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Hydrogen recovery from the purge stream of an HDA process using the concept of Mass Exchange Networks

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ABSTRACT

In this paper we use the concept of Mass Exchange Networks to design the hydrogen recovery from the purge stream of an HDA Process by implementing a recently proposed counter current gas permeation equipment to exchange hydrogen between the purge and the toluene feed to the process. This design would correspond to the final design refinement step in the Douglas [1,2] hierarchical process design procedure, proposed by Fischer and Iribarren [3]. The goal of this design is recovering part of the hydrogen available in the purge stream, and results in a process alternative different from other flow sheet recently proposed by Bouton and Luyben [4], also resorting to gas permeation membrane units, but in a traditional arrangement. Two different types of available zeolite ceramic membranes were studied, of different permeability and selectivity. The here proposed mass exchange design recovers a similar amount of hydrogen as the process alternative proposed by Bouton and Luyben [4] who use a less expensive type of polymeric membrane, but need a compressor to recycle the permeate stream because they use transmembrane pressure as the driving force. The here proposed design at actual cost of zeolite membranes allows an 153.9% increase of the Net Annual Savings with respect to the pressure driven membrane system when using the less selective ceramic membrane, while this figure descends to a 32.61% when using the most selective (which is also the most expensive alternative).

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1. Introduction

The design of a new process following the hierarchical procedure by Douglas [1,2] consists in generating increasingly more detailed versions of the process, starting from a few number of process blocks (e.g. reaction, separations) interconnected by process streams. The design procedure progressively adds detail guided by heuristics, which recommend among the options available at each stage of the design (e.g. recycle of streams, alternative unit operations). At the end of

the procedure the process streams defined in previous levels are heat integrated.

On the other hand, the technique for Mass Exchange Networks (MEN) synthesis by El-Halwagi and Manousiouthakis [5], El-Halwagi [6,7] dictates mass exchanging between process streams in a (as much as possible) counter current arrangement. This technique takes as input information, the list of streams to be integrated: their flows and inlet-outlet concentrations.

Fischer and Iribarren [3] propose to apply the concept of MEN at two levels of the Douglas [1,2] hierarchical process

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design procedure. First at an earlier stage, just after the reaction is defined. If the reaction requires operating conditions with components in excess which must be removed after the reactor, the concept of MEN is used as an additional heuristic rule (in competence with the other Douglas heuristics): “Explore the implementation of a Mass Exchanger between the streams exiting and entering the reactor”.

And second, at the end of the hierarchical design procedure, once all process streams have been generated, as a final design refinement step, only before the heat integration (because this step still generates new process streams, liable to be heat integrated).

Applying the concept of MEN at an early stage strongly modifies the separations and recycling structure of the process. Fischer and Iribarren [8] explored this approach on the HDA Process for producing benzene from toluene, using a proposed counter current gas permeation equipment to exchange hydrogen from the reactor outlet stream (the reaction requires an excess of hydrogen that must be removed afterward) and the toluene inlet stream. This new Mass Exchanger did not completely removed the original separation and recycle structure of Douglas [1,2] process, but strongly reduced its size and cost, and rendered an interesting reduction of the overall hydrogen consumption of the process. Also, this approach is explored in an Ammonia Synthesis Loop [9] and in a Cyclohexane Synthesis Process [10].

Applying the concept of MEN at the end of the design procedure, or to an existing process, requires restricting the integration to streams entering and exiting the process, because if internal streams were integrated this could strongly change the process itself and besides, the input information to the MENs synthesis problem that one is trying to solve. Mass integration of process streams at this level of the design procedure (and restricted to streams entering and exiting the process) are deemed not to affect the operation conditions of the process.

In this paper we use the concept of MEN as a last refinement step of the traditional HDA Process, designing the hydrogen recovery from the purge stream by implementing the counter current gas permeation equipment recently proposed by Fischer and Iribarren [8] to exchange hydrogen between the purge and the toluene feed to the process. The goal of this design is recovering part of the hydrogen available in the purge stream, and results in a process alternative different from other recently proposed by Bouton and Luyben [4] also resorting to gas permeation membrane units, but to a different type of membranes and in a traditional arrangement. Both approaches are compared.

Following there is a section that formally presents the general problem to which we apply the concept of MEN in the last stage of the process design procedure, and compare it with the traditional purge recovery problem. Next, we apply the proposed approach to the original HDA Process by Douglas [1,2] and analyze the pros and cons of implementing a counter current mass exchanger resorting to two different types of available zeolite ceramic membranes (of different permeability and selectivity), comparing the results with the approach reported by Bouton and Luyben [4]. Finally, the last section draws the conclusions of this work.

2. The general problem that we are approaching

Consider a process that involves a reaction between two or more gas-phase reactants (suppose component A and B), performed at medium or high pressure, which react to form a product (suppose component C) and eventually byproducts. Usually, some of the reactant (suppose component B) 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 reactants. The reactant added in excess, after separation from the product, is recycled to the reactor, and a purge is extracted from the recycle to prevent accumulation of inert components and/or byproducts. An outline of such a process is shown in Fig. 1a.

The purge stream is rich in the reactant added in excess, so in case that this reactant is valuable, systems are designed to recover this component from the purge stream. These systems include gas separation unit operations e.g. scrubbing, adsorption, molecular sieves, and more recently, gas permeation membrane units as the gas separation operation. Gas separation membranes often operate with an important transmembrane pressure difference of 30 bar or higher Pabby et al. [11], Yampolskii and Freeman [12]. These systems are typically designed to take advantage of the medium or high

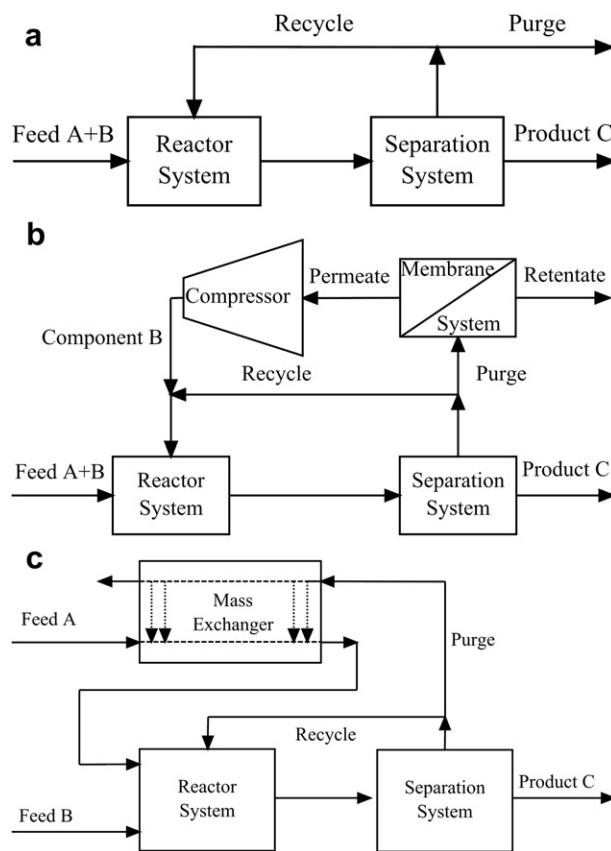


Fig. 1 – (a) Case study. (b) Traditional membrane recovery system. (c) Purge recovery applying the concept of MEN as a final design refinement.

pressure of the stream rich in the component to be recovered, resulting in a low pressure permeate stream richer in this component. The driving force for mass transfer through the membrane is the difference in partial pressure of this component, enhanced by a low total pressure in the permeate side. The permeate stream (rich in the recovered component B) ought to be recompressed to the reactor pressure. Fig. 1b shows the general structure of a recovery system like the one just described, using membranes to perform the separation. In this type of recovery system, the cost of the compression equipment is important, even larger than the cost of the membrane modules that actually perform the separation.

Applying the concept of MEN as a last design refinement step to the process depicted in Fig. 1a, leads to exchange component B between the purge stream rich in this component (that we want to recover and recycle to the reactor), and a reactor inlet stream lean in the same component (the feed of component A), in a counter current arrangement as shown in Fig. 1c. 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. In Fig. 1c this driving force is provided by the concentration gradient rather than by the transmembrane total pressure difference as is the case in Fig. 1b. Eventually we may have a considerable partial pressure gradient of the component we wish to exchange, without resorting to any compressor.

Not all of the component of interest present in the rich stream can be transferred, the limit being that its partial pressure be equal on both sides of the membrane. Depending on the process at hand, significant amounts of the desired component could be recovered without a compressor and the rest resorting to the traditional pressure driven separation membranes.

Simulation of the counter current gas permeation mass exchanger required building an ad hoc module, because it has an extra inlet stream and depending on the concentrations on both sides of the membrane, the flux of some components may be toward the opposite side of the membrane. The module to perform this exchange is described in detail in Fischer and Iribarren [8] and was developed in Aspen Custom Modeler V7.2 to be used in Aspen Plus V7.2 to simulate the mass exchange of hydrogen in the recycle and separation system of the HDA Process.

3. The HDA process

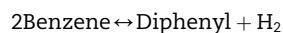
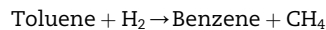
3.1. Overview

To illustrate the new process alternative generated when implementing the concept of MEN at the end of the design, we use the well-known process HDA (hydrodealkylation of toluene to benzene) by Douglas [1,2]. To assess the steady-state process alternatives generated we use Aspen Plus V7.3 with Peng Robinson equation of state as the physical property model. We also used Aspen Energy Analyzer Aspen V7.3 and Aspen Process Economic Analyzer V7.3 in this paper.

This traditional process designed by Douglas [1,2], before heat integration which is the last level of decisions in the

hierarchy, is presented in Fig. 2. The most relevant streams for a production of 125 kmol/h of benzene are presented in Table 1.

The reactions of interest are:



The reaction is homogenous and takes place in the range of 621–667 °C (below this temperature range the rate of reaction is too low and above, hydrocracking reactions are detrimental) and a pressure ca. 35 atm. An excess of hydrogen (5:1 minimum) is necessary to prevent coking at the reactor. The gas leaving the reactor is quickly quenched to 621 °C to prevent coking in the next heat exchanger. The fresh feed streams of toluene and hydrogen are heated and mixed with the recycle stream before being fed into the reactor. The stream exiting the reactor contains hydrogen, methane, benzene, toluene, and diphenyl. Most of the hydrogen and methane are separated from the aromatics 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 methane (which is an impurity of hydrogen feed and also produced by the reaction) in the process. Some of the liquid stream leaving the flash is used to quench the hot gases leaving the reactor. The remaining liquid stream goes through a distillation train. Because not all of the hydrogen and methane could be separated by the flash, they are removed in a stabilizer distillation column. Benzene is separated in the second distillation column, and the third column separates toluene from diphenyl.

3.2. Traditional membrane recovery system

Bouton and Luyben [4] proposed a membrane system that can be added to the traditional process of Douglas [1,2] to recover the hydrogen available in the purge stream. This membrane system does not change the operating conditions of the process and reduces the amount of fresh hydrogen feed. In this alternative Bouton and Luyben [4] take the purge after the compressor, as is shown in Fig. 3.

They use a polymer type membrane with a permeance of 0.201 kmol/m² bar h and a selectivity of 110 for hydrogen with respect to methane. They optimized the recovery system as regards the membrane area and the pressure downstream of the membrane, while maintaining constant the amount of methane purged by varying the ratio of purge to recycle streams.

They found optimal economic conditions with a membrane area of 229 m², operating at 41.85 bar upstream and 8.84 bar downstream of the membrane. With this configuration they were able to reduce the consumption of hydrogen in 77.04 kmol/h. The permeate stream is 95.9 kmol/h and requires a power of 100.3 kW and 85.6 kW for the secondary recirculation compressors (considering an isentropic efficiency of 0.7). This alternative requires a 0.22% increase of toluene feed to keep constant the production of benzene. The purge stream RETENTATE is smaller in 76.60 kmol/h than the purge stream prior to incorporation of the membranes and its principal component (85.9%) is methane. This stream is normally used as fuel in furnaces or boilers due to its high energy value.

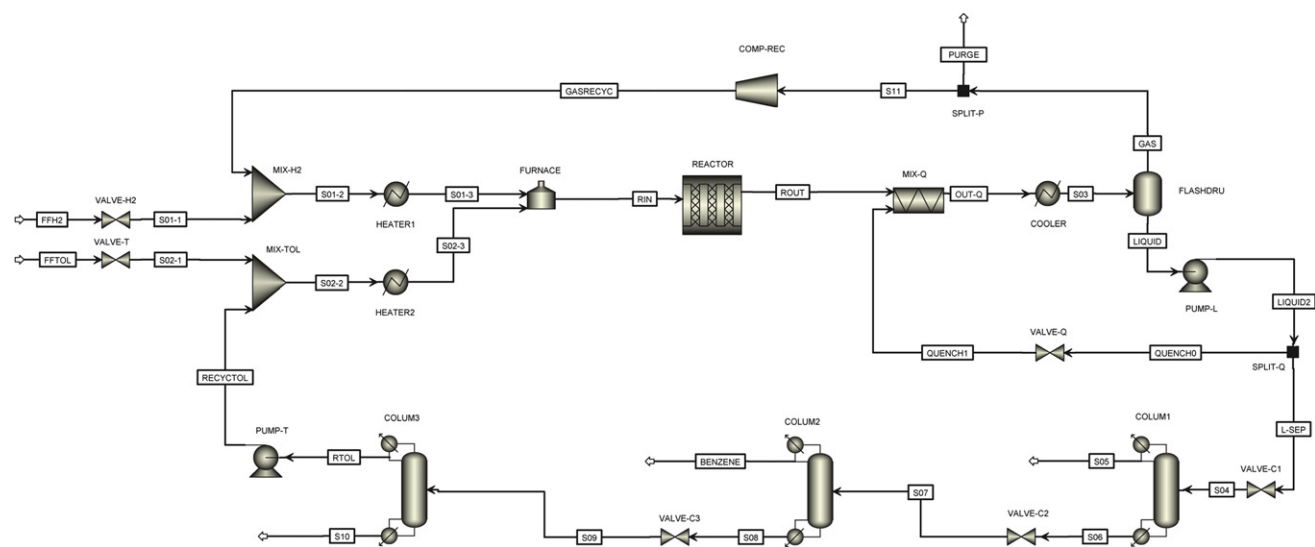


Fig. 2 – HDA process flowsheet by Douglas.

3.3. Purge recovery utilizing the concept of MEN at the end of the design

Designing the purge recovery system resorting to the concept of MEN as a final stage of the process design, and restricting the integration to streams entering and exiting the process, we take as the hydrogen rich stream the process purge heated to 325 °C and as the hydrogen lean stream, the feed of toluene to the process heated to 325 °C. Fig. 4 shows the flow sheet of the process, with the inclusion of the mass exchanger between the selected streams which takes the purge after the compressor as did Bouton and Luyben [4], so we can compare our results directly with their alternative.

Slight changes will be required in the configuration of the heat exchange network to operate at the selected temperatures. Fig. 4 shows the addition of three heat exchangers (HEATER2,

HEATER3 and HEATER4), which can be accommodated by the final heat exchange network synthesis step, since there are no important changes in the initial and final temperature conditions nor in the heats exchanged.

To analyze the performance of this configuration we selected two different types of zeolite ceramic membranes that can operate at these process conditions. One is the ZSM-5 zeolite with MFI structure. Welk et al. [13] reported a membrane ZSM-5 having a permeance for hydrogen of the order of 1×10^{-6} mol/m² Pa s and a selectivity of 7 with respect to methane. The other selected membrane is a SAPO-34 zeolite with structure CHA for which Li et al. [14] reported a permeance of 3.9×10^{-8} mol/m² Pa s for hydrogen and a selectivity of 32 with respect to methane.

These membranes are still being developed and there are large variations in their performance (permeability and

Table 1 – Streams data in Douglas HDA flowsheet.

	FFH2	FFTOL	RECYCTOL	RIN	ROUT	OUT-Q	LIQUID	L-SEP	GAS	PURGE	GASRECYC	BENZENE
Temperature (°C)	30.00	30.00	146.60	621.10	667.70	621.40	48.90	49.40	48.90	48.90	74.40	105.60
Pressure (bar)	43.06	43.06	41.80	36.68	36.68	35.57	33.44	38.91	33.44	33.44	41.85	2.07
Flowrates (kmol/h)	232.23	135.04	31.50	2081.31	2081.31	2134.45	221.61	168.47	1912.84	230.31	1682.53	125.00
Flowrates (kmol/h)												
H ₂	225.27	0.00	0.00	906.20	774.92	775.14	1.00	0.76	774.14	93.21	680.93	0.00
CH ₄	6.97	0.00	0.00	986.81	1121.43	1123.80	9.84	7.48	1113.96	134.12	979.84	0.00
BENZENE	0.00	0.00	0.48	20.46	148.40	188.08	165.37	125.71	22.71	2.74	19.98	124.97
TOLUENE	0.00	135.04	30.96	167.78	33.16	42.96	40.93	31.12	2.02	0.24	1.78	0.03
DIPHENYL	0.00	0.00	0.06	0.06	3.40	4.48	4.47	3.40	0.00	0.00	0.00	0.00
Mole Frac												
H ₂	0.9700	0.0000	0.0000	0.4350	0.3720	0.3630	0.0050	0.0050	0.4050	0.4050	0.4050	0.0000
CH ₄	0.0300	0.0000	0.0000	0.4740	0.5390	0.5270	0.0440	0.0440	0.5820	0.5820	0.5820	0.0000
BENZENE	0.0000	0.0000	0.0150	0.0100	0.0710	0.0880	0.7460	0.7460	0.0120	0.0120	0.0120	1.0000
TOLUENE	0.0000	1.0000	0.9830	0.0810	0.0160	0.0200	0.1850	0.1850	0.0010	0.0010	0.0010	0.0000
DIPHENYL	0.0000	0.0000	0.0020	0.0000	0.0020	0.0020	0.0200	0.0200	0.0000	0.0000	0.0000	0.0000

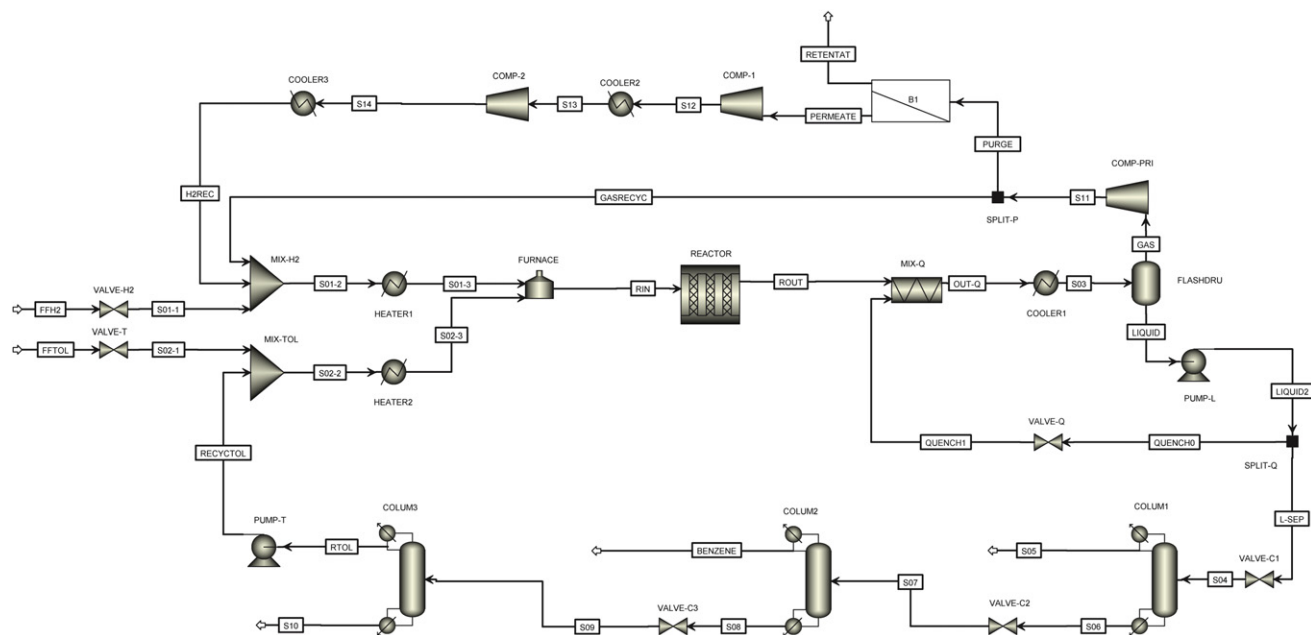


Fig. 3 – HDA flowsheet proposed by Bouton and Luyben.

selectivity) depending on the methods to produce them and subsequent treatments. We use these literature reported pure gases permeances and selectivities as an approximation to the mass exchange performance that can be expected if implemented in the process example studied here.

By recovering part of the hydrogen from the purge stream, less hydrogen is needed to be fed to the process. Thus, to maintain the original operating conditions without appreciable modifications, we controlled the input streams of both hydrogen and toluene fresh feeds. Besides hydrogen exchange, the equipment also exchanges methane, as the selectivity of the membranes used is relatively low.

We assessed the implementation of the mass exchanger in a membrane area range from 0 to 100 m² for the ZSM-5 membrane, and from 0 to 1.000 m² 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 thereof.

Methane also acts as a heat carrier, so its amount present in the recycle must be controlled too. This is achieved by slightly increasing the purge to recycle fraction, sending a larger purge stream to the mass exchanger. For larger areas of exchange, more methane permeates together with the

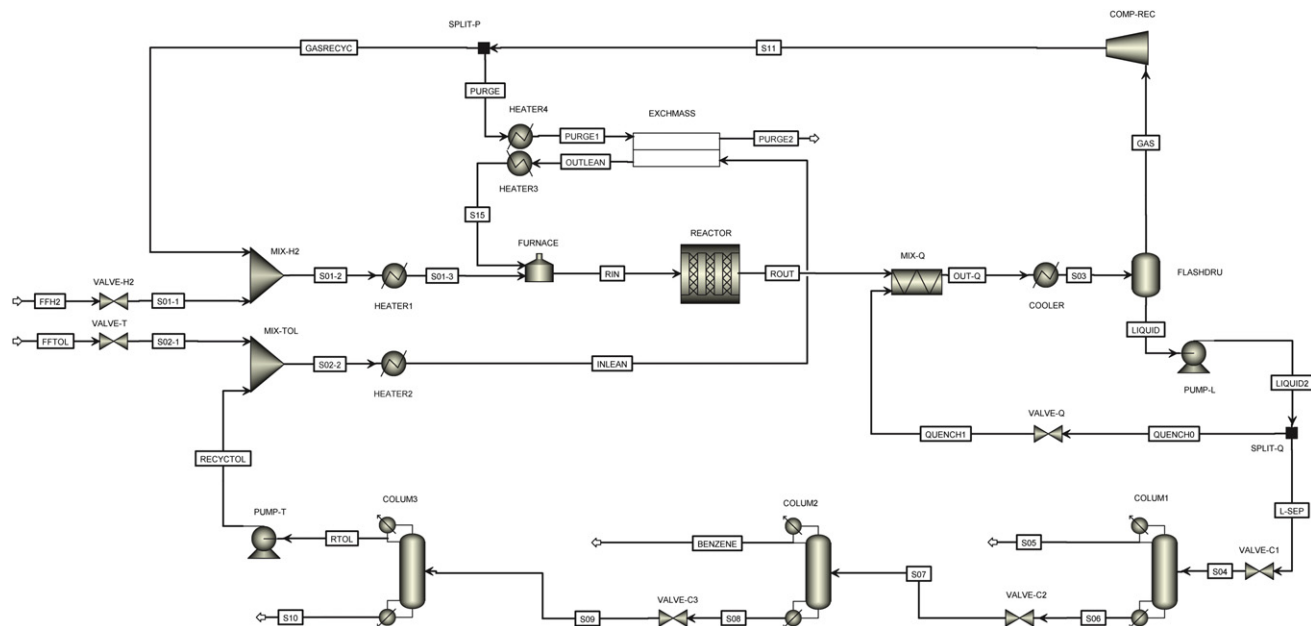


Fig. 4 – HDA flowsheet by Douglas with the inclusion of the mass exchanger.

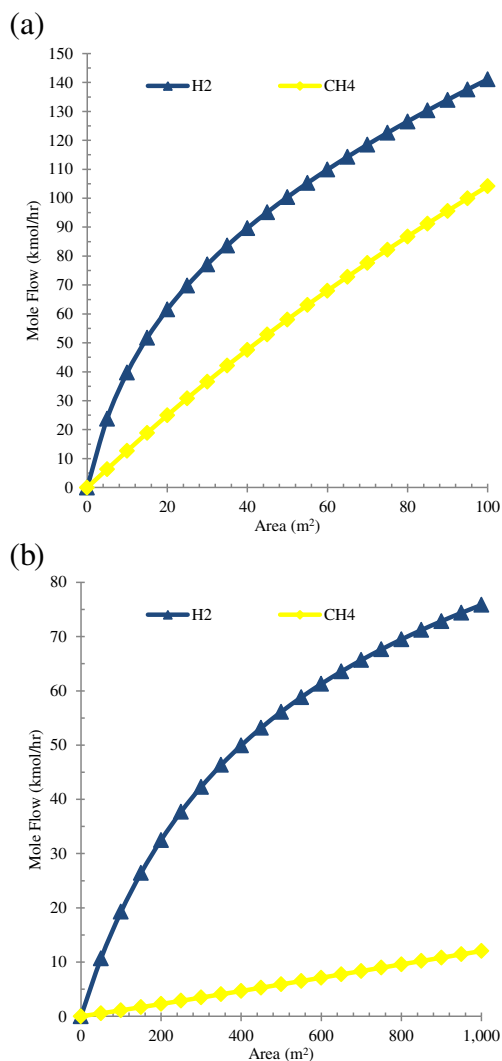


Fig. 5 – (a) Hydrogen and methane exchanged for zeolite ZSM-5. (b) Hydrogen and methane exchanged for zeolite SAPO-34.

hydrogen, so that a higher purge fraction is necessary to prevent buildup of methane in the recycle.

Fig. 5a and b shows the amounts of hydrogen and methane transferred in the area ranges analyzed for the two types of membranes.

The purge stream PURGE, in addition to hydrogen and methane, also has small amounts of toluene and benzene. As benzene and toluene do not permeate across the membrane, they stay in the residual stream PURGE2 and are lost. Thus, it takes a small amount of additional toluene to give the same amount of benzene produced.

Fig. 6a and b displays hydrogen and toluene fed to the process, and the benzene stream produced. In the range studied the hydrogen feed stream presents a reduction of 70.38 kmol/h equivalent to 30.36% for the ZSM-5 membrane and of 70.89 kmol/h equivalent to 30.58% for the SAPO-34 membrane. The toluene feed stream presents an increase of 0.66 kmol/h equivalent to 0.49% for the ZSM-5 membrane and

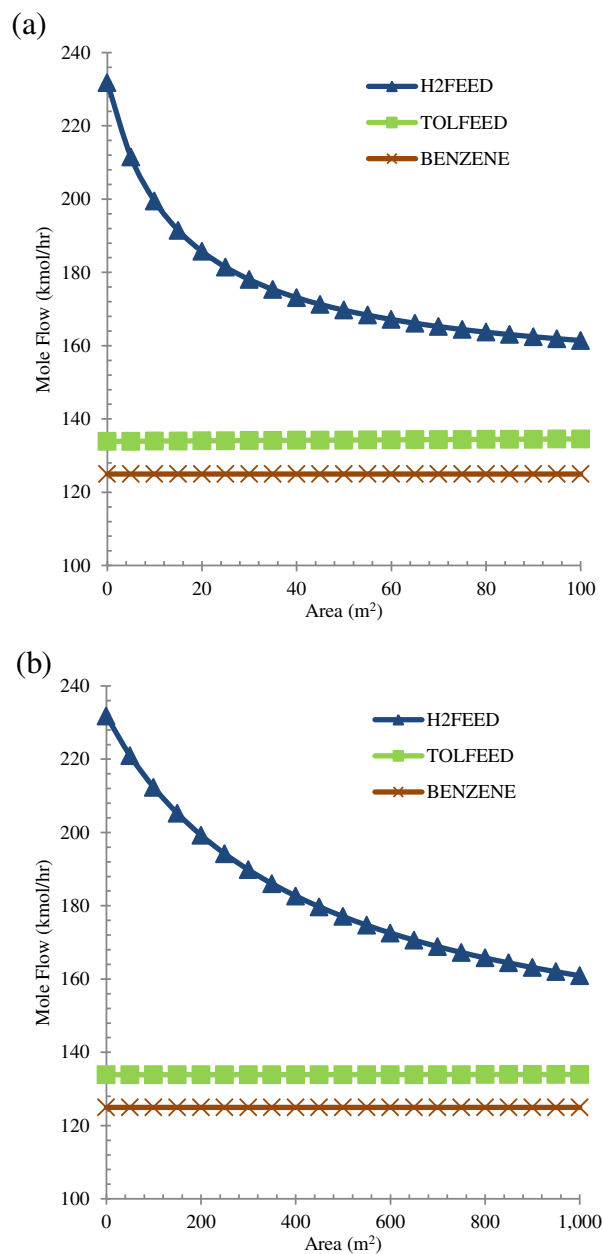


Fig. 6 – (a) Hydrogen and methane exchanged (ZSM-5). (b) Hydrogen and methane exchanged (SAPO-34).

0.06 kmol/h equivalent to 0.05% for the SAPO-34 membrane. The benzene product stream undergoes no variation because it has been set as a design target.

Although a detailed analysis of the variations of the process heat exchanger network is beyond the scope of this paper, using Aspen Energy Analyzer V7.3 we imported from Aspen Plus V7.3 the data associated with the heat exchanger network to construct the composite grand hot and cold streams of both the traditional process and the alternative with counter current membrane mass exchange. These curves are plotted in Fig. 7a, b and c (for the optimal membrane areas). Table 2 summarizes the minimum utility requirements.

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

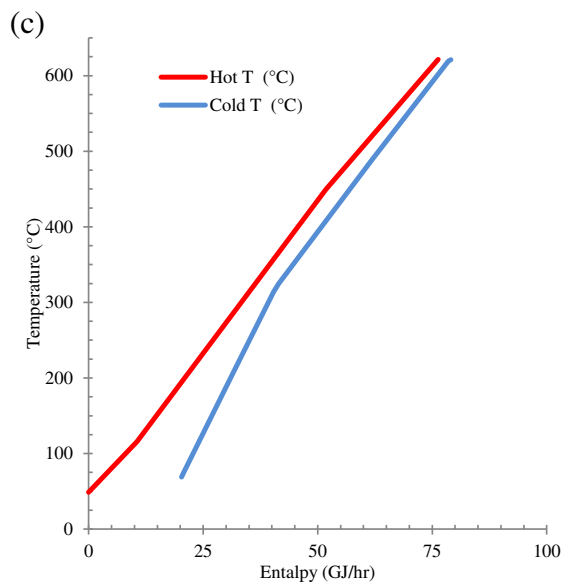
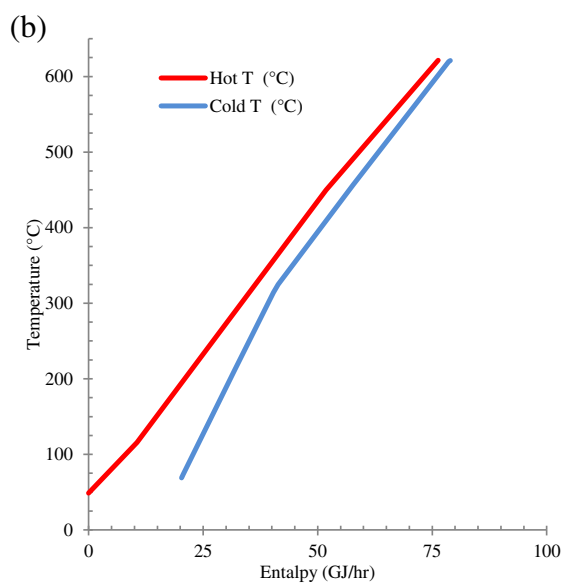
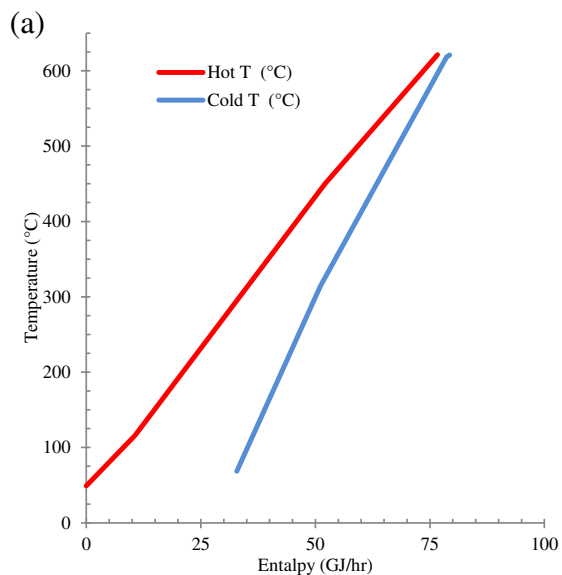


Fig. 7 – (a) Composite curves for the traditional process. (b) Composite curves for the process with the ZSM-5 membrane. (c) Composite curves for the process with the SAPO-34 membrane.

Table 2 – Summary of minimum utility requirements.

	Traditional process	Process with the ZSM-5 membrane	Process with the SAPO-34 membrane
Heating (Gj/h)	2.62	2.70	2.78
Cooling (Gj/h)	32.82	20.28	20.29

altered. The heating requirement is very similar, while the cooling requirement is a little less, so that the process alternative is beneficial. Furthermore, in all cases the composite hot curve is safely above the composite cold curve.

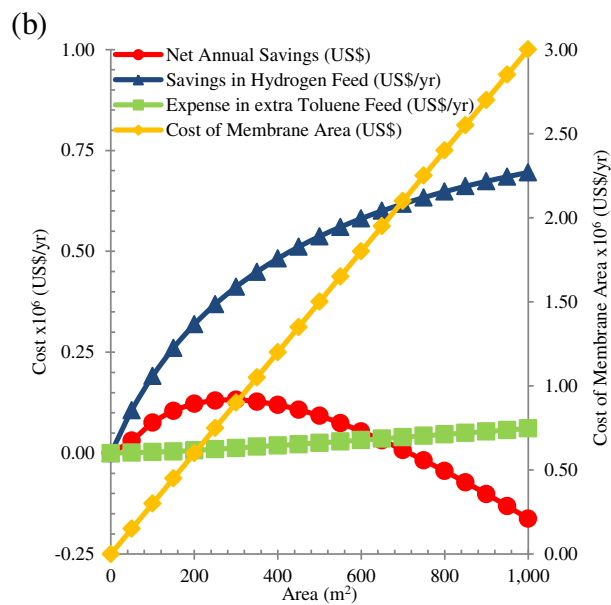
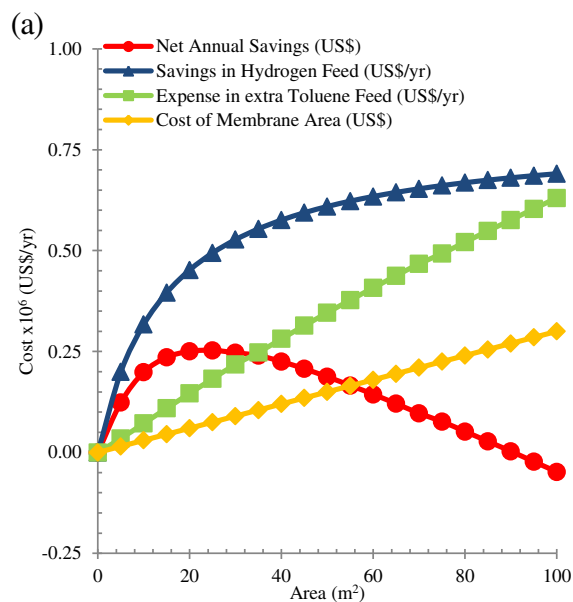


Fig. 8 – (a) ZSM-5. (b) SAPO-34.

Table 3 – Comparison of alternatives.

	Published by Bouton and Luyben. in year 2008 (M&S Index = 1293.1)	Published by Bouton and Luyben actualized to year 2011 (M&S Index = 1536.5)	Cost of alternative with ZSM-5 membrane (area = 25 m ²)	Cost of alternative with SAPO-34 membrane (area = 300 m ²)
Reduction in hydrogen feed (kmol/h)	77.04	77.04	50.82	42.41
Savings in hydrogen feed (US\$/yr)	688,300.00	755,854.85	494,352.61	411,852.05
Heat loss in the purge stream (US\$)	–	13,040.73	6045.83	8609.86
Expense in extra toluene feed (US\$)	–	286,803.66	182,483.59	12,533.34
Electric energy cost (US\$/yr)	79,800.00	113,993.88	–	–
Capital costs				
membrane (US\$)	126,000.00	126,000.00	75,000.00	900,000.00
compressor 1 (US\$)	374,300.00	444,754.43	–	–
heat exchanger 1 (US\$)	37,300.00	44,320.97	–	–
compressor 2 (US\$)	260,700.00	309,771.52	–	–
heat exchanger 2 (US\$)	37,500.00	44,558.62	–	–
heat exchanger (heater 4)	–	–	136,100.00	134,170.00
Total capital investment (US\$)	835,800.00	969,405.54	211,100.00	1,034,170.00
Annual savings (US\$)	399,600.00	99,665.20	253,048.18	132,166.35
Return on investment (% per year)	47.81	10.28	119.87	12.78

3.4. Cost analysis

The main benefit of doing a MEN synthesis at the end of the process design is a significant reduction in the amount of hydrogen required. To compare the performance of this approach against a traditional membrane recovery, we compared the Net Annual Savings of both alternatives. Net Annual Savings are computed as the difference between Total Annual Savings and the Total Annual Cost. Total Annual Savings are the savings achieved by the reduction in hydrogen consumption. Within the Total Annualized Cost are the annualized costs of compressors, heat exchangers and membranes, and the annual cost of electricity consumed by the compressors. We also considered the extra expense due to the larger toluene consumption and the loss of heat generated burning the purge stream, because we have a smaller purge stream when using a hydrogen recovery system. We compare with the results of Bouton and Luyben [4] considering that the plant operates 8760 h/yr.

For the installed cost of the ceramic zeolite membrane modules we resorted to Babita et al. [15] who reported it is US\$3000 per m². The cost of installation of the heat exchanger HEATER4 was estimated with Aspen Process Economic Analyzer V7.3. Installation costs are annualized using a Capital Charge Factor of 0.25. We considered that the variation in the heat exchanger network cost is negligible (as argued above) and only added the cost of heat exchanger HEATER4.

We considered a cost for hydrogen of 0.5058 U.S. \$/kg and for the purge of 0.01 U.S. \$/kg. The cost of energy consumed by the compressors was determined considering an electrical-mechanical efficiency of 1 adopting the assumptions considered by Bouton and Luyben [4] and a cost of 0.07 U.S. \$/kW-h.

Fig. 8a and b plots Net Annual Savings, the amounts of Hydrogen Feed Savings, the additional expenses in Toluene Feed and the Costs for alternative membranes ZSM-5 and SAPO-34. Note that the additional expense in Toluene Feed has a strong impact in case of adopting the ZSM-5 membrane due to its low selectivity. On the other hand, for the alternative with SAPO-34 the membrane cost has a very strong impact, because of the low permeability of the membrane.

For zeolite membrane ZSM-5 the optimum NAS U.S. \$ 253,048 is reached with an area of only 25 m². The very low selectivity of this membrane produces an increase in the purge stream with its consequent loss of toluene and benzene. For the alternative SAPO-34 membranes the optimum NAS U.S. \$ 132,166 is reached with an area of 300 m².

Bouton and Luyben [4] found the optimal operating conditions for the pressure driven membrane hydrogen recovery. To compare their results with ours we updated their costs from 2008 to 2011 with the Marshal and Swift M&S Index. Table 3 compares the two alternatives for recovering hydrogen from the purge.

When comparing with the updated costs of the design by Bouton and Luyben [4] we notice that the here proposed alternative with ZSM-5 membranes presents a much lower cost of installation (85.37% lower), whereas the alternative with SAPO-34 membranes presents a slightly lower cost (8.84% lower). With ZSM-5 membranes we have a 153.9% increase in Annual Net Savings compared with the traditional separation system with polymer membranes, whereas with the SAPO-34 membranes this figure increased to a 32.61%. The return of investment is 119.87% for the alternative with ZSM-5 membranes and 12.78% for the alternative with SAPO-34 membranes.

Taking into account that the costs of the zeolite membrane may decrease rapidly with intensified use, we also predict the overall process performance using different reduction factors of the installed cost. Fig. 9 presents the Net Annual Savings with a reduction factor of two, three and four times. This figure shows that for a reduction factor of four times, the Net Annual Savings climbs to 267,111 for the alternative with ZSM-5 membranes and to 405,786 for the alternative with SAPO-34 membranes. It can be seen that the process alternative with ZSM-5 membranes is poorly sensitive to the installed cost. This is so because this alternative uses little membrane area (the ZSM-5 membrane has a large permeability). Otherwise, the alternative that uses SAPO-34 membranes is highly sensitive to the installed cost (the SAPO-34 membranes have a low permeability).

Following the traditional process design rules, we also analyzed taking the purge before the recycle compressor (to avoid spending compression costs on a waste stream). But this process alternative has a lower driving force for the hydrogen exchange. By comparing with the alternatives above (where the purge is taken after the recycle compressor), the hydrogen recovery decreased in a 25.34% and 18.06% for the ZSM-5 and SAPO-34 membranes respectively. The compression powers are reduced by 18.80% and a 12.71% respectively and the energy consumptions are lower. Overall, these process alternatives have smaller Net Annual Savings than the process alternatives that take the purge after the recycle compressor.

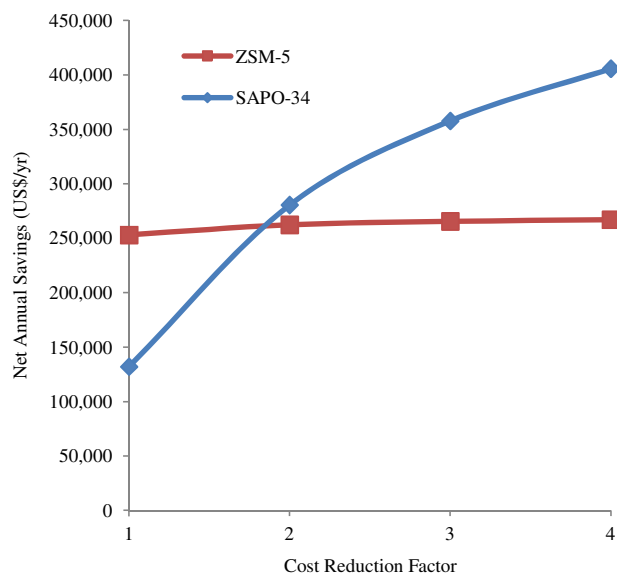


Fig. 9 – Net annual savings at different cost reduction factors.

Thus, the criteria of taking the purge after the compressor used by Bouton and Luyben [4] is also the one that gives better results in our case.

4. Conclusions

In this paper we explore the use of the concept underlying the Mass Exchange Network synthesis technology, as a heuristic in the last stage of the hierarchical process design procedure of Douglas [1,2] as proposed in Fischer and Iribarren [3]. This mass integration step was performed resorting to counter current gas permeation equipment that we already used in previous works [8–10]. This mass integration, applied at the end of the design of a new process (or to a process already designed), does not significantly changes the process conditions. In case of designing a new process, as some process conditions do change with mass integration, a more refined analysis would include a last re-optimization of the process variables, e.g. varying the purge fraction in the HDA process. This was not done here, but the process conditions were kept unchanged to enable a comparison with the reference process proposed by Bouton and Luyben [4].

We applied this procedure to the HDA traditional process resulting in a new (not previously reported in the literature) process alternative for recovering the hydrogen available in the purge stream. We explored using different types of zeolite membranes for the counter current gas permeation mass exchange and also compare the results obtained with a recovery system previously proposed by Bouton and Luyben [4] that resorts to pressure driven gas permeation with polymeric membranes.

The main benefit of implementing a counter current mass integration was a significant reduction in the amount of hydrogen required by the process. Another advantage was that the recovery system lacks the recycle compressor (and associated costs) to recycle the recovered hydrogen. For the alternative with ZSM-5 membrane we obtained an increase of 153.9% of the Net Annual Savings with respect to the traditional system, whereas for SAPO-34 membranes this figure climbed to 32.61%. We also estimated de Net Annual Savings at different reduction of the installed cost of the ceramic zeolite membranes to assess the overall performance of the process in a future scenario. In this way, for a reduction factor of four times, the Net Annual Savings respect to traditional system climbs to 168.01% for the alternative with ZSM-5 membranes and to 307.15% for the alternative with SAPO-34 membranes. These results encourage the study of a new application of the zeolite membranes in the design of hydrogen recovery systems.

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