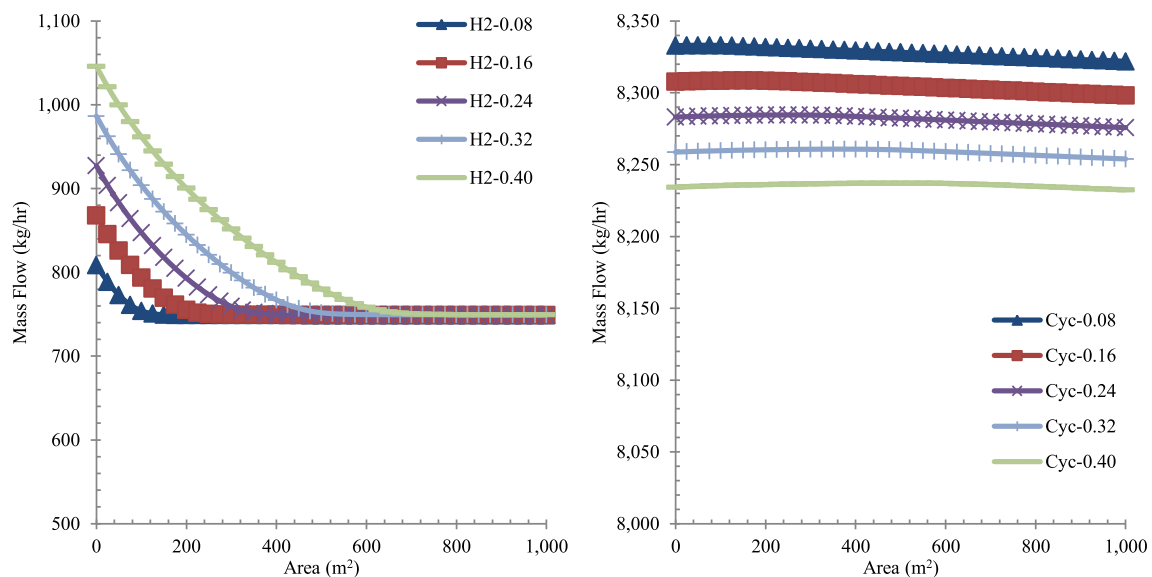


Fig. 7 – Hydrogen feed and cyclohexane produced (SAPO-34).

the steam generated in the process. The streams exiting the reactors are in the order of 290 °C and must be cooled to 175 °C before being sent to the next reactor. Considering the outlet stream of the first reactor at 285.7 °C, it is cooled in a Heat Recovery Steam Generator (HRSG) up to 200 °C. The rest of the cooling down to 175 °C is achieved by the addition of the second fraction of benzene feed. This gets the liquid benzene being vaporized, but losing 0.24 GJ/hr which could be used in the generation of steam. This also happens in the other HRSGs of the process. Overall, in the conventional process, there is no need to add energy to vaporize 3/4 of the benzene, but some of the energy available in the process to generate steam is lost.

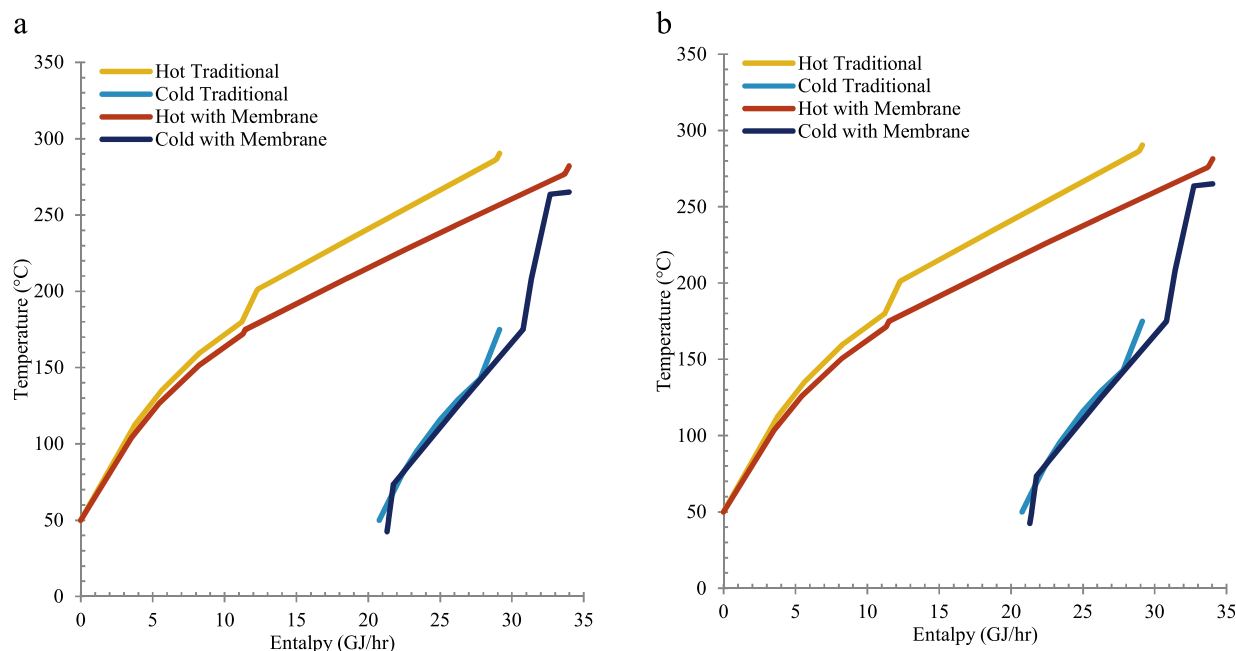
The processes with the membrane mass exchanger cannot generate the steam quality necessary for using in the evaporation of benzene. Fig. 8a shows the composite curves of the Hot and Cold streams (excluding the distillation column) of the conventional process, compared with the processes with ZSM-5 membranes, while Fig. 8b shows the composite curves of the conventional process, compared with the processes with SAPO-34 membranes. From these Figures it can be seen that the curves differ mainly in the upper-right corner. The composite curves for the conventional process with conventional membrane recovery system are similar to the curves for the conventional process and are not plotted. As the cold composite curves are still below the hot composite curves, it is possible to apply the HEN synthesis methodology to find a network that provides the energy required (at the appropriate temperatures) for the evaporation of benzene. Furthermore, part of the energy supplied for this evaporation, can be recovered by generating some extra steam from the streams exiting the reactors. Overall, the process with membrane exchanger 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.

From these Figures it is noted that the amounts of heat to be exchanged and temperature levels are not significantly altered.

In the simulations of the Process Flow Diagrams (PFD) in Aspen Plus V8.2, the HRSGs and all the Heat Exchangers are modeled as heaters or coolers, which does not affect the operating conditions of the process. Then the data from these processes are exported to Aspen Energy Analyzer V7.2 to generate a network of HRSGs and Heat Exchangers. We can find structures for the HEN to provide the heat required for evaporation of benzene without resorting to Fired Heater or an Electrical Source. We build networks for these processes and analyzed (without exhaustively finding the optimal HEN) the costs of the networks for the conventional process and for the processes with membranes. For this we used all default values of Aspen Energy Analyzer V7.2 for the costs of equipments, services and other parameters automatically provided (such as the heat transfer coefficients for gas or liquid phase). The cost of these heat exchange networks is included in the economic analysis to find the most convenient process alternative.

### Economic analysis

The main benefit of using the mass exchange heuristic at the end of the process design procedure with the inclusion of a counter-current mass exchanger is a significant reduction in the amount of hydrogen required. To compare the performance of this approach against a conventional membrane recovery system, we compared the Net Annual Income (NAI) of these alternatives. NAI are computed as the difference between Total Annual Income (TAI) from the sale of cyclohexane plus the purge stream, and the Total Annual Cost (TAC) of the main process units.



**Fig. 8 – (a) Comparison of the Composite Curves for the Process with the ZSM-5 membrane. (b) Comparison of the Composite Curves for the Process with the SAPO-34 membrane.**



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, and others. The cost of these items was determined in previous work using 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 compressors, the membrane unit and the steam generators with the streams exiting the reactors.

We consider centrifugal compressors driven by electric motors and find the installation cost using the correlations in Turton [22]. To compute the energy consumed by the compressors, we consider an electrical to mechanical conversion efficiency of 0.9 and an electric energy cost of US\$0.07 per kW hr. For the material streams, we take the following prices [23]: hydrogen, 0.5058 U.S.\$/kg; benzene, 1.266 U.S.\$/kg; Cyclohexane 1.292 U.S.\$/kg and Purge 0.010 U.S.\$/kg. For the installed cost of the ceramic zeolite membrane modules we resorted to Babita et al. [24] who report US\$3000 per m<sup>2</sup>. For the installed cost of the polymeric membrane modules we took US\$550 per m<sup>2</sup> [19]. The capital costs were annualized with a Capital Charge Factor of 0.351 and considered that the plant operates 8000 h/yr.

Fig. 9a and b plot the variations of the Net Annual Income for different purge fractions in the range of analyzed mass exchange area for the ZSM-5 and SAPO-34 membranes.

For zeolite membrane ZSM-5 the optimum NAI U.S. \$3,595,132 is reached with an area of only 5 m<sup>2</sup> with a purge fraction of 0.08. The hydrogen feed is reduced by 7.12%. The low selectivity of this membrane (in the medium and high range exchange area) produces an increase of methane in the synthesis process, decreasing the amount of cyclohexane produced. For the alternative SAPO-34 membranes the

optimal NAI U.S. \$3,508,337 is reached with an area of 100 m<sup>2</sup> with a purge fraction of 0.08. The hydrogen feed is reduced by 6.74%. This alternative has a lower reduction of hydrogen feed and it is reached at a larger exchange area, with a slightly lower NAI.

Considering that for the ZSM-5 membranes the optimum is reached with only 5 m<sup>2</sup> of exchange area, the cost the membrane has a low influence in the location of the optimum. Otherwise, for SAPO-34 membranes, the optimum is reached at 100 m<sup>2</sup>, where the cost of the membrane has a significant influence on the locus of the optimal point. If in a future scenario, the cost of zeolite membranes is lower, this would not significantly improve the optimal when using the ZSM-5 membranes. Instead, this would represent a significant improvement for the optimal alternative when using SAPO-34 membranes. For example, if we assume that the future industrialization of these membranes will produce a reduction in the cost 4:1, then the alternative with SAPO-34 membrane, would have almost the same cost reduction than the alternative with ZSM-5 membrane.

On the other hand, when comparing with the conventional membrane recovery system we notice that the here proposed alternative with ZSM-5 membranes presents a much lower cost of installation, whereas the alternative with SAPO-34 membranes presents a larger cost of installation.

If we compare the reduction in hydrogen feed to the process in the alternative with ZSM-5 membranes with the conventional membrane recovery system, the reduction is greater (7.12% versus 6.25%). Additionally, it is more efficient energetically, as it requires no compression energy to reuse the hydrogen recovered.

Table 2 shows a comparison of the most important parameters considered for the alternatives studied.

We also analyzed all the alternatives taking the purge after the recycle compressor (which contradict traditional process

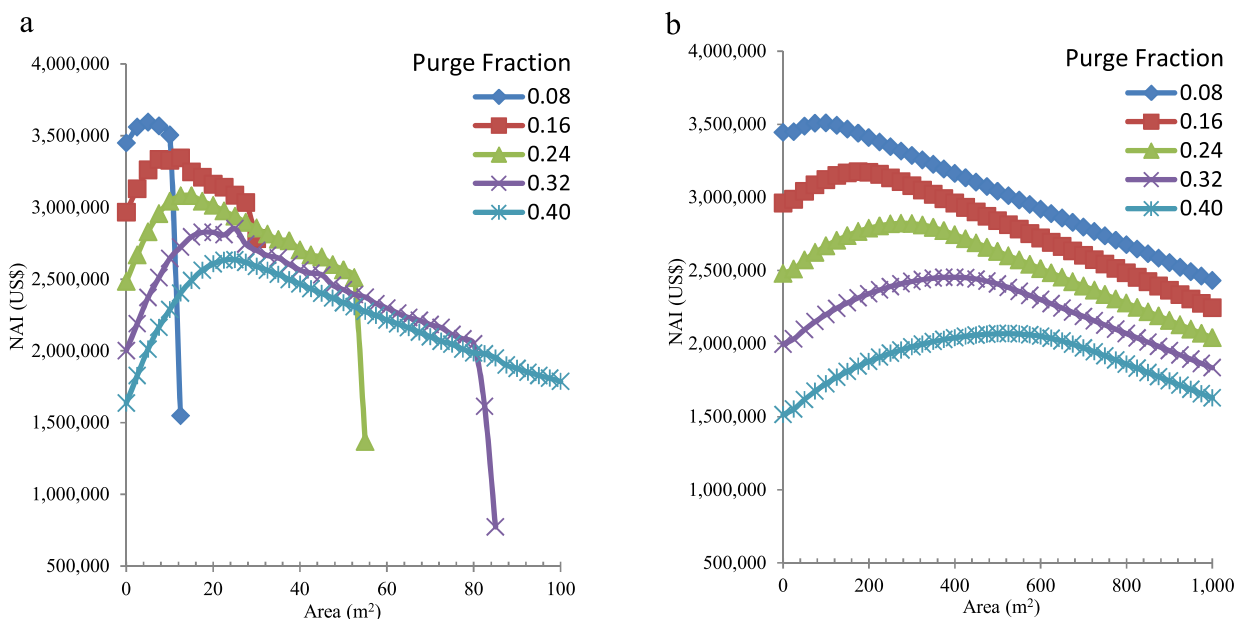


Fig. 9 – a Net Annual Income as a function of ZSM-5 Membrane Area. b Net Annual Income as a function of SAPO-34 Membrane Area.

**Table 2 – Comparison of alternatives.**

	Alternative without membrane recovery system	Alternative with conventional membrane recovery system	Alternative with ZSM-5 membrane	Alternative with SAPO-34 membrane
Membrane area (m <sup>2</sup> )	–	30	5	100
Reduction in hydrogen feed (kmol/hr)	–	20.827	23.703	22.455
reduction in per cent (%)	–	6.25	7.12	6.74
Savings in hydrogen feed (US\$/yr)	–	204,462.55	138,707.39	220,492.41
Electric energy cost (US\$/yr)	–	14,877.80	–	–
Capital Costs				
membrane (US\$)	–	16,500.00	15,000.00	300,000.00
secondary recycle compressor (US\$)	–	107,571.09	–	–
Net Annual Income (US\$)	3,449,046.68	3,591,119.13	3,595,131.79	3,508,337.11
Increase of the Net Annual Income (%)	–	4.12	4.24	1.72

design rules, because they spend an additional compression cost on a waste stream), because they increase the driving force at the membrane modules. But these process alternatives have a slightly lower NAI.

In a previous work [15] on the Cyclohexane process, we used the mass exchange heuristic at the higher hierarchy, reaching a reduction of 3.59% in hydrogen consumption. Moreover, it produced an important reduction of 40% of the costs associated with the recycle compressor. Applying the mass exchange heuristic at an earlier stage in the hierarchical design procedure, leads to major changes in the process, significantly reduces the recycle compressor cost (and energy for operating it), reduces hydrogen feed, and changes the heat exchange network. On the other hand, applying the mass exchange heuristic at a final stage in the hierarchical procedure, produces minor changes in the process (principally in the heat exchange network). This is an advantage if the purpose of the study is to improve an existing process. As generally the cyclohexane plants are integrated to an industrial complex (or refinery), the changes in the heat exchange network can be easily handled.

## Conclusions

In the cyclohexane synthesis process analyzed in this paper, we applied the mass exchange heuristic at the end of the hierarchical design procedure by Douglas [3,4], once all process streams have been generated, and as a final design refinement step only before heat integration. Applying this heuristic, we 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 produced at the optimum point. The hydrogen consumption was reduced by 7.12%, thereby improving the environmental performance of the process, concerning raw materials usage. In order to properly analyze the overall economic impact we compare the Net Annual Income of the alternatives studied. The Net Annual Income of the process with ZSM-5 membrane was optimal, presenting a maximal increase of 4.24% with a membrane area of 5 m<sup>2</sup> with respect to the conventional design process and slightly larger than that of the conventional membrane recovery system. These results are promising and represent a new application of zeolite membranes as

countercurrent mass exchangers in the industry with intensive use of hydrogen.

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