Monomer recovery in polyolefin plants

This article outlines the application in polyolefin plants of a membrane based process, VaporSep, for separating and recovering hydrocarbons from nitrogen – in particular, the treatment of resin degassing vent streams

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Chemical feedstocks, or monomers, such as ethylene and propylene, are the single largest operating cost in the manufacture of polyolefins. Due to the intensely competitive nature of the industry, monomer losses in vent streams are a major concern for producers. Typical losses for a plant range from 1 to 2 per cent of the feed and can account for 2000 to 4000 tons/year of lost monomer. Assuming a cost of $350/ton, these vent streams represent a significant opportunity for recovery and recycling of raw materials

A membrane-based process called VaporSep, to separate and recover hydrocarbons and nitrogen in polyolefin plants, has been developed by MTR. The process is based on a polymeric membrane that selectively permeates hydrocarbons, compared to light gases such as nitrogen and hydrogen. This article describes how the process is applied to resin degassing vent streams in polyolefin plants.

In conventional membranes, the separation is accomplished primarily by differences in diffusion rates due to differences in molecular size. In contrast, the VaporSep membrane separates on the basis of solubility.

This "reverse selective" membrane allows large hydrocarbon molecules to permeate much faster than smaller molecules such as nitrogen, hydrogen, or methane. The reverse selective effect is due to the higher solubility of large hydrocarbon molecules in the membrane polymer.

The membrane is a thin-film composite polymer that is 10 to 100 times more permeable to hydrocarbon compounds than to nitrogen. The membrane, shown in Figure 1, consists of three layers: a non-woven fabric which serves as the membrane substrate (support web); a tough, durable and solvent-resistant microporous layer which provides mechanical support without mass transfer resistance, and a non-porous, defect free selective layer which performs the separation.

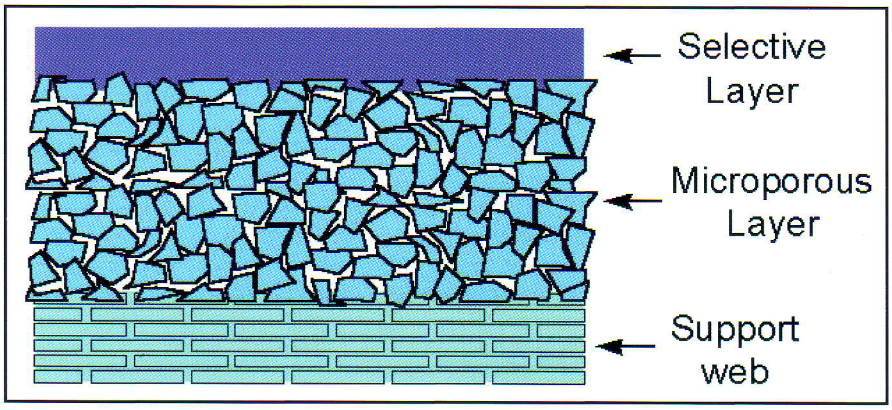

***Figure 1** The three-layer VaporStep membrane*

After manufacture as flat sheet, the membrane is packaged into a spiral-wound module, as shown in Figure 2. The feed gas enters the module and flows between the membrane sheets. Spacers are added on the feed and permeate side to create flow channels.

As the hydrocarbon preferentially permeates through the membrane, 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.

Resin degassing vent streams

In a typical polyolefin plant, propylene, ethylene, catalysts, and solvents are contacted at pressure in a reactor to produce polyethylene and polypropylene. The raw polymer product is produced in powder form and contains significant quantities of unreacted monomers and other raw materials.

These hydrocarbons must be removed before the polymer can be extruded and shipped to the customer. The hydrocarbons are removed from the powder by

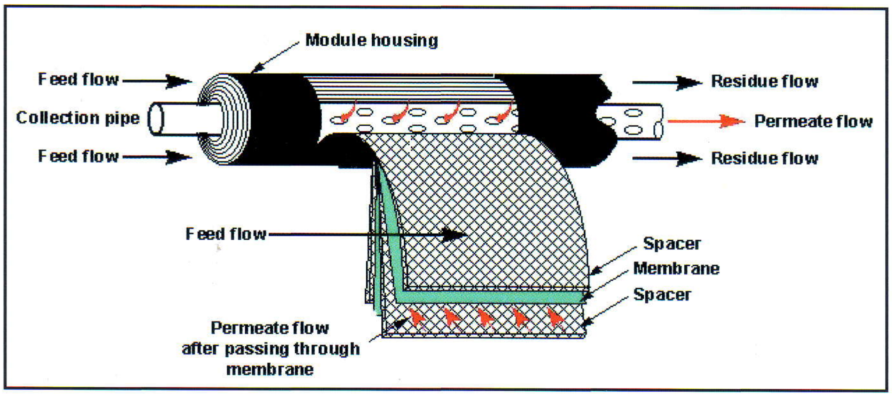

***Figure 2** How the membrane is packaged into a spiral-wound module*

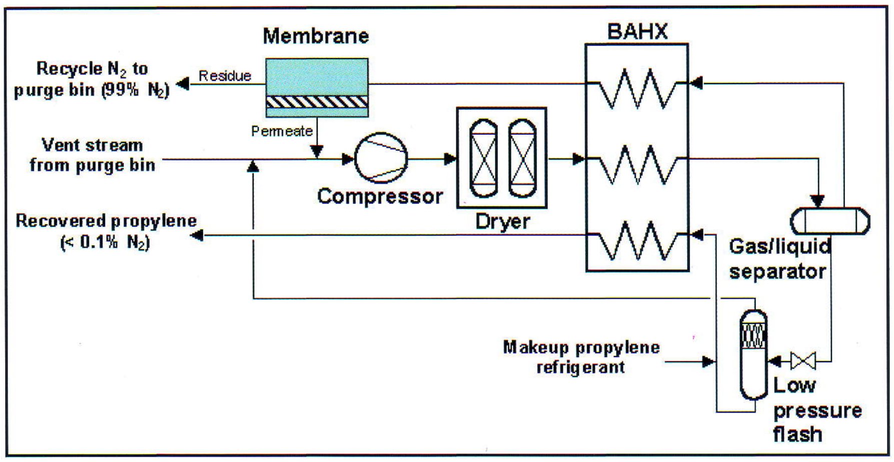

Figure 3 Schematic of propylene recovery unit

PRU performance	
Feed composition (#/hr)	
Ethane	7
Nitrogen	1730
Propane	230
Propylene	730
Water	3
Total	**2700**
Propylene recovered (#/hr)	715
Propylene recovery (%)	98
Nitrogen recovered (#/hr)	1729
Nitrogenrecovery (%)	99
Nitrogen purity (vol%)	99
Power consumption (kW)	330
Value of recovered nitrogen ($000/yr)*	300
Value of recovered propylene ($000/yr)*	1050
Capital cost ($000)	1700

*Based on $350/ton propylene and $40/ton nitrogen

Table 1

using hot nitrogen in a stripper column, also known as the purge bin. In many plants, the vent gas from the purge bin is sent to the flare and both the hydrocarbon and nitrogen content is lost.

In an average polyolefin plant, the value of the monomers in this stream is in excess of $1 million/year. In addition, the value of the nitrogen represents an additional $0.5 million annually. Beyond these monetary incentives, eliminating or minimising the amount of hydrocarbons to be sent to the flare provides meaningful environmental benefits.

Plant application

Eight propylene recovery units (PRU) have been constructed to separate and recover propylene and nitrogen in polypropylene plants. The process schematic for one of these units is shown in Figure 3. This scheme is referred to as the self-refrigerating cycle as the recovered liquid propylene is flashed and vaporised at a lower pressure to provide the refrigeration required by the process.

The propylene/nitrogen feed stream enters the PRU at atmospheric pressure. The gas is compressed by an oil-flooded, screw compressor to a pressure of approximately 200psig and then fed into a molecular sieve adsorbent dryer to remove moisture. The gas then enters a brazed aluminum heat exchanger (BAHX) and is cooled to approximately –25°C.

A portion of the propylene condenses inside the BAHX and the resulting two-phase mixture flows into the gas/liquid separator. The recovered liquid propylene stream is flashed to 15psig and vaporised to provide the refrigeration required. In addition, a small amount of additional propylene may be required to make up for heat gain and other system inefficiencies. This make-up propylene is approximately 5 per cent of the propylene in the feed gas. The gas stream from the separator (nitrogen and propylene vapour) flows back through the BAHX (for refrigeration recovery) and then enters the membrane section.

The membrane is much more permeable to hydrocarbons than to nitrogen, so the stream is separated into a purified nitrogen residue stream and a propylene-enriched permeate stream. The permeate stream is recycled back to the inlet of the compressor. The residue stream is sent back to the purge bin.

The advantages of this design are that virtually no refrigeration is required and that the recovered propylene contains a very low concentration of dissolved nitrogen (less than 0.1 vol%). The performance of this PRU is summarised in Table 1. Based on a value of $350/ton for propylene and $40/ton for nitrogen, this project has a payback time of only 15 months. An alternative to the process scheme in Figure 3 is to provide an

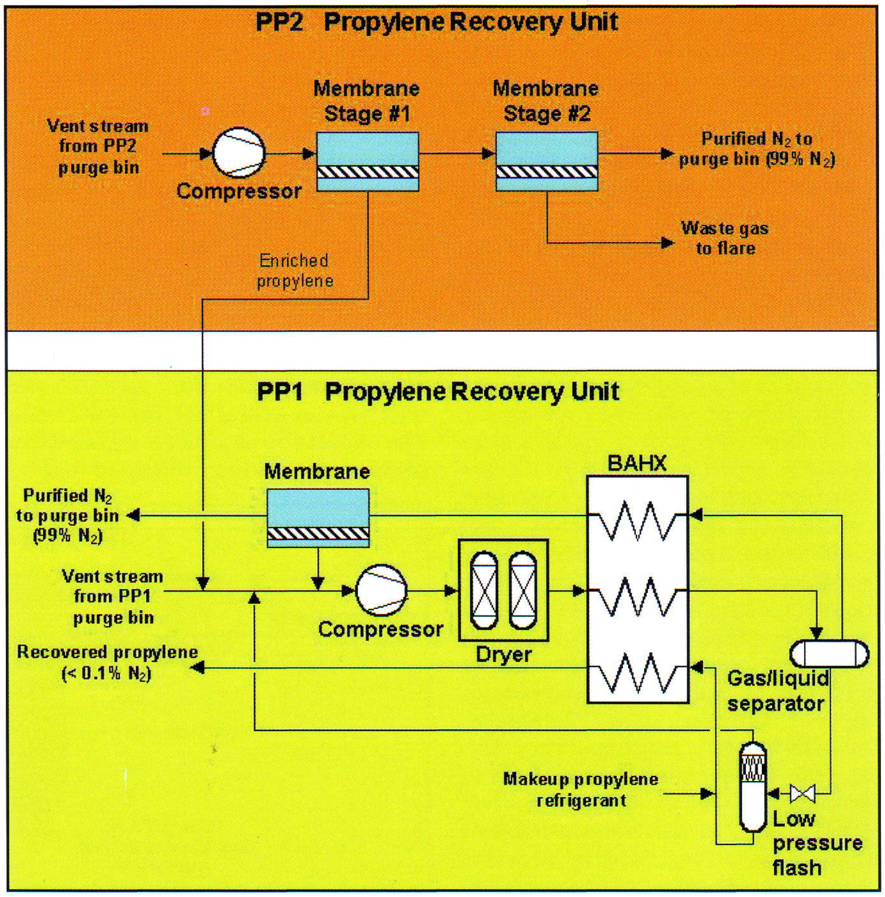

Figure 4 Process flow scheme of one of the propylene recovery units

external source of refrigeration. The propylene is then recovered as a high-pressure liquid, which may be sent directly to the reactor or to a distillation column for additional purification. In this case, the recovered propylene will contain close to 2 vol% dissolved nitrogen.

The process flow diagram for another PRU is shown in Figure 4. In this case, the customer had an existing PRU in his polypropylene plant No. 1 (PP1). Several years ago, the company decided to build a new polypropylene plant (PP2).

For this new plant, the company wanted to construct a membrane-based PRU and to improve the performance of the unit for PP1 with the addition of a membrane system. The existing unit for PP1 consists of a three-stage reciprocating compressor with a BAHX and uses the self-refrigerating cycle.

The unit recovers 80 per cent of the propylene in the feed, but since the nitrogen is only purified to 92 vol%, it is not pure enough to recycle to the purge bin and must be sent to flare. In addition to the 2000 pounds/hour of nitrogen that is lost, an additional 125 pounds/hour of propylene is also burned.

The total value of this stream is close to $400 000/year. The company also experienced difficulties with the compressor as the hydrocarbon concentration in the feed gas was too low and caused the compressor to overheat. To prevent overheating, propylene vapour was added to the compressor feed.

To avoid the expense of a completely new PRU for the new polypropylene plant No. 2, the customer planned to send the PP2 purge bin vent to the existing PP1 PRU. Although the PP2 unit had some excess capacity, it was not enough to handle the entire stream from PP1. The VaporSep system was therefore used to concentrate the stream from PP1 so that it could be handled by the PP1 PRU. An additional benefit of this scheme was that adding the concentrated scheme from PP2 eliminated the compressor overheating problem.

The feed stream from PP2 is initially compressed to 14bara and cooled to 35°C. The gas then enters the membrane section where it is separated into a propylene-enriched permeate and a nitrogen-enriched stream. This stream is further purified to 99 per cent in a second membrane stage and sent back to the purge bin. The permeate from the second membrane stage is sent to flare. The permeate stream from the first membrane stage is mixed with the feed from PP1 and sent to the existing PRU. By mixing the two streams, the hydrocarbon concentration is increased from 30 to 40 wt%. The increase in concentration solved the temperature problem in the compressor and allowed the company to eliminate the addition of propylene vapour. The gas is compressed to 400psig, cooled, and then partially condensed in the BAHX. The liquid and vapour are separated.

The liquid is flashed to 15psig and returned to the BAHX to provide cooling before being returned to the polypropylene process. The vapour is sent back through the BAHX and into the membrane section.

The purified nitrogen stream is recycled back to the purge bin, while the propylene enriched permeate is sent to the inlet of the compressor.

In summary, the combined membrane system provided four important benefits to the customer. First, propylene and nitrogen were separated and recovered from the new plant, PP2. Second, the propylene and nitrogen recovery performance of the existing PRU was enhanced. Third, the feed gas composition for the PP1 compressor was increased from 30 wt% hydrocarbon to 40 wt%, which eliminated the compressor overheating problem.

Finally, the payback time for the combination of PP1 and PP2 was less than one year. The performance of each PRU is shown in Table 2.

PRU performance

Feed composition (#/hr)*	PP1	PP2
Ethane	8	0
Ethylene	1	0
Nitrogen	1940	1750
Propane	14	180
Propylene	124	1220
Water	0	5
Total	**2087**	**3155**
Propylene recovered (#/hr)	107	1180
Propylene recovery (%)	87	96
Nitrogen recovered (#/hr)	1920	1440
Nitrogen recovery (%)	99	82
Nitrogen purity (vol%)	99	99
Power consumption (kW)	N/A	300
Value of recovered nitrogen ($000/yr)**	200	150
Value of recovered propylene ($000/yr)**	160	1750
Capital cost ($000)	400	1000

*The feed composition for PP1 is for the membrane section only
**Based on $350/ton propylene and $25/ton nitrogen

Table 2

Polyethylene plant application

In the manufacture of high density polyethylene (HDPE), the resin degassing vent stream contains a large quantity of iso-butane. Three butane recovery units (BRU) have been constructed to separate and recover iso-butane. The process design combines compression-condensation with membranes as shown in Figure 5. The hydrocarbon/nitrogen mixture enters the BRU. The mixture is compressed by an oil-flooded, screw compressor to a pressure of approximately 250psig and then fed into a shell and tube condenser. A portion of the hydrocarbons condenses inside the condenser. The two-phase, liquid/gas mixture flows into the high pressure liquid/gas separator.

The gas stream from the separator (nitrogen and hydrocarbon vapour) flows into the membrane modules, where it passes across the surface of the membrane. This membrane separates the stream into a hydrocarbon-depleted residue stream and hydrocarbon-enriched permeate stream.

The permeate stream is then recycled back to the inlet of the compressor. The residue stream, which is stripped of

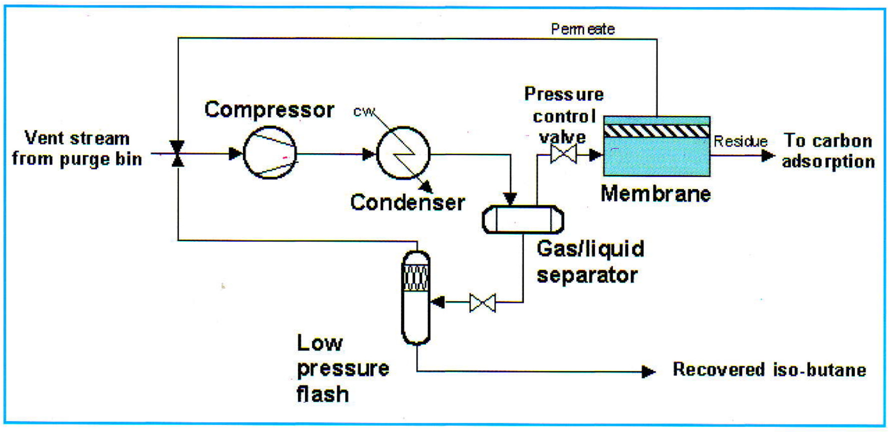

Figure 5 Process design combining compression-condensation with membranes

BRU performance	
Feed flow rate (#/hr)	4000–8000
Iso-butane feed concentration (wt%)	55
Iso-butane recovered (#/hr)	2300–3000
Iso-butane recovery (%)	66–98
CO_2 removal (%)	90–98
Power (kW)	400
Value of recovered butane ($000/yr)*	2200
Capital cost ($000)	1300

*Based on $175/ton iso-butane

Table 3

hydrocarbons, is sent to an existing carbon adsorption unit. To remove dissolved CO_2 from the recovered hydrocarbons, the liquid from the high pressure separator is flashed to 15psig in a low pressure separator. The vapour from the low pressure separator is recycled back to the inlet of the compressor, while the liquid is pumped up to 300psig and sent to a storage tank before recycle to the polyethylene process.

In addition to removal of CO_2 from the iso-butane liquid, the BRU was designed to accommodate a feed flow rate ranging from 4000 to 8000 pounds/hr. This design feature was accomplished by maintaining a high condenser pressure and allowing the membrane feed pressure to vary. The compressor capacity, which is fixed, is the sum of the feed flow rate and the permeate flow rate.

As feed flow rate increases, the membrane feed pressure decreases to reduce the membrane driving force and thus the permeate flow.

Alternatively, as the feed flow rate decreases, the membrane feed pressure increases to increase the membrane driving force and the permeate flow. A summary of the BRU performance is shown in Table 3. The simple payback time is less than 8 months, indicating a very attractive investment.

Conclusion

VaporSep has been successfully applied in polyethylene and polypropylene plants for the separation and recovery of monomers and nitrogen from resin degassing vent streams. The systems provide many important benefits. Hydrocarbon recovery is 90 per cent or higher, depending on the value of the monomers. Nitrogen recovery is optimised, based on its value, and ranges from 65 to 99 per cent, with purity of 99 vol%t. Flaring is minimised or eliminated completely. The recovery units are supplied as complete skid-mounted packages. The systems are simple, requiring at most a single stage compressor. Typical payback times are short ranging from six to 15 months.

Six VaporSep units are currently operating in resin degassing service and two units have been running for more than two years. Four additional units are expected to come onstream in the next few months. Other VaporSep applications in polyolefin plants include ethylene recovery from reactor purge streams and ethylene and propylene recovery from distillation column overhead streams.

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