Maximising membranes

Marc L. Jacobs and Douglas E. Gottschlich, Membrane Technology & Research, Inc., USA, **discuss two casestudies of hydrocarbon recovery systems installed and operated by polyethylene producers in the USA.**

The single largest operating cost in the manufacture of polyethylene is the cost of the feedstock. In the case of a gas phase polyethylene plant, which produces either high density polyethylene (HDPE) or linear low density polyethylene (LLDPE), the feedstock is typically a combination of monomers such as ethylene, butene and hexene-1. For a liquid or slurry phase polyethylene process producing HDPE, the feedstock is ethylene, hexene-1 and a diluent such as isobutane used to keep the catalyst and polymer in solution. Typical plant efficiency, as measured by the lb of feedstock or monomer per lb of polymer produced, ranges from 1.025 - 1.050 (with a theoretical limit of 1.00). The difference between these efficiency values and the theoretical limit is primarily due to vent streams, which are not recovered in the process. Since polyethylene is a commodity polymer, producers compete mainly on price. As a result, plant profitability is strongly influenced by operating efficiency. Based on the average monomer cost of US$ 300/t, the difference in efficiency between 1.025 and 1.050 for a 300 000 tpy plant represents more than US$ 2.2 million/yr in lost monomer. These losses represent a significant opportunity for recovery and recycling of raw materials. In addition to monomers, nitrogen is another raw material that is used in both gas phase and slurry phase polyethylene processes. By purifying the nitrogen and recycling it back into the process, additional savings can be made. Furthermore, recovery of hydrocarbons provides the environmental benefit of reduced flaring. In some urban areas where emission restrictions are becoming more stringent, this benefit can represent real savings.

Membrane Technology and Research, Inc. (MTR) based in the USA, has developed a membrane based process called VaporSep® to separate and recover hydrocarbons and nitrogen. The enabling technology is a polymeric membrane that selectively permeates hydrocarbons, compared to light gases such as nitrogen and hydrogen. This article describes how the process has been applied in polyethylene plants. Two casestudies of VaporSep units, which have been installed and operated by polyethylene producers in the USA, will be discussed in detail.

Separation of membranes

In most gas separation membranes, the separation is accomplished primarily by differences in diffusion rates according to variations in molecular size. In contrast, the VaporSep membrane separates according to differences in solubility. This membrane behaves in a counterintuitive manner by allowing large hydrocarbon molecules to permeate much faster than smaller molecules such as nitrogen, hydrogen or methane. The behaviour 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 nitrogen. A cross section is shown in Figure 1. The membrane consists of three layers: a non woven fabric, which serves as the membrane substrate; a robust,

Table 1. INRU performance summary		
Feed composition (No./hr)	Nitrogen	2800
	Ethylene	30
	Isobutane	1000
	Hexene-1	170
	Total	**4000**
Isobutane recovery (%)		> 99.5
Annual value of isobutane* (US$ 000)		1300
Nitrogen recovery (%)		65
Nitrogen purity (volume %)		99.9
Annual value of nitrogen** (US$ 000)		200
Power required (kW)		370
Installed cost (US$ 000)		2500
Simple payback (months)		20
*Based on US$ 300/t. **Based on US$ 30/t.		

Table 2. Hydrocarbon recovery unit performance summary		
Feed composition (No./hr)	Nitrogen	200
	Ethylene	300
	Butane	300
	Total	**800**
Hydrocarbon recovery (%)		> 90
Annual value of hydrocarbons* (US$ 000)		700
Installed cost (US$ 000)		400
Simple payback (months)		7
** Based on US$ 300/t for ethylene and butene.*		

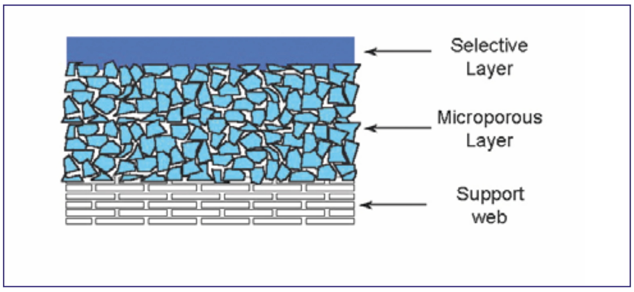

Figure 1. The VaporSep membrane.

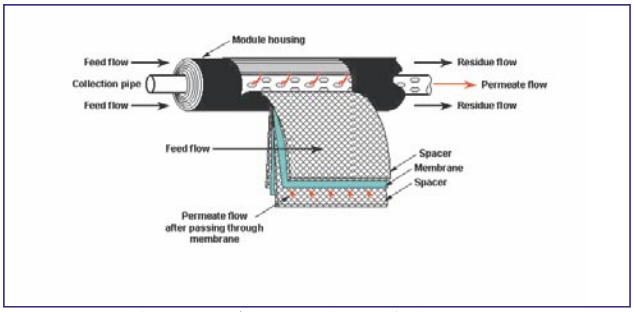

Figure 2. The spiral wound module.

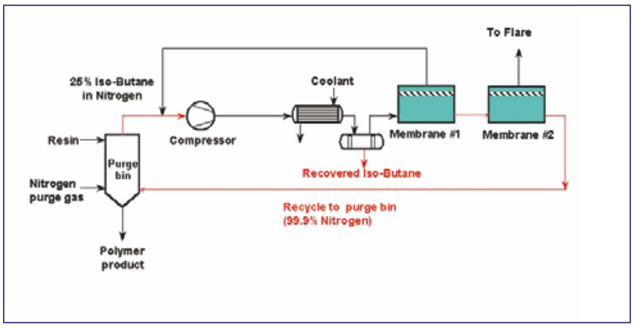

Figure 3. Diagram of INRU.

solvent resistant microporous support layer, which provides mechanical support; and a dense, defect free selective layer, which performs the separation. The selective layer is cross linked to the microporous layer, thus preventing any delamination or separation of the two layers.

The membrane is produced as a flat sheet and then packaged into the arrangement shown in Figure 2. This type of packaging is referred to as a spiral wound module. Spiral wound is 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, creating a membrane envelope. A spacer material is placed inside to create a flow channel for the permeate stream, and the edges of the envelope are glued. The 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 diameter and area of the module are reached. In the module, the gas enters and flows into the feed channel. The hydrocarbon only permeates the membrane once and then the gas spirals inward to a central collection pipe. Nitrogen 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 a particular application.

MTR supplies membrane based systems as a complete, skid mounted package. The skid can include only the membranes and their pressure vessels, or additional components such as rotating equipment (compressors and pumps), heat exchangers, gas/liquid separators and other items necessary for optimal performance. The systems are compact and contain few (if any) moving parts, making installation simple and inexpensive.

The casestudies described below represent two very different ways of using the VaporSep membranes. In the first example, a large membrane system treats a low pressure stream to recover hydrocarbons and nitrogen. The system includes a compressor, heat exchangers and PLC based control system. In the second example, a small membrane system treats a high pressure stream to recover ethylene and other hydrocarbons. This system consists of the membranes plus a small pretreatment section.

Resin degassing casestudy

In the liquid slurry polyethylene process, ethylene, hexene-1 and isobutane are contacted in a reactor to produce polyethylene. The raw polymer product is produced in powder form and contains significant quantities of unreacted monomers and diluent. These hydrocarbons must be removed before the polymer can be extruded and shipped to the customer. The final step in hydrocarbon removal uses hot nitrogen in a stripping column known as the purge column. Some plants use a conventional approach to recovery with high pressure and low temperature condensation. In this case, only a portion of the hydrocarbons and none of the nitrogen is recovered. In many other plants, because of the expense and moderate recovery of the condensation process, the vent gas from the purge column is sent to the flare, and both the hydrocarbon and nitrogen content are lost.

A diagram of the process used to separate and recover the hydrocarbons and nitrogen from the purge column offgas is shown in Figure 3. The system is referred to as the isobutane nitrogen recovery unit (INRU). The process is a combination of compression, condensation and membrane vapour separation. The feedstream from the purge column is initially compressed by an oil flooded screw compressor to approximately 280 psia and then cooled to -13 ˚F. A portion of the hydrocarbons condenses and is separated from the remaining gas stream in a gas/liquid separator. The gas stream leaving the separator (which still contains a significant quantity of isobutane) is fed to the first membrane stage (membrane no. 1). This produces two streams: a low pressure hydrocarbon enriched permeate stream and a nitrogen enriched residue stream. The permeate stream is returned to the inlet of the compressor and the residue stream is further purified in a second membrane stage (membrane no. 2). This purifies the nitrogen to greater than 99.9 vol%.

The design of the INRU is summarised in Table 1. The installed system cost was approximately US$ 2.5 million, resulting in a simple payback time of 20 months, a very attractive investment. In addition to the financial incentive, eliminating or minimising the amount of hydrocarbons and nitrogen to be sent to the flare, reduces CO_2 and NOx formation, which represents a significant environmental benefit.

The INRU was commissioned in late 2001 and it has been in service for more than 12 months (Figure 4). Actual performance of the unit has been equal to or better than design.

Figure 4. Isobutane nitrogen recovery unit.

Reactor purge stream recovery casestudy

In a large number of processes, only a fraction of the feed reacts during a single pass through the reactor to form the desired product. As a result, the unreacted feedstock is recycled back to the reactor. In this recycle process, contaminants build up to unacceptable levels over time and must be purged from the reactor. However, in addition to the contaminants, monomers are also purged and their value lost.

In the manufacture of gas phase polyethylene, nitrogen is added to the reactor to convey the catalyst into it. The nitrogen must be purged from the reactor, taking a substantial quantity of ethylene and other comonomers with it. This stream is normally sent to the flare, resulting in significant monomer loss.

A diagram of the process used to separate and recover ethylene and butene from nitrogen is shown in Figure 5. The feedstream from the reactor enters the system at approximately 300 psig and 200 ˚F. The gas is filtered to remove polymer fines and then cooled to 90 ˚F. The gas enters the membrane, producing a hydrocarbon enriched permeate stream and a hydrocarbon depleted residue stream. The permeate stream is sent to the inlet of the existing reclaim compressor for recycle to the reactor, and the residue is sent to the flare. A summary of the system design is shown in Table 2.

Two VaporSep units were commissioned in mid 1998 and both units have been onstream for more than four years. A photograph of one of the units is shown in Figure 6. Membrane life has been more than four years, as the original membranes were replaced in Q3 2002. The units required no maintenance or operator attention prior to membrane replacement, which is a simple procedure requiring less than eight hours.

Conclusion

VaporSep systems have been successfully applied to both gas phase and liquid slurry polyethylene processes for the separation and recovery of monomers and nitrogen. The systems provide many important benefits.

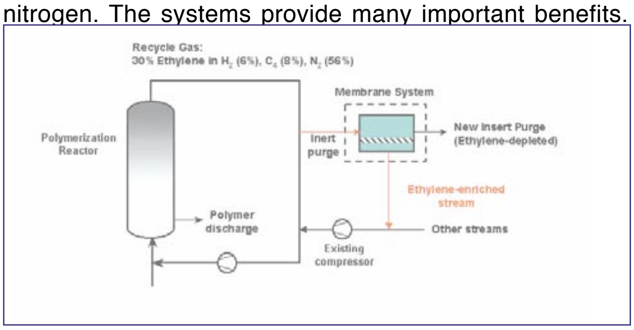

Figure 5. Diagram of hydrocarbon recovery unit.

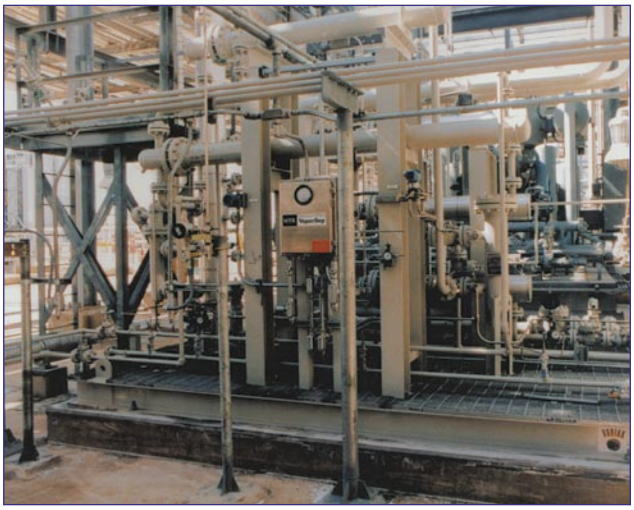

Figure 6. A hydrocarbon recovery unit.

Hydrocarbon recovery is 90% or higher depending on the value of the monomers. Nitrogen recovery is optimised based on its value, and ranges from 65 to 99% with purity of 99.9 vol%. Payback times are short, ranging from seven to 20 months; flaring is significantly reduced.

The recovery units are supplied as a complete skid mounted package, minimising installation costs. No moving parts were required for the hydrocarbon recovery unit, while only a single stage compressor was supplied for the INRU.

Currently, 17 VaporSep units are operating in polyethylene service. The cumulative operating experience of these units is more than 60 years and membrane life, on average, has been more than three years. ■