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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.

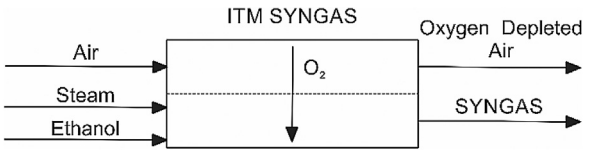


**Fig. 1.** ITM Syngas Membrane Configuration.

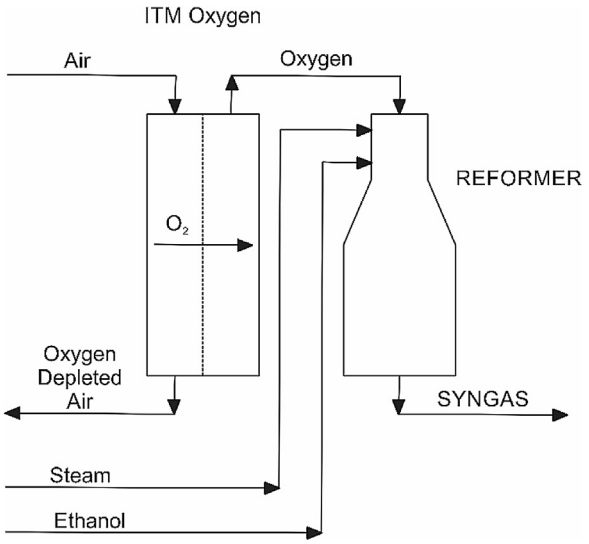


**Fig. 2.** ITM Oxygen Membrane in Conventional Configuration.

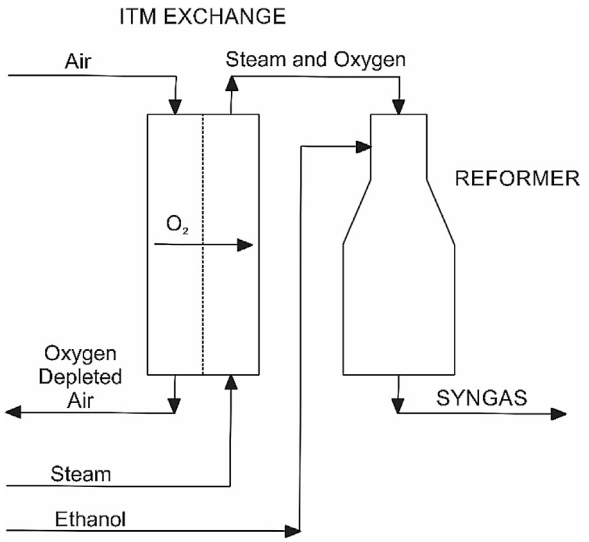


**Fig. 3.** ITM Oxygen Membrane in Counter-Current Configuration with a Process Sweep Stream.

## 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