# Achieving ethylene efficiency

Marc L. Jacobs, Membrane Technology & Research Inc., USA, and Barry J. Billig, Scientific Design Company Inc., USA, discuss a membrane process to recover ethylene in EO and VAM plants.

Ethylene oxide (EO) and vinyl acetate monomer (VAM) are produced by catalytically reacting oxygen and ethylene. Methane is added as a diluent to ensure that the reactor is operating outside of the explosive range. As only a fraction of the feed reacts during a single pass through the reactor, the unreacted gas is recycled back to it, and because both oxygen and ethylene are not 100% pure, process contaminants such as argon from the oxygen and ethane from the ethylene build up over time. These must be purged from the reactor to control their composition. However, when these impurities are purged, ethylene and methane are also lost. Given that ethylene is an expensive feedstock ranging between US$ 400 - 800/t, losses represent a substantial operating cost. For a 300 000 tpy ethylene oxide plant the ethylene loss in the argon purge represents close to US$ 1 million/y. For a similar size VAM plant, ethylene losses are even greater. These represent a significant opportunity for recovery and recycling of raw materials. In some cases, a portion of the methane may also be recovered and recycled in the process, providing further savings.

Membrane Technology and Research Inc. (MTR), based in Menlo Park, California, USA, has developed a membrane based process called VaporSep to separate and recover ethylene from argon in EO and VAM plants. The enabling technology is a polymeric membrane that selectively permeates hydrocarbons such as ethylene but not light gases such as argon. More than 60 clients now use this technology in polyethylene, polypropylene and polyvinylchloride plants. This article describes how the process is applied in EO and VAM plants, as well as looking at case studies of ethylene recovery units (ERUs) that have been installed.

## VaporSep membranes

In most gas separation membranes, the separation is accomplished primarily by using differences in diffusion rates due to differences in molecular size. In contrast, the VaporSep membrane separates due to differences in solubility; the membrane allows large hydrocarbon molecules to permeate much faster than smaller molecules such as nitrogen, hydrogen or argon. This counter intuitive performance is due to the higher solubility of large hydrocarbon molecules in the membrane polymer compared to the light gases.

The membrane is a thin film composite that is 10 - 100 times more permeable to hydrocarbon compounds than to argon. It consists of three layers (Figure 1): a nonwoven fabric that serves as the membrane substrate; a robust, solvent resistant microporous support layer that provides mechanical support; and a nonporous, selective layer that performs the separation. The selective layer is cross linked to the microporous layer, thus preventing any delamination or separation of the two layers.

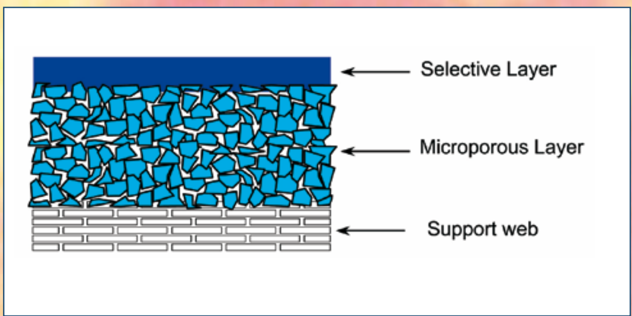


**Figure 1. The VaporSep membrane.**

**Table 1. EO ERU performance summary**

| | |
|---|---|
| Ethylene recovery (#/hr) | 290 |
| Ethylene recovery (%) | 75 |
| Value of recovered ethylene (US$/y)* | 620 000 |
| Methane recovered (#/hr) | 150 |
| Value of methane recovered (US$/y)** | 215 000 |
| System cost (US$) | 550 000 |
| Simple payback (months) | < 8 |

**Based on US$ 500/t  ** Based on $ 7.00/1000 ft³*

The flat membrane sheets are packaged in a module that is spiral wound (Figure 2), a common technique used to produce membrane modules for water purification applications such as reverse osmosis. To fabricate a module, the membrane sheet is initially cut to a specific length and folded in half. A spacer material is placed inside to create a flow channel for the permeate stream and the edges of the membrane envelope are glued together. The membrane envelope is then wrapped and secured in place around the collection pipe. This process is repeated with additional membrane envelopes separated by spacers until the specified mass transfer area of the module is reached.

In the module, the gas enters and flows into the feed channel. Hydrocarbons such as ethylene permeate through the membrane only once before the gas spirals inward to a central collection pipe. Argon and other light gases are rejected and exit as the residue stream. The membrane modules are placed into pressure vessels and configured in series and parallel flow combinations to meet the requirements of the particular application.

The membrane based systems are supplied as complete, skid mounted packages. The skid includes the membranes and their pressure vessels, plus additional components such as heat exchangers, gas liquid separators and the instrumentation and control necessary for optimal performance. The systems are compact and contain no moving parts, making installation simple and inexpensive.

## EO case study

Ethylene oxide is one of the most important commodity chemicals in the world today. Current production is more than 14 million tpy and the annual growth rate is expected to be close to 7%. Typically, it is produced through the catalytic oxidation of ethylene with 99.6+% pure oxygen. The application of the membrane within the ethylene oxide production process is shown in Figure 3. Ethylene, oxygen and methane are fed into the reactor. Methane serves to ensure that the reactor is operating in a safe condition, outside the region where explosions and unwanted levels of combustion are attained during the reaction. Ethylene oxide is produced along with $CO_2$ and water as byproducts. The mixture is sent to the water based scrubber to recover the ethylene oxide. After the $CO_2$ is removed by absorption with hot potassium carbonate, ethylene and oxygen makeup are added to the unreacted gases and are recycled back to the reactor. Due to the presence of impurities such as argon in the oxygen and ethane in the ethylene, a portion of the gases in the reactor loop are purged to control the concentration in the reactor feed. Traditionally, this stream is used as fuel in a boiler or incinerator.

The purge gas contains approximately: 20 - 30% ethylene; 10 - 12% argon; 1 - 10% $CO_2$; 1 - 3% ethane; 50% methane; and 4 - 5% oxygen. This purge gas enters the membrane system at approximately 20 bar and 30 ˚C. Ethylene preferentially permeates the membrane, producing an ethylene enriched permeate stream and an argon enriched residue stream. The permeate stream is then recompressed back into the reactor loop via the reclaim compressor, which is typically part of a standard ethylene oxide unit and is used to recover

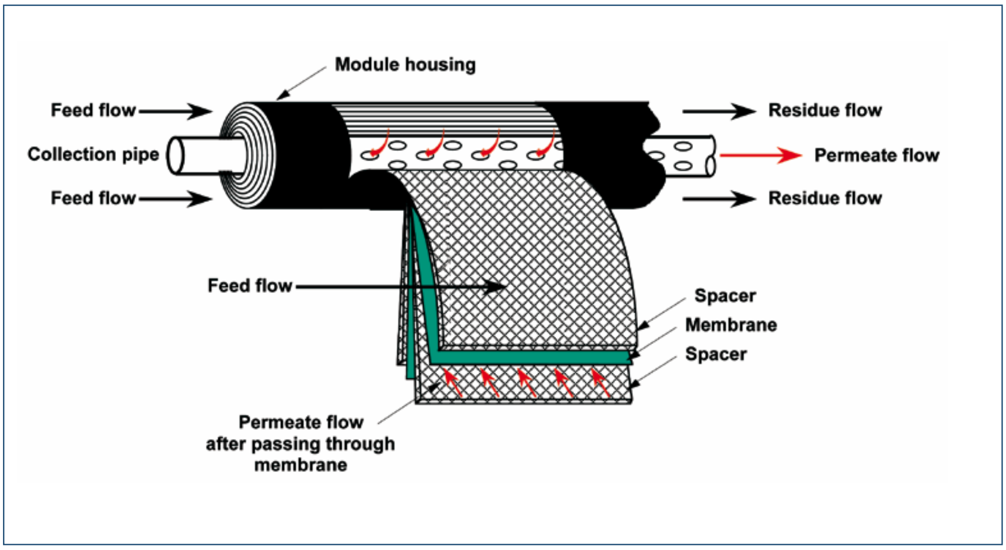


**Figure 2. The spiral wound module.**

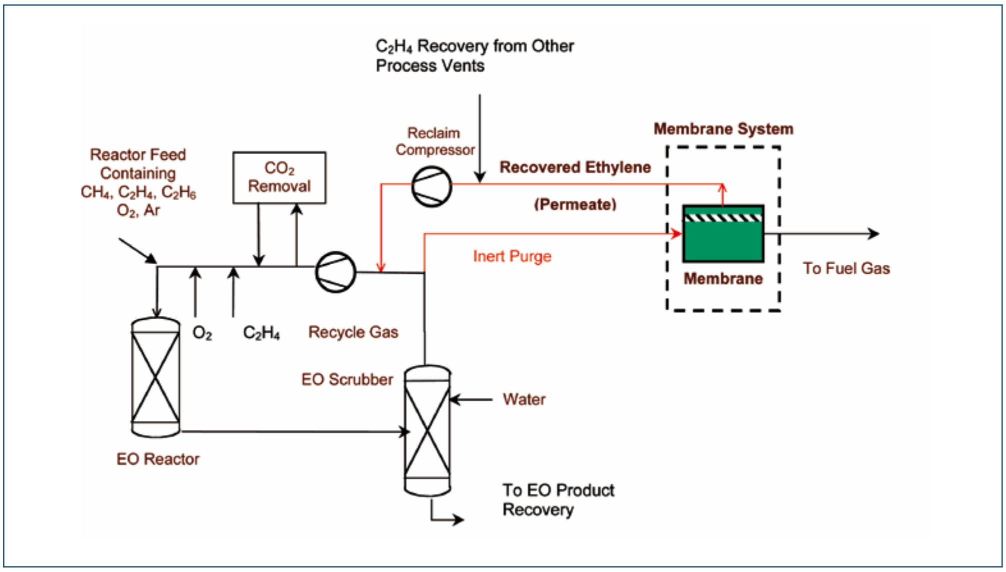


**Figure 3. Schematic of EO plant ERU.**

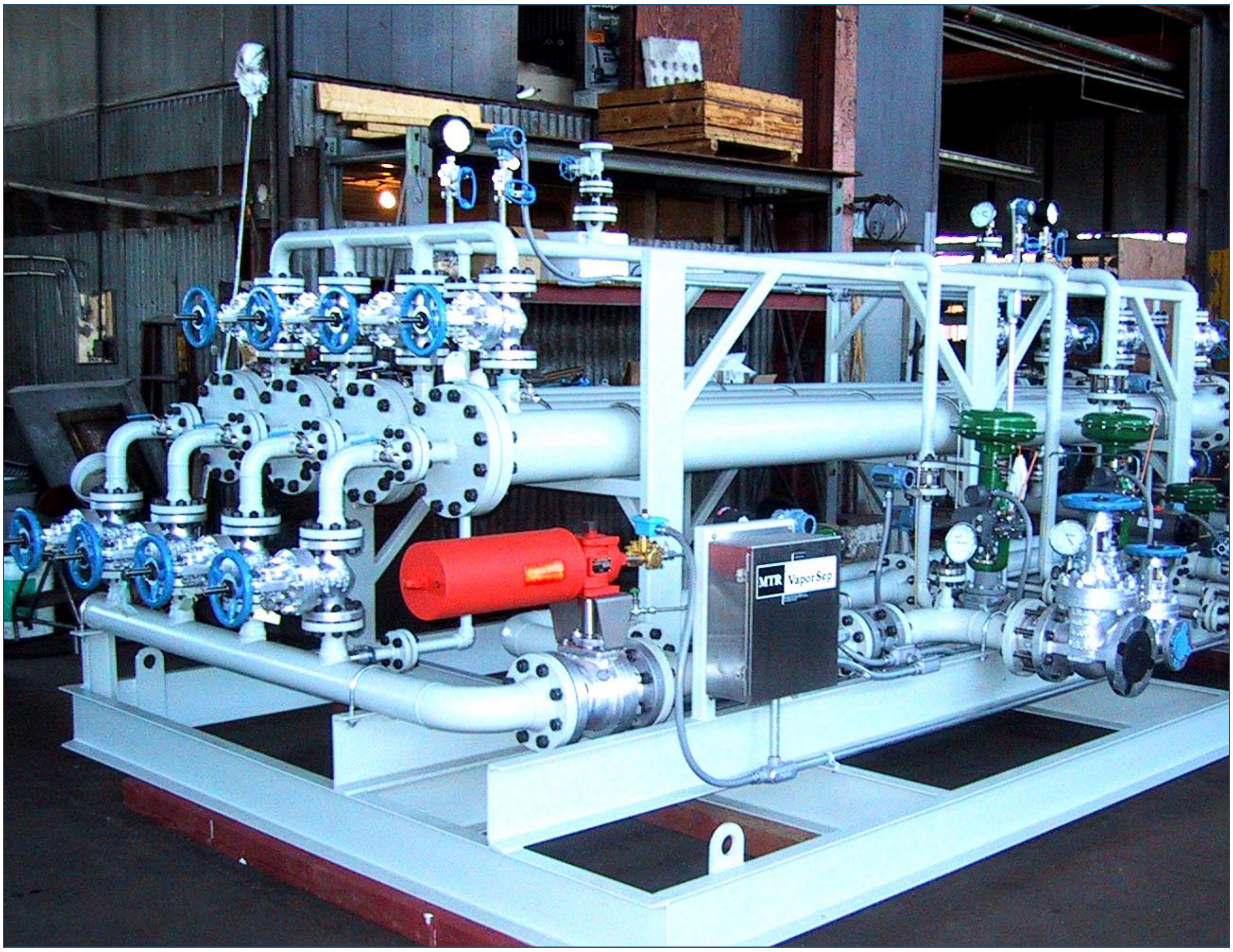


**Figure 4. An ethylene recovery unit.**

ethylene from other process vent streams. As ethane also preferentially permeates the membrane, there is the potential for buildup of ethane in the system. However, this buildup is mitigated by two factors: the ethane concentration in polymer grade ethylene is very low; and, as long as the recovery of ethylene is not too high (greater than 90%), the remaining ethane will be removed from the reactor loop through the residue stream. Based on actual field data from operating units, no ethane buildup has been observed. The residue stream, which has been stripped of the ethylene, is used in a boiler or incinerator.

The design of the ERU is summarised in Table 1. The system cost was approximately US$ 550 000, resulting in a simple payback time of less than eight months. The ERU is also easily installed in existing plants and as the ERU involves no additional mechanical machinery, it adds no complication to the existing plant operation.

## VAM case study

Vinyl acetate is another important commodity chemical, with production in excess of 4 million tpy. It is produced by bubbling ethylene gas up through acetic acid and combining this mixture with oxygen. The gases leaving the reactor are cooled, partially condensing the mixture, with the condensed liquid then purified in the distillation section downstream. The vapour is first sent to the $CO_2$ removal system and then returned to the reactor where the unreacted gases are combined with the feed gases. Similar to ethylene oxide, a purge stream from the reactor loop must be provided to remove argon, ethane and any other impurities. For VAM production, the purge gas contains a much higher concentration of ethylene (more than 65%), and the remaining components are $CO_2$ (20%), argon (5%) and methane (10%). The feed pressure and temperature are 10 bar and 35 ˚C, respectively. Table 2 summarises the performance of the ERU, which provides a payback of less than nine months.

**Table 2. VAM ERU performance summary**

| | |
|---|---|
| Ethylene recovered (#/hr) | 460 |
| Ethylene recovery (%) | 70 |
| Value of ethylene (US$/y)* | 980 000 |
| System cost (US$) | 700 000 |
| Simple payback (months) | < 9 |

** Based on US$ 500/t for ethylene*

## Conclusion

VaporSep systems have been successfully applied to both EO and VAM plants for the separation and recovery of ethylene from argon. The systems provide many important benefits. Hydrocarbon recovery is 70% or higher, and a portion of the diluent gas, methane, is also recovered. Payback times are short, in the range of 5 - 12 months. Hydrocarbon burning is reduced.

The recovery units (Figure 4) are supplied as a complete skid mounted package, minimising installation costs. No moving parts were required. Currently, seven VaporSep units are operating in EO and VAM plants. The cumulative operating experience of these units is more than 15 years, and one ERU has been in service for more than five years, without requiring any membrane replacement. ■