Recovery of Valuable Feedstocks in the Polyolefin Industry Using Membranes

by

Marc Jacobs
Doug Gottschlich
Frank Buehner
David Koch

Membrane Technology and Research, Inc.
1360 Willow Road
Menlo Park, CA 94025-1516
(650) 328-2228

Prepared for Presentation at:
Spring AIChE National Meeting
Houston, Texas
March 9 - 11, 1999

Background

Due to the high cost of raw materials, efficient use of chemical feedstocks is a major concern in polyolefin manufacturing. For example, monomer loss from polyolefin plant vent streams typically ranges from 1 to 2 percent of the total plant feedstock. With 300 polyolefin plants worldwide, and total capacity in excess of 60 million tonnes per year, worldwide monomer losses are costing the industry nearly 500 million dollars per year.

Membrane Technology and Research, Inc. (MTR) has developed a membrane-based process to separate and recover propylene, ethylene, and other hydrocarbons from nitrogen in polyolefin plant vents. The process, called VaporSep®, uses a membrane that selectively permeates hydrocarbon vapors compared to nitrogen. This paper describes how VaporSep® is used to recover valuable monomers from resin degassing vent streams, distillation column vents stream, and reactor purge streams.

The membrane is a high flux, thin film composite type that is 10 to 100 times more permeable to hydrocarbons than to nitrogen. The membrane shown in Figure 1, consists of three layers; a non-woven fabric which serves as the membrane substrate; a solvent-resistant microporous support layer for mechanical strength; and a defect-free selective layer which performs the separation.

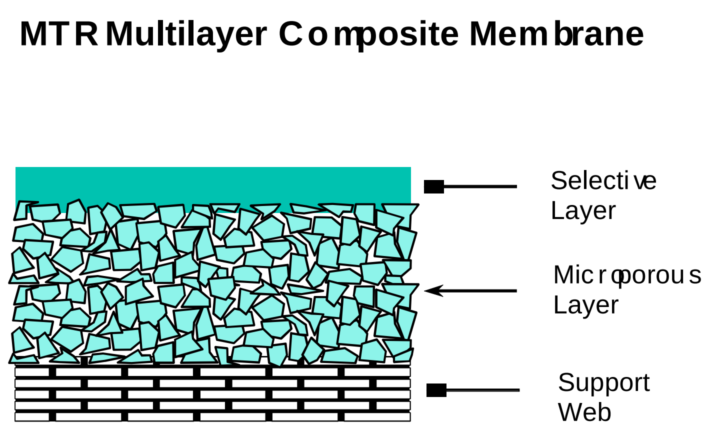

Figure 1

The membrane is manufactured as flat sheet and packaged into a spiral-wound module as shown in Figure 2. The feed gas enters the module and flows between the membrane sheets. Spacers on the feed and permeate side of the membrane sheets create flow channels. The hydrocarbon vapor preferentially passes through the membrane and spirals inward to a central permeate collection pipe. Nitrogen is rejected by the membrane and exits as the residue.

MTR Spiral Wound Module

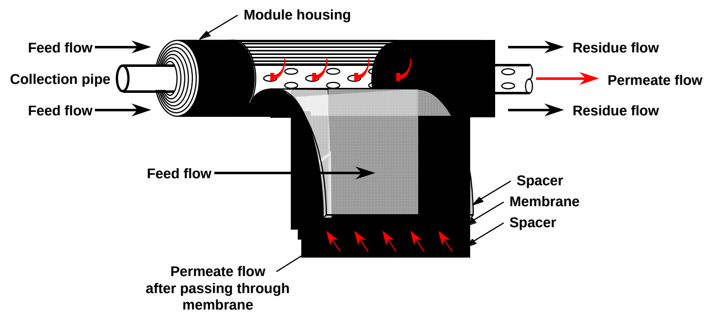

Figure 2

Resin Degassing Vent Streams

Raw polyolefin product is produced as a powder and contains significant amounts of unreacted hydrocarbons. Before the powder can be extruded, these unreacted hydrocarbons must be removed. The hydrocarbons are removed from the powder by 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 a typical polyolefin plant, the value of the monomers in this stream is in excess of $1 million per year. Moreover, the value of the nitrogen represents an additional $0.4 million annually.

In the manufacture of High Density Polyethylene (HDPE), the resin degassing vent stream contains a substantial quantity of iso-butane. Two butane recovery units (BRU) to separate and recover iso-butane have been installed in the Gulf Coast. The process design combines compression-condensation with membranes as shown in Figure 3.

The feed stream is compressed to 13 Bara and then partially condensed with cooling water in a shell and tube heat exchanger. The vent from the condenser, which still contains a significant fraction of hydrocarbons, passes across the surface of the hydrocarbon selective membrane. The membrane separates the gas into two streams: a permeate enriched in hydrocarbon vapor, and a residue stream depleted in hydrocarbons. The permeate stream is recycled back to the inlet of the compressor. The residue stream which contains a small amount of carbon dioxide and oxygen (as well as nitrogen), is sent to flare. The condensate is the recovered hydrocarbon stream. A summary of the unit performance is shown in Table I below.

Hydrocarbon Recovery from HDPE

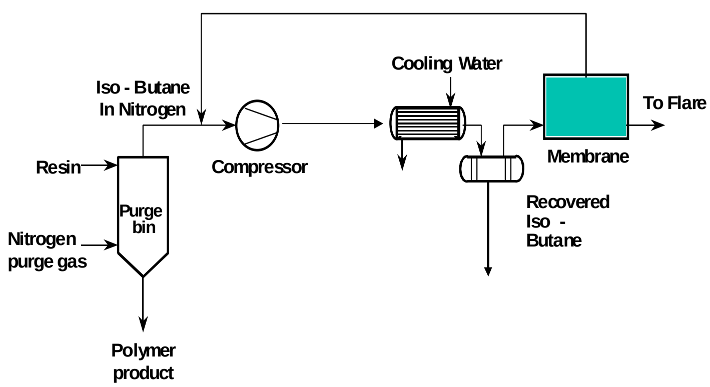

Figure 3

Table I - System Performance Resin Degassing -- HDPE	
Feed Composition (kg/hr)	
Nitrogen	750
Carbon Dioxide and Oxygen	45
Iso-Butane	1,050
Water	5
Total	1,850
Iso-Butane Recovered (kg/hr)	1,020
Iso-Butane Recovery (%)	97

Power Consumption (kw)	400
Value of Recovered HC ($000/yr)*	2,000
Capital Cost ($000)	1,300

* Hydrocarbons valued at $200/tonne

Three Propylene Recovery Units (PRU) are in operation to recover propylene in polypropylene plants, with five additional units under construction. The process design that was used for several of these PRU is illustrated in Figure 4. The hydrocarbon or nitrogen feed stream is compressed by an oil-flooded, screw compressor to a pressure of approximately 13 Bara and then fed into a molecular sieve type adsorbent dryer to remove moisture. The gas then enters a shell and tube condenser and is cooled down to approximately

-25 ^{o}C. The coolant for the condenser is supplied from a stand-alone refrigeration unit. A portion of the hydrocarbons condense inside the exchanger and the resulting liquid/gas mixture flows into a gas-liquid separator. The gas stream from the separator (nitrogen and hydrocarbon vapor) is sent to an economizer exchanger (for refrigeration recovery) and then enters the membrane modules. The membrane is much more permeable to the hydrocarbons than to nitrogen, so the stream is separated into a hydrocarbon-depleted residue stream and hydrocarbon-enriched permeate stream. At this point, the permeate stream is recycled back to the inlet of the compressor. The residue stream is further purified in a second membrane stage.

The permeate stream from the second stage is utilized to regenerate the dryer and then sent to flare. The liquid stream from the separator is used to pre-cool the condenser feed and is then pumped to the propylene-propane splitter column for purification. The performance of the system is summarized in Table II below.

Table II -- System Performance Resin Degassing -- PP	
Feed Flow Rate (kg/hr)	2,700

Feed Composition (volume %)	
Hydrogen	1.0
Nitrogen	84.4
Propane	0.3
Propylene	14.0
Water	0.3
Hydrocarbons Recovered (kg/hr)	450
Hydrocarbon Recovery (%)	91
Nitrogen Recovered (kg/hr)	900
Nitrogen Recovery (%)	50
Nitrogen Purity (volume %)	99
Power Consumption (kw)	630
Coolant Requirements (kw)	60
Value of Recovered Nitrogen ($000/yr)*	600
Value of Recovered HC ($000/yr)*	1,700
Capital Cost ($000)**	2,400

* Propylene valued at $400/tonne; nitrogen valued at $75/tonne
** Includes the low temperature refrigeration unit

Propylene Recovery Unit

Cooling Water

Wet Resin Recovered HC

Figure 4

Application of VaporSep® for Reactor Purge Streams in Polyethylene Plants.

In the production of Linear Low Density Polyethylene (LLDPE) or HDPE, nitrogen is added to the reactor to control the partial pressure of ethylene. The nitrogen is later purged from the reactor, taking a substantial quantity of ethylene and other co-monomers with it. This stream is normally sent to flare, resulting in monomer losses in excess of $500,000 per year.

A simplified flow diagram of this application is shown in Figure 5. One similar unit has been in service for two years and two additional units have been in service for six months. The objective of the VaporSep unit is to remove a fixed amount of nitrogen and to recycle the enriched hydrocarbons back to the reactor. Since the feed stream is at 300 barg, no feed compressor is required. The vent from the reactor is initially fed to a heat exchanger to cool the stream and to condense any higher boiling hydrocarbons. After the exchanger, the membrane separates the feed into a hydrocarbon enriched permeate stream and a hydrocarbon depleted residue stream. The permeate is sent to an existing compressor for recycle back into the reactor while the residue is sent to the flare. The performance is summarized in Table III below.

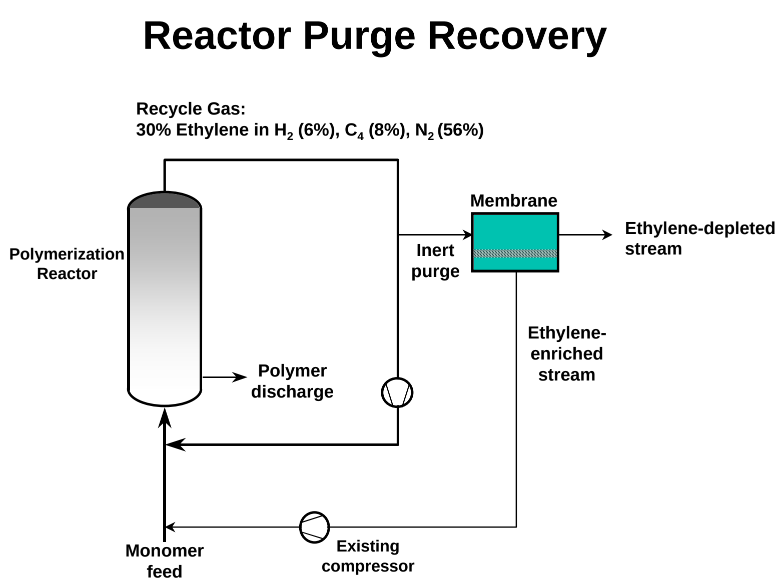

Figure 5

Table III -- System Performance **Reactor Purge -- LLDPE/HDPE**

Feed Composition (kg/hr)	
Hydrogen	2
Nitrogen	78
Ethylene	150
Ethane	3
1-Butane	132
Total	365
Hydrocarbons Recovered (kg/hr)	
Ethylene	132
1-Butane	129
Hydrocarbon Recovery (%)	
Ethylene	88
1-Butane	98
Value of Recovered HC* ($000/yr)	700
Capital Cost ($000)	300

* Ethylene and Butane valued at $300/tonne

Application of VaporSep for Distillation Column Vent Streams in LDPE Plant

Ethylene supply and purity are very important aspects of polyethylene production. At polymer plants where an olefin plant is on-site, ethylene purification is accomplished in an ethylene-ethane splitter column within the olefin process train. However, many polyethylene plants are stand-alone and purchase feedstocks from refineries or other sources by pipeline. For stand-alone plants, purification of the feedstock is sometimes achieved in a separate C_2 splitter column. When nitrogen and other light gases (hydrogen and methane) are present in the feed, they build up in the overhead of the column and must be vented. This vent stream also contains a significant amount of ethylene, which in a typical plant is valued at more than $500,000 year.

The VaporSep system is shown in Figure 6. The objective of the unit is to remove a fixed amount of the lights and to recycle the enriched ethylene back into the column. Since the stream is at 20 Bara, no feed compressor is required. The vent from the overhead condenser of the column is fed to the membrane.

The membrane separates the feed into an ethylene enriched permeate and an ethylene depleted residue. The permeate is sent to an existing compressor and then recycled back to the column while the residue is sent to the flare. The performance is summarized in Table IV below.

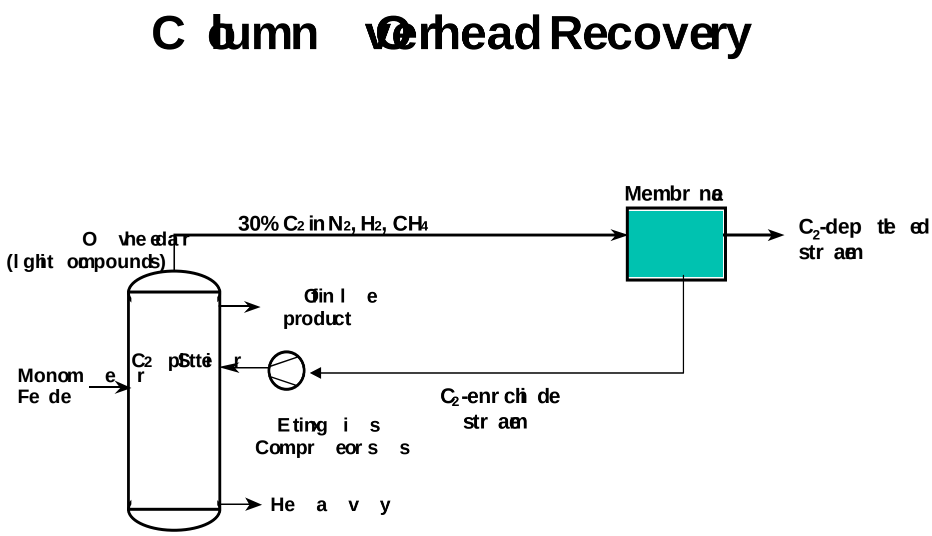

Figure 6

Table IV- System Performance Distillation Column -- PE	
Feed Composition (mole %)	
Hydrogen	18
Nitrogen	19
Methane	30
Ethylene	33
Ethylene Recovered (kg/hr)	135
Value of Recovered Ethylene ($000/yr)*	370
Capital Cost ($000)	200

* Ethylene valued at $300/tonne

Benefits of VaporSep

The equipment provided for resin degassing streams is supplied as a complete skid-mounted package with only one piece of rotating machinery. For the reactor and column vents, the equipment required is even simpler, containing only membrane modules. Payback times based on installed costs, range from 12 to 24 months.

Eight VaporSep units are currently in service in polyolefin plants and several units have been in operation for over 24 months. Five systems are in the pre-commissioning phase with start-up scheduled in the next 3 to 6 months. Three additional units are now under construction. In summary, VaporSep is a proven process with compelling economics for recovering monomers, co-monomers, and nitrogen from resin degassing streams, reactor vents, and distillation column vents in polypropylene and polyethylene plants.