

## Potential of Membrane Operations in Redesigning Industrial Processes. The Ethylene Oxide Manufacture

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Ethylene oxide is a widely used petrochemical intermediate and its production is a representative example of selective catalytic oxidation of a valuable hydrocarbon feedstock (ethylene). The present trend of increasing production volumes, raw material costs and plant size for ethylene oxide manufacture justifies a continuous effort for improving production efficiency, according to a logic of sustainable growth and process intensification.

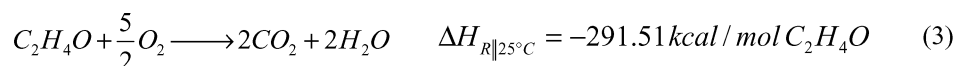
In the development of environmental friendly and highly efficient energy processes, membrane operations for both reaction and separation purposes are becoming a realistic alternative to conventional technologies due to an excellent flexibility to tolerate fluctuations in feed conditions, operational simplicity and reliability, absence of moving parts, low footprint and weight.

In the present study, the opportunity to integrate different membrane operations in the ethylene oxide manufacturing cycle for achieving benefits in terms of environmental impact and energetic aspects has been analysed. This approach would allow a better material utilization by a separation/recycle scheme and a safer distribution of the reactants, resulting also in a reduced loss of valuable components, waste streams production and lower utilities consumption.

### 1. Introduction

Ethylene oxide (EO) is one of the most important petrochemical intermediates with a global production and consumption both around 19 Mt in 2009. EO consumption is forecast to average growth of 5% per year from 2009 to 2014, and around 3% per year from 2014 to 2019. The major application for ethylene oxide is in the manufacture of (mono) ethylene glycol, which accounts for more than 70% of total EO consumption. Production of ethoxylates consumes another 11%, and smaller amounts are used to make higher glycols, ethanolamines, glycol ether, and polyols (Devanney, 2010).

Today, EO is mainly manufactured by catalytic direct oxidation of ethylene. Depending on the source of the oxidizing agent, it is possible to distinguish two different options: air- and oxygen-based processes. In the first process, air or oxygen enriched air streams are fed to the reactor, whereas in the second process oxygen at purity level higher than 95% is used. The main reactions involved in the EO synthesis on silver supported catalysts are the following:



Industrial reactors operate under recycle conditions in packed-bed multitubular configuration at 200-300°C and 10-20 bar. In order to guarantee a high selectivity and to keep the gas reaction composition outside of the flammable region, the per pass conversion is maintained low. Methane is typically added to the feed stream in the oxygen-based process as a diluent in order to shift the flammable limit (Othmer and Kirk, 2004). As a feature of partial oxidation processes, the total ethylene oxidation is much more exothermic than partial oxidation causing hot spots and catalyst deactivation. Therefore, catalyst inhibitors such as halides are used for suppressing the undesirable oxidation of ethylene to carbon dioxide and water without altering the primary reaction.

Membrane operations can be beneficially integrated at different levels in a petrochemical plant as already shown for an ethylene production plant by steam cracking (Bernardo et al., 2004). Membrane processes have several advantages than many other conventional separation techniques (e.g., distillation, extraction, absorption and adsorption). They are compact and easy to scale-up, fully automated and with no moving parts; they do not require energy-intensive phase changes or potentially expensive adsorbents and/or difficult to handle solvents (Bernardo and Drioli, 2010; Clarizia, 2009).

In the present analysis, membrane operations, replacing both conventional separation and reacting units, are proposed in order to redesign the ethylene oxide manufacture. This strategy follows a logic of process intensification and is aimed at reducing equipment volumes, as well as material and energy consumption and waste production.

## 2. Description of the approach

Typically, in industrial production cycles, the enhancement of process productivity is accomplished by new catalysts and reactor engineering improving. An alternative approach, discussed in the present study, is based on the implementation of new reactor concepts such as membrane reactor or the integration of membrane units, less depending on large scale economy, in the conventional production cycles.

In both EO processes it is possible to distinguish three main strictly related sections:

- a) reaction system, constituted by a series of packed bed reactors in order to enhance the global conversion and handle the reaction heat;
- b) EO recovery, carried out by means of adsorption and stripping towers;
- c) EO purification, performed in distillation columns.

The proposed membrane units, localized in all the different sections of the plant, are the following:

- Gas separation membrane systems to recovery valuable raw material ( $C_2H_4$ ), undesired product ( $CO_2$ ) and additional components ( $CH_4$ , Ar, etc.), and to enrich the  $O_2$  concentration in the feed stream;
- Membrane contactors for recovering EO and eventually  $CO_2$  as alternative to membrane gas separation;
- Membrane reactors for the conversion of ethylene to ethylene oxide.

Figure 1 is a schematic flow-sheet for the redesigned air-based process, while Figure 2 shows the opportunities for membrane systems in an oxygen-based process.

Membrane integration in existing plants  
*Air process*

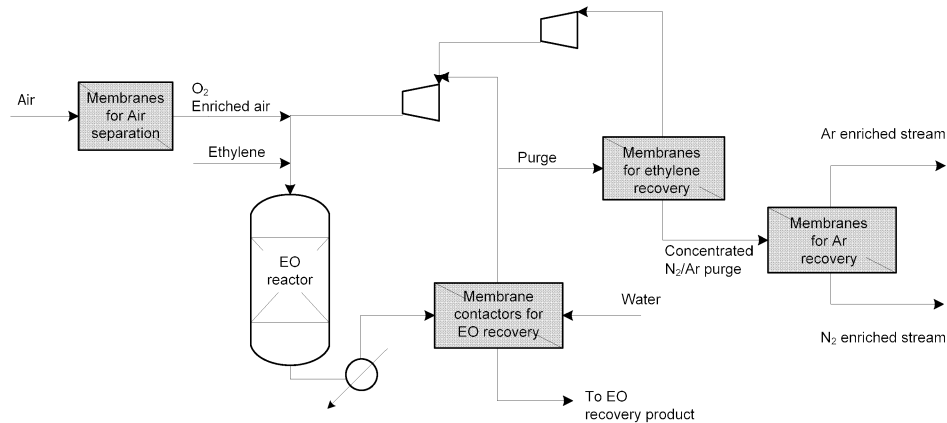


Figure 1. Membrane units in a simplified air-based ethylene oxide manufacture plant.

Membrane integration in existing plants  
*Oxygen process*

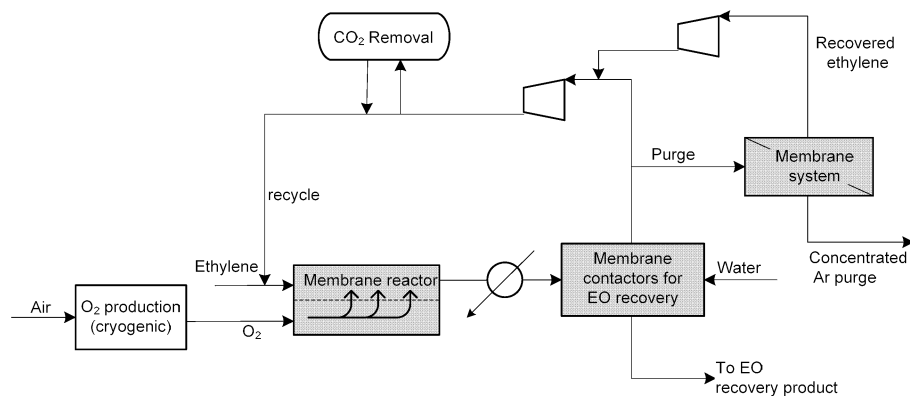


Figure 2. Membrane units in a simplified  $O_2$ -based ethylene oxide manufacture plant.

Gas separation systems equipped with polymeric membrane modules are already commercially available for recovering some unreacted ethylene from the reactor purge streams (Baker, 2008); at the same time similar separation systems can be integrated in order to obtain oxygen enriched air instead of cryogenic or pressure swing adsorption air separation units in the air-based process, for CO<sub>2</sub> removal or Argon recovery from the purge in the O<sub>2</sub>-based alternative.

The first option (purge treatment) gives the opportunity to reduce hydrocarbons losses (*e.g.*, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>) with a resulting lower make-up into the reactor. As a consequence of increasing ethylene price and more stringent environmental restrictions, significant cost savings can be achieved, particularly in large size plants, as showed in Table 1.

*Table 1: Economy of the ethylene and methane recovered in EO manufacture process.*

		<b>2005</b>	<b>2010</b>
<b>Ethylene recovery (75%)</b>	130 kg/h	620,000 \$/y	1.05 million \$/y
<b>Methane recovery</b>	70 kg/h	215,000 \$/y	121,500 \$/y

The recovery data are taken from Jacobs and Billig (2005), but the prices for ethylene and methane are updated at present. Ethylene price passed in only 5 years from \$500/ton to \$990/ton and thus its recovery becomes very economically interesting even if the methane (natural gas) price, in the same period, is reduced from \$7/1000 ft<sup>3</sup> to ca. \$4.5/1000 ft<sup>3</sup>. At the same time, the membrane integration approach represents a valuable action of environmental protection, avoiding hydrocarbon incineration. These vent streams represent a significant opportunity for recovery and recycling of raw materials.

The operations of scrubbing/absorption, employed in the plant separation section for the EO recovery, can be successfully accomplished in membrane contactor systems, which are much more compact than traditional packed towers. In fact, the polymeric membrane facilitates a controlled flow of gas into the solvent and provides high gas-liquid contact surface area. This physical separation of the liquid and gas flows eliminates foaming and channelling problems that can occur in classical solvent absorption processes. On the basis of a more efficient contact between gas and liquid phases as discussed by Stanojevic et al. (2003), a reduction of the volume of equipment and a decrease of the transfer unit values occur. Similar systems are usually considered in CO<sub>2</sub> separations: in this case the transfer of carbon dioxide through a non-selective membrane before chemically absorption into a solvent is involved. Therefore, these advantages can be achieved also in O<sub>2</sub>-based EO plants concerning the CO<sub>2</sub> removal section.

The above considered membrane systems are all developed at a commercial stage, while less diffuse is the industrial use of membrane reactors. As proved on laboratory scale (Mallada et al., 2000), partial oxidation processes can benefit from the adoption of an inert membrane reactor configuration in which a mesoporous ceramic membrane is used for the controlled addition of the oxidant. Not only side reactions are reduced, and thus selectivity is enhanced, but reaction rate is controlled and it is possible to select the

operating conditions to maintain the oxygen concentration in the reaction zone below the minimum value for explosion. In this way, the formation of explosive mixtures inside the reactor may be avoided, irrespective of the concentration of the hydrocarbon. In the EO process, the application of this new concept of reactor should be effective to restrict flammability range, avoiding the use of inert components to dilute the feed gas mixture. Furthermore, taking advantage of the specific capability of these devices to couple mass and heat transport between feed-retentate and permeate sides, the downstreams exiting from the reactor keep the thermal requirements for the subsequent purification steps. On the other hand, the membrane reactor type suggested for this application is characterized by a competitive cost, differently from the still expensive Pd-based membrane reactors widely investigated for H<sub>2</sub>-involving reactions (dehydrogenation reactions). In addition, an appropriate catalyst distribution is easier in these reactors to fit the kinetic of the desired reaction subtracting the oxidant from the reaction ambient after EO generation. As discussed by Bernardo et al. (2010), membranes are successfully applied to the production of oxygen enriched air to be used in chemical and related industries, in the medical field, food packaging, etc. In industrial furnaces and burners, OEA (25-35% O<sub>2</sub>) injection results in higher flame temperatures and reduces the volume of parasite nitrogen to be heated; this means lower energy consumption. In EO air-based process, the use of oxygen enriched air reduces the nitrogen presence in the recycle approaching the performance of O<sub>2</sub>-based process without the drawback of more restrict flammability ranges.

### 3. Conclusions

Petrochemical industry, which is highly energy and capital intensive, might significantly benefit from innovative technologies such as membrane operations, owing to the necessity of meeting stringent environmental standards, to control production cost and final products quality. Thus, in analogy with other applications where membrane units have been proved effective for improving the efficiency of industrial productions, their use in EO manufacture is suggested. A more controlled O<sub>2</sub> supply in a membrane reactor favours the desired reaction and reduces the flammability range, improving the safety of the process. The potential increase of reactor cost is balanced by the enhancement of the selectivity for the process. In the EO recovery section the more efficient contact between the gas and liquid phases in membrane contactors determines a lower unit size with respect to conventional absorption/stripper towers, avoiding flooding and channeling phenomena. A moderate oxygen enrichment of air can be performed more efficiently by membranes than by pressure swing adsorption and by cryogenic techniques due to the higher capability to tolerate changes in productivity of existing plants. Membrane gas separation is an efficient system to recovery unconverted ethylene, methane and also argon from the purge stream reducing hydrocarbon losses with benefits in terms of environment protection and cost saving. CO<sub>2</sub> removal from the oxygen-based cycle can be performed by membrane contactors or gas separation membranes as alternative to a conventional hot K<sub>2</sub>CO<sub>3</sub>-based absorption process.

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