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Oxygen integration of autothermal reforming of ethanol with oxygen production, through ion transport membranes in countercurrent configuration

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ABSTRACT

In this work, we propose a new arrangement for integrating an Autothermal Reforming of Ethanol process with oxygen production with the technology of ITM membranes. In the conventional configuration O_2 is first separated from the air and then injected in the reforming process, while in the new configuration O_2 is depleted from the air in a counter-current arrangement with a reforming process stream, used as sweep gas. We took from the literature a process for Autothermal Reforming of Ethanol in its optimal operating condition, and scaled it up to pilot size. We assessed the performance of both configurations with Aspen Plus V8.7 and found that the configuration in counter-current arrangement with a process sweep stream has a reduction of the total annualized cost of 27.3% with respect to the conventional separation configuration. Furthermore, we optimize the operating conditions and ancillary structure of the counter-current integrated process, achieving a total annualized cost reduction of 72.2% with respect to the conventional design.

1. Introduction

In a previous work (Fischer and Iribarren, 2016) we used the mass exchange heuristic rule that we proposed earlier (Fischer and Iribarren, 2011; Fischer and Iribarren, 2013a; Fischer and Iribarren, 2013b; Fischer and Iribarren, 2014) to integrate streams within a process, to integrate streams belonging to different processes (located closely). Specifically, analyzed different design alternatives for the integration of a gasification process with the oxygen production process through Ion Transport Membranes (ITM). In the present work, we study the possibilities of integrating the oxygen production process with a process for Autothermal Reforming (ATR) of Ethanol, with the ITM oxygen membranes, for both the conventional separation configuration and the counter-current exchange arrangement.

Following, there are brief overviews of the ATR of Ethanol and the ITM oxygen and syngas processes. Subsequently, we assess different integration strategies: the conventional separation system design using ITM oxygen membranes and the separation system arrived at by using the ITM oxygen membranes in a counter-current arrangement with a process stream as sweep gas. Afterward, we analyze the economic impact of adopting the here proposed new design and compare it with conventional separation designs. Finally, we draw the conclusions of this work.

1.1. Overview of autothermal reforming of ethanol

Normally, the ATR of Ethanol is fed with oxygen (or eventually with air in some cases), water (as water steam) and Ethanol or bio-Ethanol. The reforming can be carried out with different catalysts, while the molar fraction of the components (or reagents) proposed in the literature are quite different, especially in the amount of steam respect to ethanol (Ni et al., 2007; Vaidya and Rodrigues, 2006). The ratio of steam to ethanol, influences in the products and co-products obtained, as well as in avoiding the cooking of ethanol (Vaidya and Rodrigues, 2006). The steam acts as a heat wheel, absorbing heat from the ethanol partial reaction with oxygen, and providing heat to the Water Gas Shift (WGS) reactions. The temperature, and the pressure at which reforming takes place, is also the subject of numerous publications (Vaidya and Rodrigues, 2006). Typically, the ethanol conversion is favored at high temperature, although this is slightly counterproductive with the WGS

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reaction. The vast majority of studies are carried out at atmospheric pressure (we assume this is because of laboratory limitations), although at the industrial scale it is common that the processes be carried out at a medium pressure in the range 15–30 bar (Gaurav and Valerie, 2013). Also, the increased pressure is slightly counterproductive in the WGS reaction, although it greatly decreases the size of the equipment. Moreover, the pressure at which the reforming is carried out, is strongly set by the pressure needed at the downstream process (which will use the hydrogen generated). This is so because in this way the overall costs of compression can be reduced (Higman, 2008).

1.2. Overview of ITM oxygen and syngas membranes

ITM membranes are being developed for syngas and for oxygen production, in both cases the membrane function is to permeate the O_2 contained in an air feed stream (Miller et al., 2014; Bose, 2009; Dyer et al., 2000). In the ITM syngas configuration, one side of the membrane is fed with air at a relatively low pressure, while the other side is fed with methane (or another component to be reformed) and steam at a pressure up to 30 bar (Miller et al., 2014). This configuration has the great advantage that the oxygen separation from air and the reforming are carried out in a single-unit operation, which is expected to provide a compact installation with important cost savings and improved energy efficiency. On the one hand, as the oxygen reacts when coming in contact with methane, the oxygen partial pressure in the reforming stream it is very low, thus obtaining a very large driving force through the ITM syngas membrane. On the other hand, the oxygen reaction with methane causes a high temperature, which quickly deteriorates the membrane surface, reducing considerably the ITM syngas membrane lifetime. Moreover, being a compact equipment (separation and reaction in a single unit), it is impossible to use it to revamp an existing reform facility, leaving its application only for completely new facilities. In the ITM oxygen membranes (in the conventional separation configuration) the driving force for the oxygen transport through the membrane is achieved either by compressing the feed air, or performing vacuum on the oxygen permeate side. This configuration has the advantage that it is very simple, and the oxygen permeated can be used in any different application. Furthermore, as in this application there is no reaction on the surface, the lifetime of the ITM oxygen membrane is very long. In this configuration, ITM oxygen membranes can be used to revamp an existing reforming facility by replacing the Air Separation Unit (ASU) as it is proposed for thermal power plants by different researchers (Möller et al., 2006; Foy and Yantovsky, 2006; Yantovsky et al., 2009, 2004).

In this work, ITM oxygen membranes are proposed to be used in a counter-current arrangement with a process sweep stream, as a mass exchanger. In this configuration, the driving force (partial pressure) for the oxygen is large, and as a process feed stream (that would next be merged with the O_2 stream in the conventional process) is used as a sweep stream, the oxygen permeated does not need to be separated from the sweep gas. We previously proposed this ITM oxygen membrane configuration for a gasifier (Fischer and Iribarren, 2016), and here explore if it can be useful to integrate an ATR with the oxygen separation. Also, this configuration can be used to revamp an existing ATR of ethanol (replacing the ASU).

Figs. 1–3 show schemes for the different configurations described above.

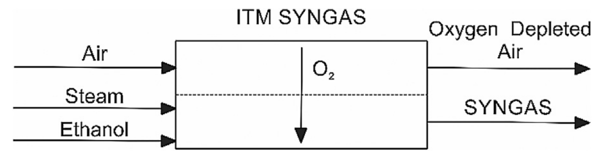

Fig. 1. ITM Syngas Membrane Configuration.

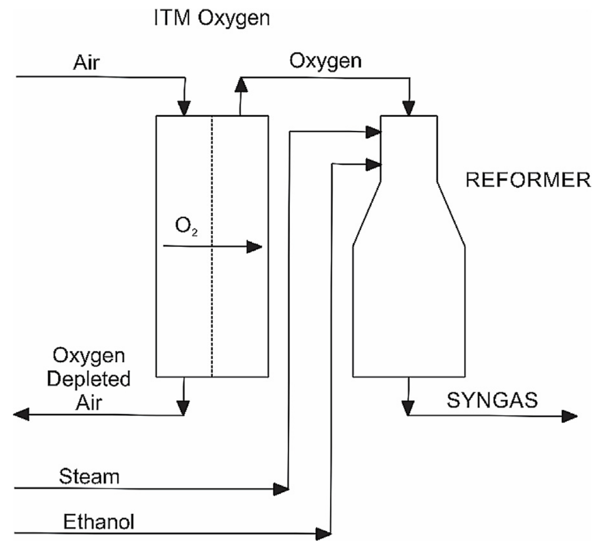

Fig. 2. ITM Oxygen Membrane in Conventional Configuration.

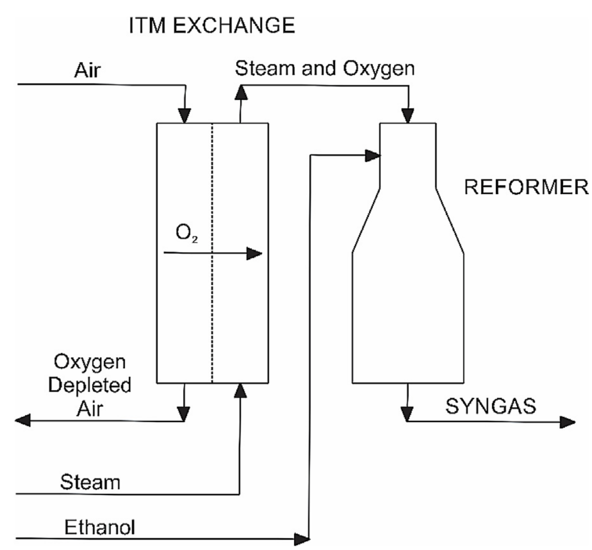

Fig. 3. ITM Oxygen Membrane in Counter-Current Configuration with a Process Sweep Stream.

2. Case of study: integration of an ATR of ethanol process, and the ITM process of oxygen separation

We selected the ethanol reforming conditions proposed by (Casanovas et al., 2006) as the study case for this work. These authors study the ethanol reforming over different supported catalysts in the range of temperature of °C (548–723 °K.) and at atmospheric pressure (1.013 bar). They found that the larger production of hydrogen with a total conversion of ethanol occurs at a temperature of 450 °C utilizing ZnO-supported palladium catalyst. Given that the objective of the present work is not to study the operating variables of the ethanol reforming process, but rather consider its integration with the oxygen separation process, we will take the conditions established in their paper, even if the ethanol reforming is performed at atmospheric pressure. Anyway, if the reforming of ethanol is carried out at industrial pressures (15–30 bar (Gaurav and Valerie, 2013)), the product fraction molar

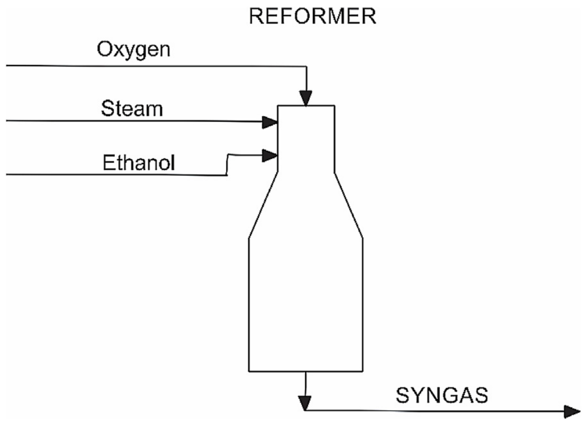

Fig. 4. Scheme of the ATR process.

would be modified slightly. In this ethanol reforming process, the ratio of water to ethanol (13:1) is particularly high, while the ratio of oxygen to ethanol (0.5:1) is the most utilized. This high ratio of water to ethanol favors the performance in the exchange methodology proposed here. Usually, industrial scale reformers process thousands of Nm^3 of Ethanol (Higman, 2008; Klerk, 2011). However, for our study, we considered a reforming process in smaller scale (or pilot scale) that process 2.5 Nm^3/h of Ethanol (liquid state). In this case, the requirements of the reformer are 43.33 kmol/h of ethanol, 21.67 kmol/h of oxygen, 563.32 kmol/h of water, and produces about 2012.58 Nm^3/h of Syngas (H_2 and CO_2). Fig. 4 shows a schematization of the ATR process.

For the ITM oxygen membranes modules we, used the models developed in Aspen Custom Modeler (ACM) V8.2 and their detailed description can be seen in our previous work (Fischer and Iribarren, 2016). For the ITM oxygen membranes operating temperature we selected 900 °C because at this temperature the membrane has a good permeability (Baumann et al., 2011) without substantial degradation (Yantovsky et al., 2009).

As ITM oxygen membranes operate at high temperature, it is necessary to consider the residual heat recovery from the effluents. In this paper, we assume that the heat recovery generates steam at different pressures that could be used in steam turbines similarly than in our previous work (Fischer and Iribarren, 2016). Figs. 5 and 6 present the flow sheets (in their optimal operating point) for the conventional separation configuration and for the configuration in counter-current with the sweep stream. The design alternatives have inherent characteristics and to facilitate comparison between them, we seek that they be as similar as possible, but essentially differ in using either the conventional O_2 separation or the counter-current arrangement. These configurations are similar to the configurations that we used for oxygen integration between ITM oxygen membranes and a gasifier (Fischer and Iribarren, 2016). Furthermore, the arrangements used for the compressor-turbine-generator are similar to a gas turbine and this is studied by several authors (Yantovsky et al., 2009; Stadler et al., 2011; Smith and Klosek, 2001).

As shown in the flow-sheets, the main differences (besides the configuration of the permeation modules) between both alternatives are in how the feed air is heated and in the heat recovery scheme for the permeate stream. For the conventional separation configuration, the air temperature is elevated up to the selected operating temperature, using the heat of the oxygen permeate, and afterward with a direct fired heater (the simplest alternative). For the configuration with sweep stream in counter-current, only a direct fired heater is used (after the air compression), since the energy of the sweep stream plus the permeated oxygen is used for heating the steam from the reformer as they have similar MCp (mass multiplied by heat capacity at constant pressure).

For both alternatives, we have fixed the amount of oxygen needed by the reformer (21.67 kmol/h) and the total pressure of the reformer (1 atm), while we have as variables the input air flow rate, air compression, mole fraction of residual oxygen in the air and the permeation area. These design variables are determined in each case by optimization of the economic performance of the whole process.

2.1. ITM oxygen membranes in conventional configuration

For this case, we have as design variables the pressure above the membrane, the air flow rate and the membrane area required. However, we cannot freely vary these variables. For example, the minimum air flow rate must contain more oxygen than the amount we want to permeate, and in turn, at the end of the permeate module, we must still have a positive partial pressure gradient (driving force). Moreover, the maximum flow rates are determined by economic considerations.

Fig. 7 shows how the membrane area required varies when air flow rate varies ranging from 137 to 450 kmol/h, for a set of air pressures from 10 to 45 bar in increments of 5 bar.

In Fig. 7 it can be seen (in addition to that for lower pressures, more area is needed) the minimum air flow rate for each pressure analyzed, and that it is larger when the air pressure is reduced. This is so, since the driving force (the oxygen partial pressure difference) depends on the total pressure and the molar fraction of oxygen in the air stream. So, when the total pressure is decreased, the partial pressure can be recovered only by a larger molar fraction of oxygen in the stream. The oxygen partial pressure in the air stream must be maintained above 1 atm (the pressure at the low pressure side).

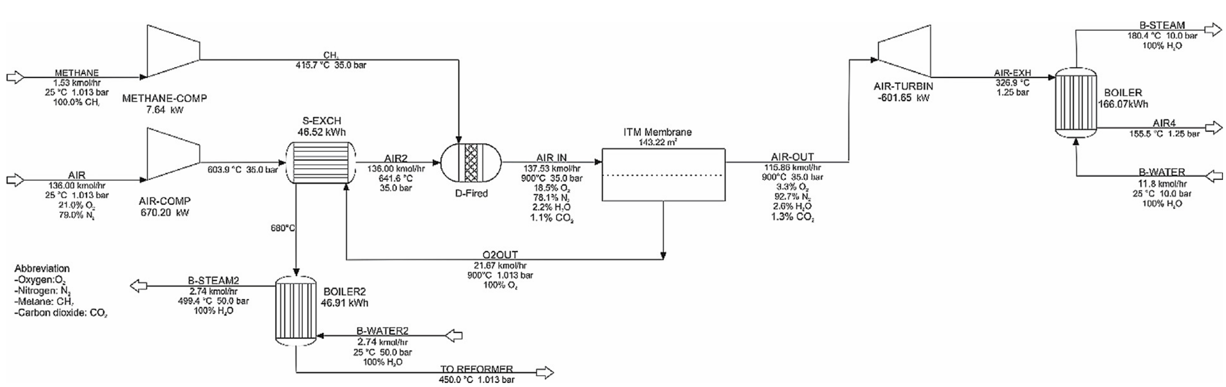

Fig. 5. Flow sheet for ITM oxygen membrane in the conventional separation configuration.

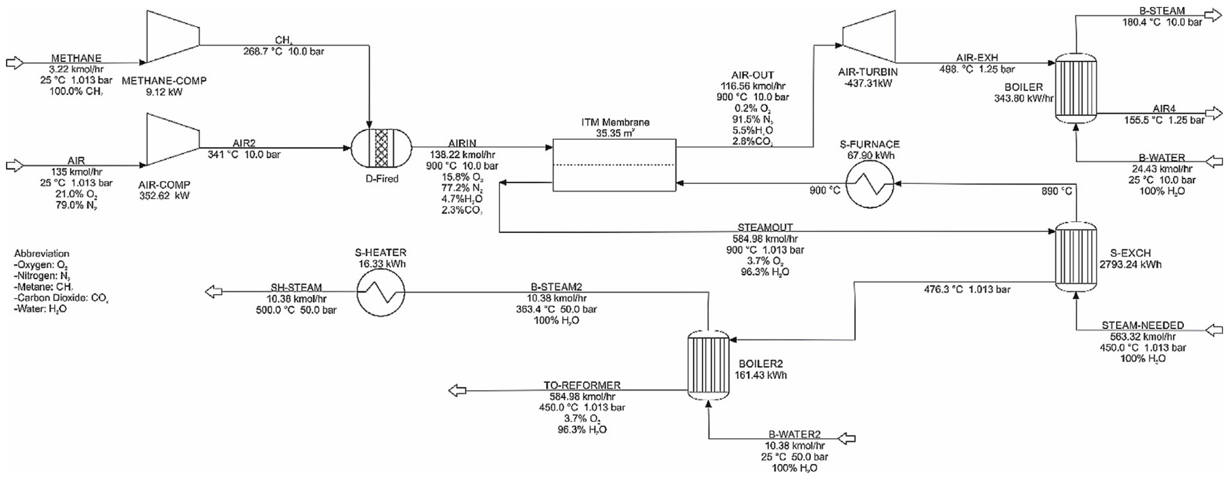

Fig. 6. Flow sheet for ITM oxygen membrane in counter-current configuration with the sweep stream, as a mass exchanger.

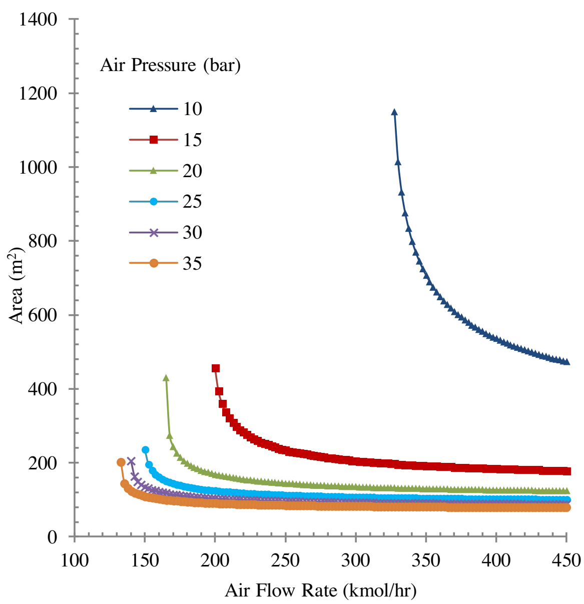

Fig. 7. Membrane area required when air flow rate varies from 137 to 450 kmol/h, for a set of air pressures from 10 to 45 bar.

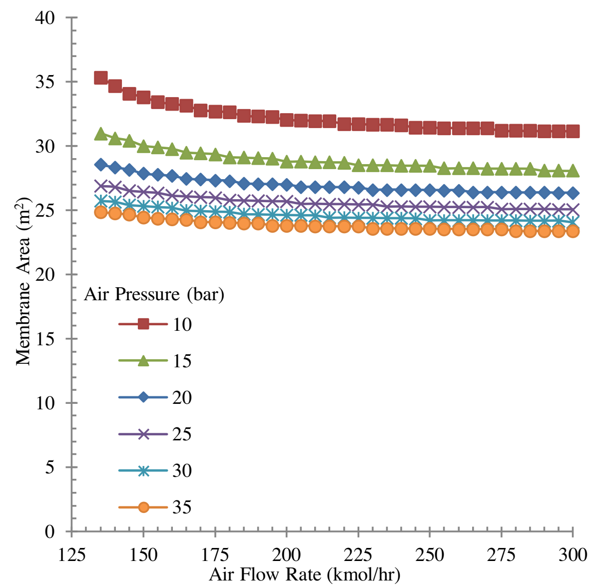

Fig. 8. Membrane area required when air flow rate varies from 135 to 300 kmol/h, for a set of air pressures from 10 to 45 bar.

2.2. ITM oxygen membranes in counter-current arrangement with sweep stream

For this alternative, the pressure of the sweep stream (steam) and its flow rate are fixed by the pressure and flow rate needed in the ATR of ethanol (563.32 kmol/h and 1 atm). In this configuration, the partial pressure of oxygen in the air exiting the permeate module can be smaller than in the conventional configuration. Furthermore, the partial pressure of oxygen in the steam exiting the permeate module can not exceeding the partial pressure of oxygen in the inlet air stream. This means than there are a minimum flow rate for the sweep stream (steam). In the case study adopted here, the amount of steam is 26 times larger than the amount of oxygen required, and the oxygen reaches a molar fraction of only 0.0370 in this condition. This means that even if the air is at atmospheric pressure, the driving force for the oxygen is important. In this case, the minimum air flow rate is close to 135 kmol/h, containing a little more oxygen that the one needed by the ATR. Fig. 8 shows how the required membrane area varies when the air flow rate varies from 135 to 300 kmol/h, for a set of air pressure from 10 to 35 bar in increments of 5 bar.

From Fig. 8 it can be seen that in the counter-current arrangement the membrane area required and its variation are lower than in the conventional configuration. This is because along the whole permeate module, the driving force obtained is larger than for the conventional configuration, and its variation is less. In the counter-current arrangement, the oxygen concentration increases on the low side of the membrane from where the steam enters towards where it leaves. In the conventional configuration, the oxygen partial pressure at the permeate side is constant: it is the total pressure at low pressure side, i.e. 1 atm.

2.3. Economic assessment

In order to compare the economic performance of the mass exchanger in a counter-current arrangement vs. the conventional separation, we computed the Total Annualized Cost (TAC) of the main process units involved in the integration of the production of oxygen with the reformer.

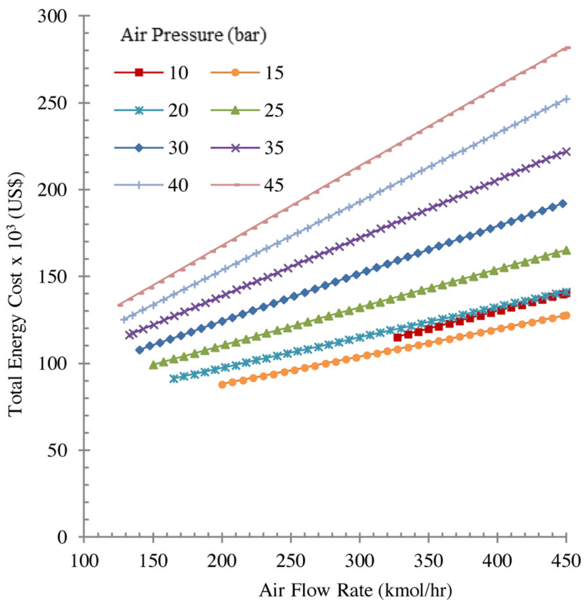

Fig. 9. Total Annual Energy Cots for ITM oxygen membrane in conventional configuration in the range of 125–450 kmol/h of feed air and a set of pressures at the high pressure side of the membrane.

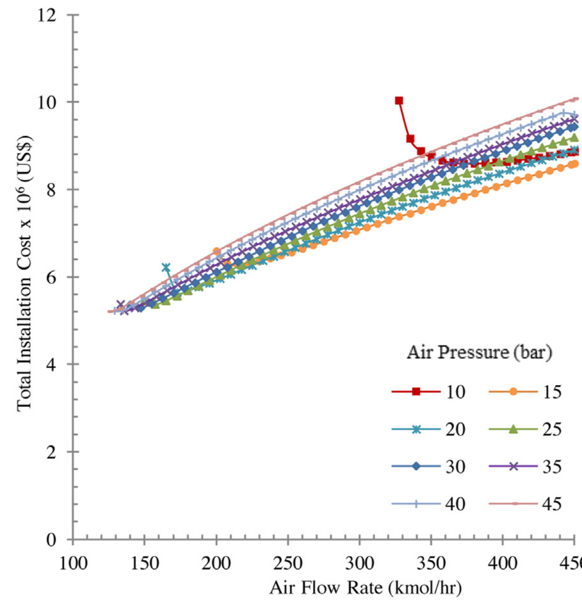

Fig. 10. Total Installation Cots for ITM oxygen membrane in conventional configuration in the range of 125–450 kmol/h of feed air and a set of pressures at the high pressure side of the membrane.

The TAC includes the equipment installation costs (of the main equipment) annualized using a Capital Charge Factor (CCF) of 0.351. To estimate the installation cost of the principal equipment, we use the correlations in Turton et at. (Turton et al., 2008) and update the cost using the Chemical Engineering Plant Cost Index (CEPCI) of 576.1 for year 2014. We considered an axial compressor and axial turbine with 0.85 isentropic efficiency (Korpela, 2011) for compressing and expanding the air respectively (for high pressure and large flow rates). We also consider a centrifugal compressor (with 0.72 isentropic efficiency) driven by an electric motor to compress the methane. For heat exchangers and the boiler, we considered shell and tube heat exchangers with fixed tubes for large heat exchange areas and spiral tube-shell for small areas. For the cost of the ITM membrane modules we referred to Bose (Bose, 2009) who reported a cost of €3000 m^2, from which €1500 correspond to the ITM membrane tubes and €1500 to the membrane module shells. With a conversion factor of 1.15 U.S.$ per € it amounts to a total cost of U.S.$ 3450 m^2 of membrane area. Also, we considered a membrane life-time of five years, and the CCF of 0.351 of their installed cost covers both amortization and annual maintenance cost.

The TAC includes purchases of methane for heating, electricity and income from selling the steam produced. To compute the energy consumed by the compressors, we considered an electrical to mechanical conversion efficiency of 0.9 and an electric energy cost of US$ 0.07 per kW-h, while for steam we considered US$ 0.009 kW-h. For methane, we take a price of 0.2327 U.S.$/kg (ICIS, 2015).

Figs. 9–11 show the Total Annual Energy Cost (sum of the cost of steam, methane and electric energy), Total Installation Cost (sum of the installation cost of main equipment) and TAC for ITM oxygen membrane in the conventional configuration in the range of 125–450 kmol/h of feed air, for a set of pressures at the high pressure side of the membrane.

From Fig. 11, it can be noticed that the lower TAC is located in the down left corner, but this is not seen very well. Therefore, we reproduce the TAC of the down left corner of Fig. 11 in Fig. 12 for the sake of clarity.

From Fig. 12, it can be seen with more clarity than the minimum TAC is located at a feed air flow rate of 136 kmol/h and a pressure

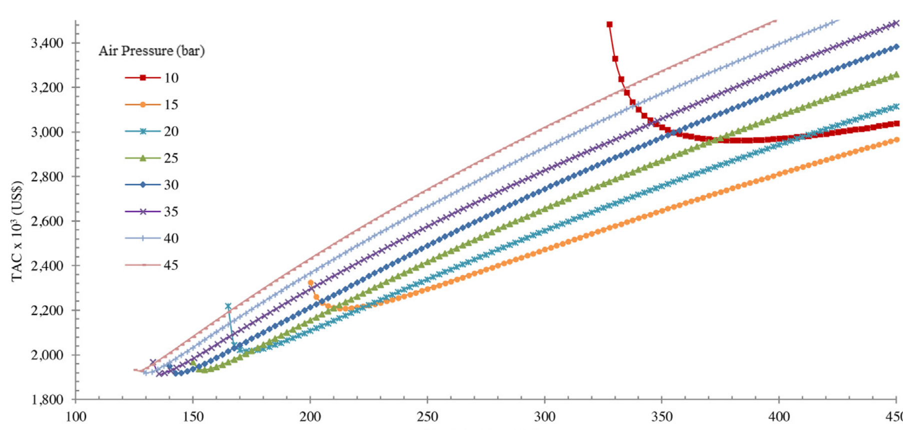

Fig. 11. TAC for ITM oxygen membrane in conventional configuration in the range of 125–450 kmol/h of feed air and a set of pressures at the high pressure side of the membrane.

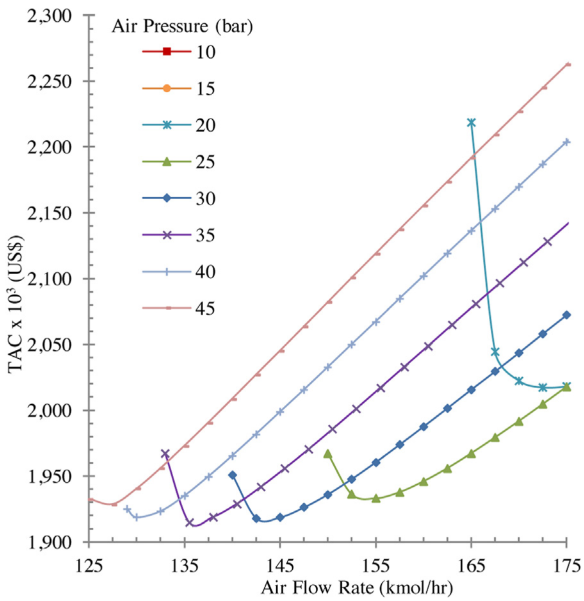

Fig. 12. Reproduction of TAC for ITM oxygen membrane in conventional configuration in the range of 125–175 kmol/h of feed air, for a set of pressures at the high pressure side of the membrane.

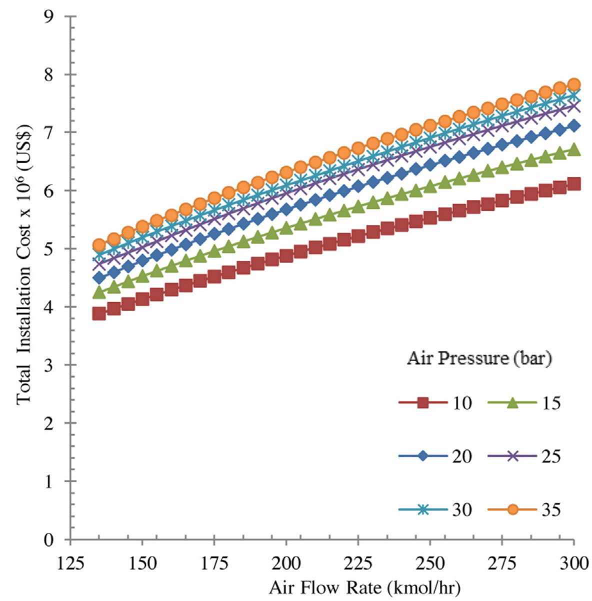

Fig. 14. Total Installation Cots for the ITM oxygen membrane in counter-current configuration in the range of 135–300 kmol/h of feed air and a set of pressures at the high pressure side of the membrane.

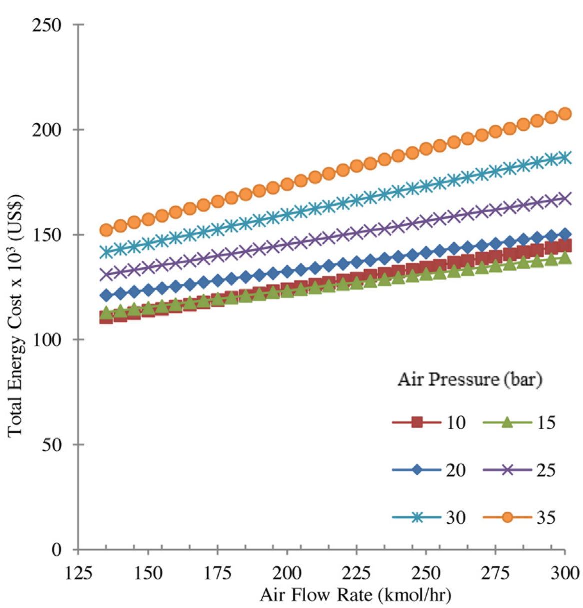

Fig. 13. Total Annual Energy Cots for the ITM oxygen membrane in counter-current configuration in the range of 135–300 kmol/h of feed air and a set of pressures at the high pressure side of the membrane.

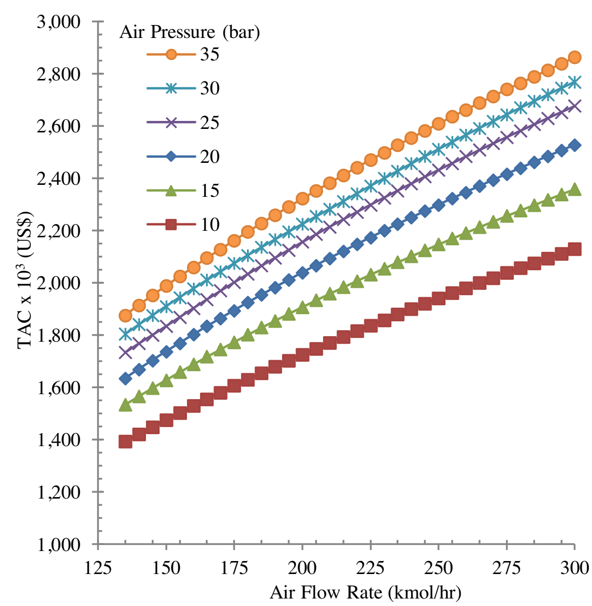

Fig. 15. TAC for ITM oxygen membrane in counter-current configuration in the range of 135–300 kmol/h of feed air and a set of pressures at the high pressure side of the membrane.

of 35 bar, with a value for TAC of U.S.$ 1,914,978. At this point, the membrane area is 143.22 m^2.

Table 1 summarizes the main costs that compose the TAC for this alternative, at the optimal operating pressure (35 bar) in the air side.

Figs. 13–15 show the Total Annual Energy Cost, Total Installation Cost and TAC for the ITM oxygen membrane in counter-current configuration with sweep stream vs. the air flow rate in the range of 135–300 kmol/h for a set of pressures at the air side.

From Fig. 15 it can be seen that for the considered range of pressures and feed air flow rates the TAC decreases when decreasing both variables, without finding a minimum for any of them. The lowest TAC in the variables space explored occurs at an air flow rate of 135 kmol/h and a pressure of 10 bar with a TAC = 1,392,994 U.S. $/yr. At this point, the membrane area is 35.35 m^2.

Table 2 summarizes the main costs that compose the TAC for this alternative, at the optimal operating pressure (10 bar) in the air side.

Since the curves (of Fig. 15) start very close to the minimum feed air flow rate (which is a process constraint), this suggests that by reducing the pressure below 10 bar, it may be possible to further reduce the TAC. But reducing the pressure below 10 bar would change the flow sheet proposed for this configuration. For low pressures and low flow rates, it is no longer convenient to use axial compressors and turbines, nor the recovery of the residual enthalpy of the oxygen depleted air through turbines. Therefore, we will explore a new low pressure counter-current process.

Table 1
Main Costs in the Total Annual Cost for 35 bar operating pressure in the air side.

Air Flow Rate (kmol/h)	Revenue by Steam (US$)	Cost of Methane (US$)	Cost of Electric Energy (US$)	Cost of Air Compressor and Air Turbine (US$)	Cost of Boilers, Exchangers and Furnaces (US$)	Cost of Membrane Area (US$)
133,0	16.457	47.554	52.459	4.292.886	282.361	698.811
135,5	16.760	48.564	52.031	4.347.101	282.674	494.096
143,0	17.612	51.584	50.714	4.506.355	283.549	407.282
150,5	18.491	54.701	49.133	4.661.276	284.441	374.311
158,0	19.345	57.733	47.776	4.811.228	285.354	355.677
165,5	20.199	60.762	46.400	4.957.046	286.281	342.800
173,0	21.178	63.914	44.760	5.099.444	287.374	332.551
180,5	22.037	66.947	43.405	5.237.712	288.326	325.337
188,0	22.897	69.982	42.026	5.372.635	289.286	319.380
195,5	23.792	73.145	40.376	5.504.788	290.245	313.906
203,0	24.654	76.187	38.993	5.633.532	291.214	309.789
210,5	25.514	79.226	37.613	5.759.450	292.184	306.280
218,0	26.375	82.263	36.237	5.882.700	293.155	303.248
225,5	27.268	85.472	34.515	6.003.868	294.102	300.016
233,0	28.139	88.496	33.146	6.122.172	295.100	297.654
240,5	29.001	91.539	31.758	6.238.225	296.075	295.561
248,0	30.014	94.581	30.372	6.352.110	297.328	293.686
255,5	30.881	97.623	28.986	6.463.928	298.310	291.996
263,0	31.747	100.666	27.601	6.573.772	299.291	290.464
270,5	32.661	103.910	25.770	6.682.188	300.269	288.297
278,0	33.534	106.941	24.393	6.788.318	301.258	287.098
285,5	34.402	109.988	22.997	6.892.738	302.237	285.926
293,0	35.270	113.036	21.601	6.995.497	303.214	284.845
300,5	36.138	116.083	20.205	7.096.661	304.190	283.845
308,0	37.006	119.129	18.810	7.196.291	305.165	282.917
315,5	37.874	122.176	17.415	7.294.446	306.137	282.052
323,0	38.742	125.223	16.020	7.391.179	307.109	281.246
330,5	39.610	128.270	14.626	7.486.541	308.078	280.491
338,0	40.536	131.546	12.714	7.580.981	309.047	279.166
345,5	41.411	134.598	11.307	7.673.741	310.024	278.500
353,0	42.280	137.650	9.900	7.765.267	310.990	277.873
360,5	43.150	140.701	8.493	7.855.600	311.953	277.282
368,0	44.019	143.753	7.086	7.944.777	312.915	276.723
375,5	44.888	146.805	5.680	8.032.834	313.875	276.195
383,0	45.758	149.857	4.273	8.119.808	314.834	275.694
390,5	46.627	152.908	2.867	8.205.730	315.791	275.219
398,0	47.496	155.960	1.461	8.290.632	316.746	274.768
405,5	48.365	159.009	52	8.374.545	317.699	274.329
413,0	49.234	162.063	−1.318	8.457.474	318.650	274.055
420,5	50.103	165.112	−2.760	8.539.509	319.601	273.530
428,0	50.972	168.166	−4.133	8.620.597	320.549	273.279
435,5	51.842	171.215	−5.572	8.700.836	321.498	272.800
443,0	53.062	174.596	−7.697	8.780.581	322.940	271.774
450,0	53.645	177.435	−8.992	8.853.878	323.406	271.592

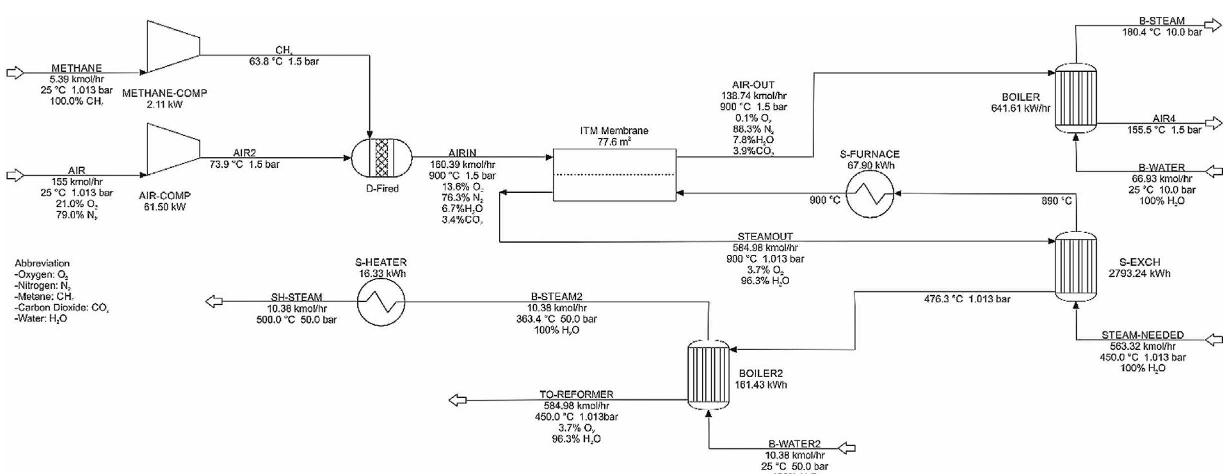

Fig. 16. Flow sheet for ITM oxygen membrane in counter-current configuration with the sweep stream, at low air stream pressure.

For a low pressure ITM oxygen membrane configuration, it is convenient to consider a centrifugal compressor driven by an electric motor, and not using a turbine to take advantage of the high pressure of the oxygen depleted air stream, but just recover its thermal energy in a heat exchanger. We explored the economic performance of a flow sheet taking into account the above consid-

Table 2
Main Costs in the Total Annual Cost for 10 bar operating pressure in the air side.

Air Flow Rate (kmol/h)	Revenue by Steam (US$)	Cost of Methane (US$)	Cost of Electric Energy (US$)	Cost of Air Compressor and Air Turbine (US$)	Cost of Boilers, Exchangers and Furnaces (US$)	Cost of Membrane Area (US$)
135	39.859	122.253	−51.490	3.104.129	543.960	121.967
140	40.982	125.960	−55.313	3.184.217	544.718	119.629
145	42.267	129.869	−59.425	3.263.469	545.666	117.679
150	43.388	133.549	−63.241	3.340.347	546.464	116.675
155	44.675	137.484	−67.373	3.416.580	547.406	115.402
160	45.800	141.171	−71.186	3.490.585	548.209	114.808
165	46.925	144.860	−74.995	3.563.261	549.011	114.330
170	48.288	148.905	−79.293	3.635.820	550.044	113.197
175	49.419	152.603	−83.114	3.706.033	550.858	112.861
180	50.550	156.302	−86.935	3.775.093	551.673	112.575
185	51.901	160.327	−91.227	3.844.063	552.711	111.663
190	53.037	164.034	−95.047	3.910.938	553.525	111.481
195	54.174	167.741	−98.878	3.976.822	554.347	111.293
200	55.402	171.750	−103.153	4.042.610	555.199	110.549
205	56.686	175.463	−106.976	4.106.546	556.245	110.449
210	57.829	179.178	−110.817	4.169.613	557.075	110.316
215	58.972	182.892	−114.656	4.231.806	557.903	110.201
220	60.227	186.979	−119.027	4.294.113	558.752	109.506
225	61.380	190.701	−122.878	4.354.655	559.594	109.413
230	62.681	194.424	−126.728	4.414.414	560.671	109.328
235	63.830	198.146	−130.578	4.473.414	561.504	109.251
240	64.978	201.869	−134.428	4.531.682	562.337	109.181
245	66.258	206.015	−138.901	4.590.233	563.202	108.492
250	67.416	209.746	−142.739	4.647.066	564.030	108.492
255	68.569	213.477	−146.618	4.703.295	564.874	108.395
260	69.884	217.208	−150.460	4.758.822	565.951	108.395
265	71.040	220.939	−154.341	4.813.777	566.800	108.300
270	72.193	224.671	−158.185	4.868.072	567.620	108.300
275	73.494	228.859	−162.746	4.922.779	568.506	107.611
280	74.658	232.598	−166.605	4.975.907	569.340	107.611
285	75.815	236.337	−170.465	5.028.477	570.162	107.611
290	76.973	240.077	−174.354	5.080.541	571.004	107.540
295	78.129	243.816	−178.215	5.132.038	571.825	107.540
300	79.479	247.555	−182.076	5.183.019	572.948	107.540

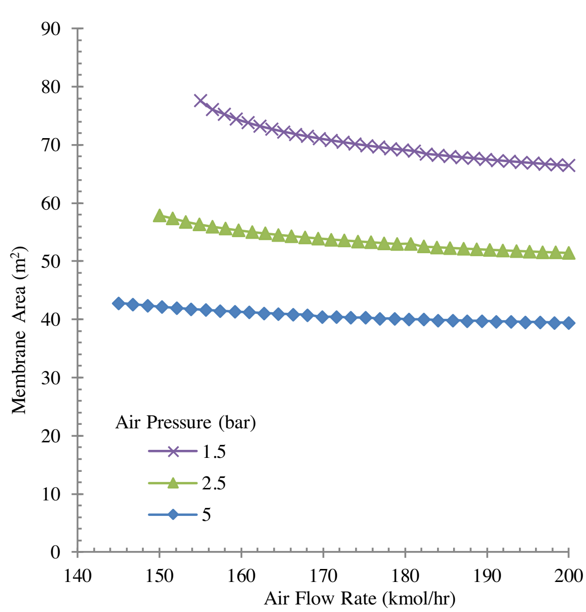

Fig. 17. Membrane area required when the air flow rate varies from 145 to 200 kmol/h, for air pressures at 1.5, 2.5 and 5 bar.

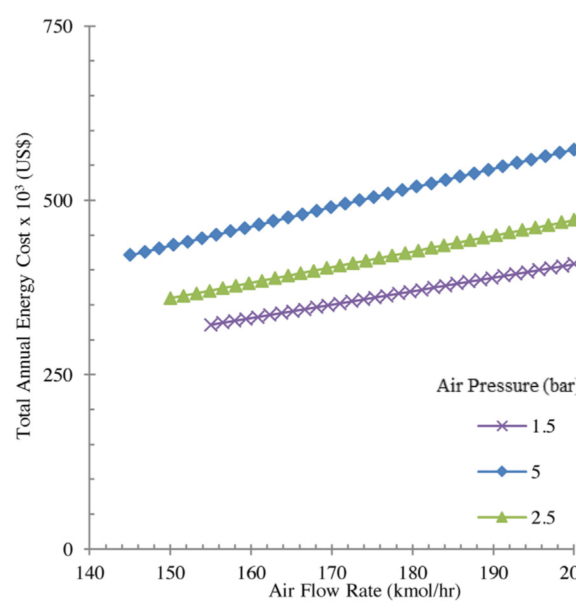

Fig. 18. Total Annual Energy Cots for the ITM oxygen membrane in counter-current configuration in the range of flow rates 145–200 kmol/h of feed air and a set of pressures at the high pressure side of the membrane.

erations. This flow sheet is presented in Figs. 16 and 17 shows how the required membrane area varies when the air flow rate varies from 145 to 200 kmol/h, for a set of air pressures from 1.5 to 5 bar. The Total Annual Energy Cost, Total Installation Cost and the TAC are plotted in Figs. 18–20, for the same air flow rates and set of pressures.

The TAC (in Fig. 20) shows a similar behavior as the previous counter-current process shown in Fig. 15, with the minimum TAC located at the air flow rate and pressure lower bounds. However a considerably lower minimum TAC of 532,959 U.S.$/yr was found at

Table 3
Main Costs in the Total Annual Cost for 1.5 bar operating pressure in the air side.

Air Flow Rate (kmol/h)	Revenue by Steam (US$)	Cost of Methane (US$)	Cost of Electric Energy (US$)	Cost of Air Compressor and Air Turbine (US$)	Cost of Boilers, Exchangers and Furnaces (US$)	Cost of Membrane Area
155	86.779	191.187	43.341	266.493	557.088	267.728
156	87.638	192.771	43.747	268.851	557.553	262.624
158	88.420	194.365	44.153	271.206	557.876	259.844
159	89.214	195.958	44.559	273.557	558.242	256.953
161	90.005	197.551	44.964	275.905	558.597	254.678
162	90.795	199.144	45.370	278.250	558.950	252.704
164	91.585	200.738	45.776	280.591	559.301	250.951
165	92.374	202.331	46.182	282.929	559.651	249.367
167	93.163	203.924	46.587	285.264	560.000	247.921
168	93.953	205.518	46.993	287.595	560.349	246.589
170	94.742	207.111	47.399	289.923	560.698	245.353
171	95.531	208.704	47.805	292.247	561.046	244.201
172	96.320	210.297	48.211	294.569	561.394	243.122
174	97.109	211.891	48.616	296.887	561.742	242.108
175	98.008	213.484	49.022	299.202	562.250	241.151
177	98.798	215.077	49.428	301.514	562.598	240.246
178	99.588	216.671	49.834	303.822	562.947	239.388
180	100.378	218.264	50.239	306.127	563.295	238.572
181	101.168	219.857	50.645	308.430	563.644	237.795
183	102.087	221.742	51.053	310.729	563.983	236.269
184	102.884	223.338	51.459	313.024	564.341	235.543
185	103.676	224.933	51.865	315.317	564.690	234.852
187	104.467	226.529	52.271	317.607	565.039	234.190
188	105.258	228.124	52.677	319.893	565.388	233.556
190	106.050	229.720	53.082	322.177	565.737	232.946
191	106.841	231.316	53.488	324.457	566.085	232.361
193	107.632	232.911	53.894	326.734	566.433	231.798
194	108.424	234.507	54.300	329.009	566.781	231.255
196	109.215	236.102	54.706	331.280	567.129	230.732
197	110.006	237.698	55.111	333.548	567.476	230.227
199	110.797	239.293	55.517	335.814	567.823	229.739
200	111.715	240.889	55.923	338.076	568.353	229.268

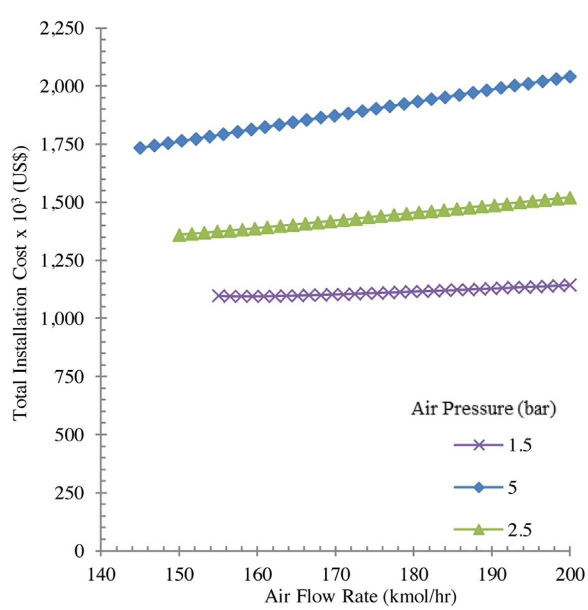

Fig. 19. Total Installation Cots for the ITM oxygen membrane in counter-current configuration in the range of flow rates 145–200 kmol/h of feed air and a set of pressures at the high pressure side of the membrane.

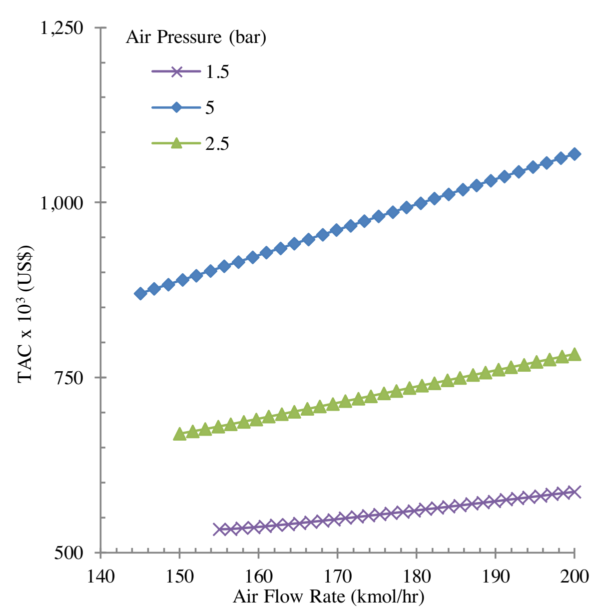

Fig. 20. TAC for ITM oxygen membrane in counter-current configuration with sweep stream, at low air stream pressure.

155 kmol/h air flow rate and a pressure of 1.5 bar. At this point, the membrane area is 77.6 m^2.

Table 3 summarizes the main costs that compose the TAC for this alternative, at the optimal operating pressure (1.5 bar) in the air side.

Tables 1–3 report the main costs of the alternatives for a range of air flow rates. To visualize their relative weights in an easy way we plotted them (at the optimum operating point) in a bar diagram in Fig. 21. From this diagram it can be seen that for both conventional and countercurrent at the medium pressure, the cost of the compressor and turbine, methane, steam and electrical energy are very close. These costs are alike because there are similar flow rates and pressures in both configurations. They differ mainly in the cost of membrane area (being lower in the countercurrent alternative) and in the cost of heat exchange equipment (being greater in the

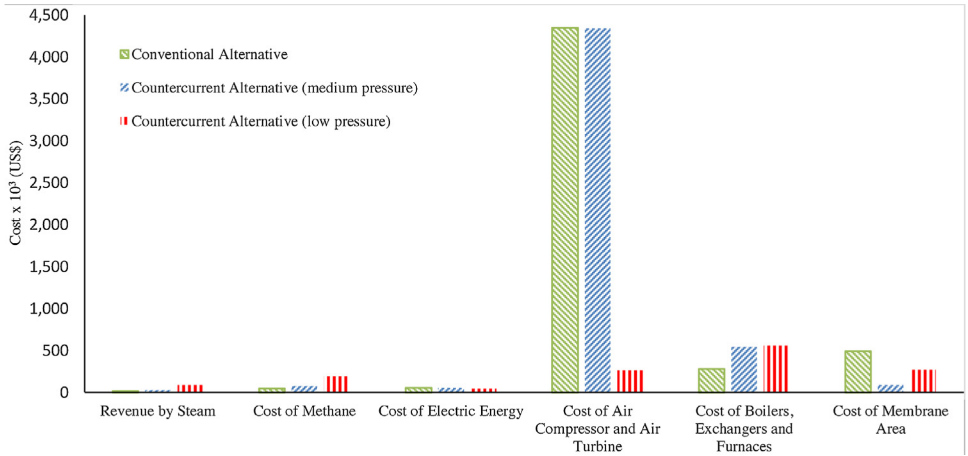

Fig. 21. Relative weights of different cost items in the process alternatives analyzed.

countercurrent alternative). Regarding to the alternative at countercurrent configuration at low pressure, the cost of the compressor (there is no turbine) is very low comparing with the previous alternatives. In this case, the pressure is low and the air flow rate slightly higher. The membrane area is higher than in the countercurrent configuration at medium pressure (there is a lower driving force for oxygen), but lower that in the conventional configuration. For this alternative, the cost of the compressor, heat exchange equipment, and membrane are in same range, while in the previous alternatives, the main cost is represented by the compressors and turbines.

3. Conclusions

In this work, we studied the integration of ITM oxygen membranes with the autothermal reforming of ethanol, in both the traditional separation configuration and with ITM membrane modules used as a mass exchanger in a counter-current arrangement with a process sweep stream. We compared their performance in different flow sheet alternatives using Aspen Plus V 8.7. To the best of our knowledge, the use of ITM oxygen membranes in a countercurrent arrangement configuration to achieve the integration of oxygen production with autothermal reforming of ethanol has not been studied previously. The here proposed configuration reduced the Total Annualized Cost in about 27.3% compared to the conventional configuration with the same flow sheet configuration. Moreover, optimizing the operating conditions and ancillary structure of the counter-current integrated process to get a low pressure process, the Total Annualized Cost is reduced in 72.2% with respect to the conventional design.

These reductions in costs are an important incentive for further study on the use of ITM oxygen membranes in the counter-current arrangement with process sweep streams. Also, as ITM oxygen membranes are the subject of several R&D projects, it is expected that in the near future they will improve their permeability and will substantially reduce their cost.

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