Monomer Recovery in Polyolefin Plants Using Membranes - An Update

By

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Introduction

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

There are three sections in the polyolefin production process where monomers are typically lost. These three sections are raw material purification, chemical reaction, and product purification and finishing. All three sections provide significant opportunities for more efficient monomer use. A schematic of the process is shown in Figure 1.

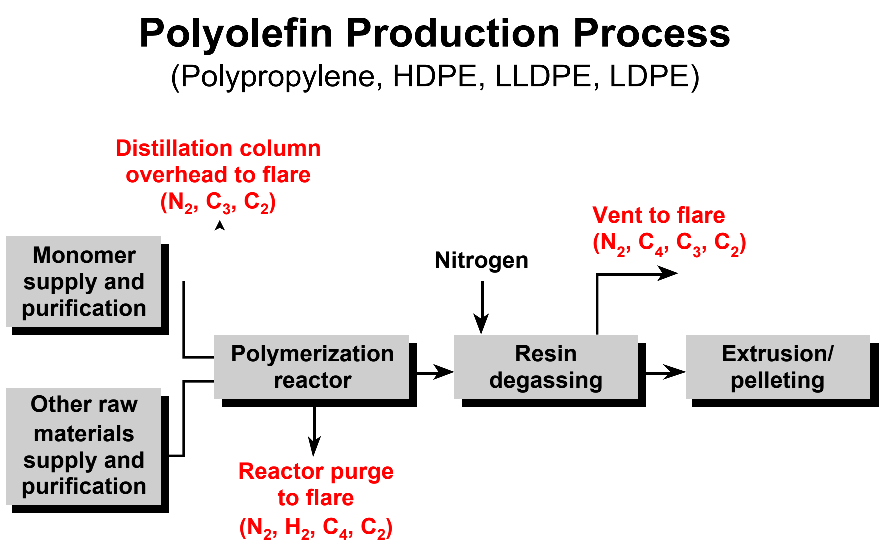

Figure 1

Membrane Technology and Research, Inc. (MTR) has developed a membrane-based process to separate and recover hydrocarbons, including propylene and ethylene, from nitrogen and light gases in polyolefin plant vents. The process, called VaporSep®, uses a membrane that selectively permeates hydrocarbon vapors compared to nitrogen and other light gases. This paper describes how VaporSep is applied to polyolefin vent streams to recover valuable monomers. Examples will be provided from each of the three process sections.

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 2, 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.

MTR Multilayer Composite Membrane

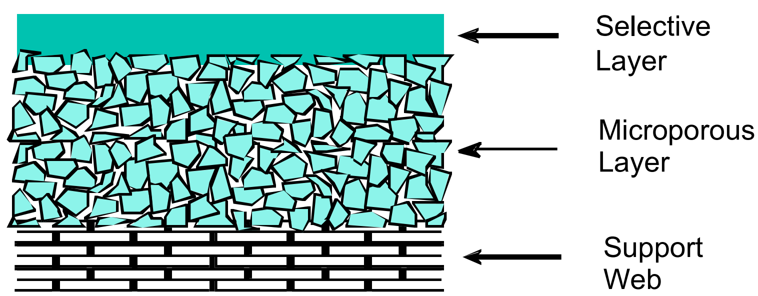

Figure 2

The membrane is manufactured as flat sheet and packaged into a spiral-wound module as shown in Figure 3. 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 permeates collection pipe. Nitrogen and other light gases are rejected by the membrane and exit as residue.

MTR Spiral Wound Module

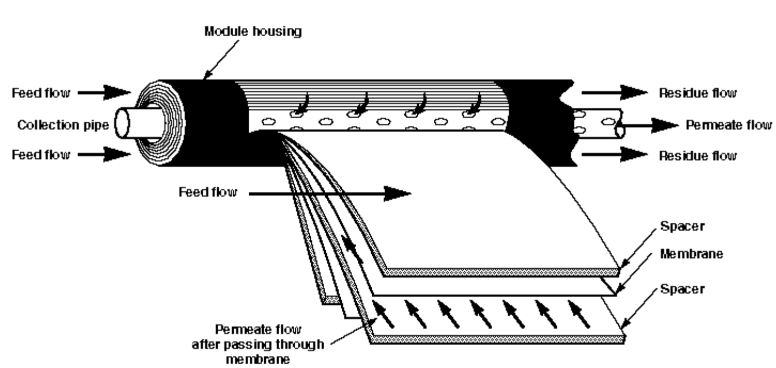

Figure 3

Application of VaporSep in the Raw Material Purification Section

Purification of raw materials is the first step in the polyolefin process. This step is very common because raw materials are not always available at the required purities. In addition, they have the capability to use low quality feedstocks which provide greater operating flexibility and lower operating costs. 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 feedstocks is 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 4. 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 300 Psig, 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 or fuel. The performance is summarized in Table I.

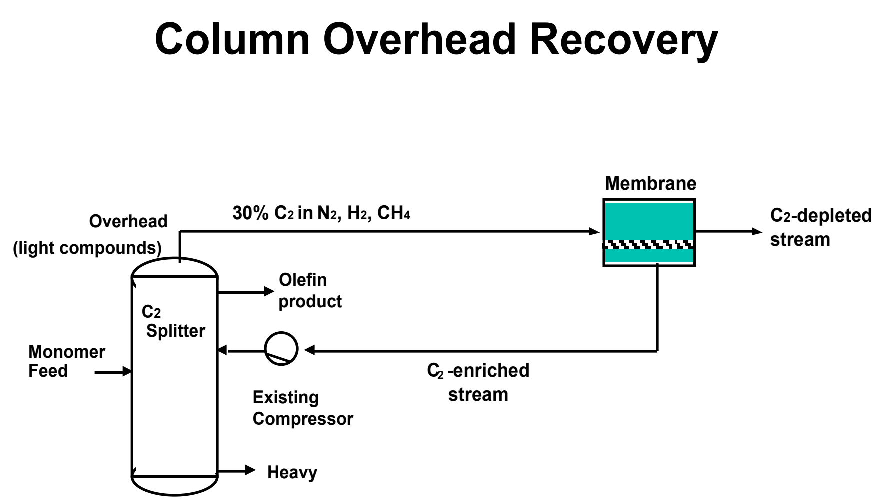

Figure 4

One unit for this application has recently been commissioned and two additional units are under active consideration. Opportunities for raw material purification are also found in polypropylene plants as well. The application is very similar, except that propylene is the vented monomer instead of ethylene.

Table I - System Performance Raw Material Purification	
Feed Composition (mole %)	
Hydrogen	18
Nitrogen	22
Methane	30
Ethylene	30
Ethylene Recovered (#/hr)	290
Value of Recovered Ethylene ($000/yr)*	370
Capital Cost ($000)	200

* Ethylene Valued at $300/ton

Application of VaporSep in the Reaction Section

In a large number of reaction processes, only a fraction of the feed reacts during a single pass through the reactor to form the desired product. After separation from the product, 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. Unfortunately, in addition to the contaminants, unreacted monomer is also lost in the purge. By applying VaporSep in the reaction section of the process, 90% of the reactant lost in the purge can be recovered.

In the production of Linear Low Density Polyethylene (LLDPE) or High Density Polyethylene (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 unit for this application has been in service for two years, two additional units have been in operation for twelve months, and a fourth unit was commissioned six months ago. 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 Psig, 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 II below.

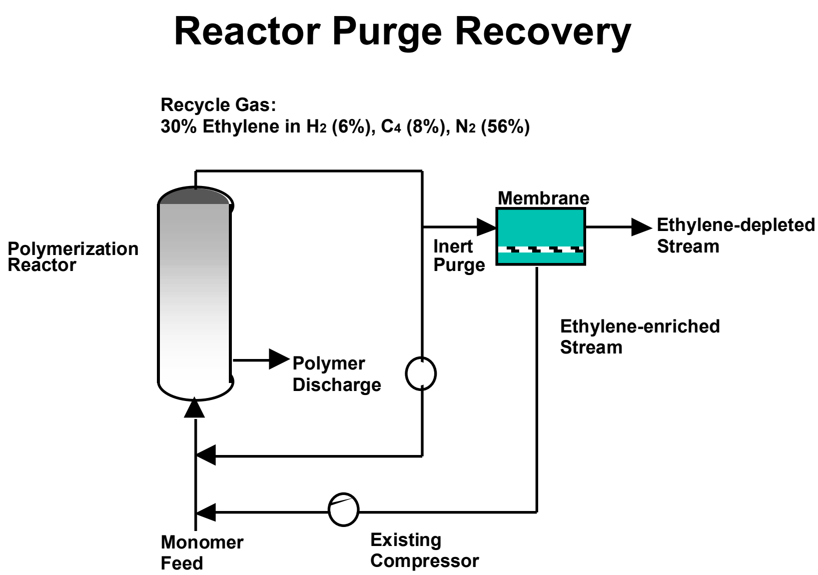

Figure 5

Table II - System Performance Reaction Section - LLDPE/HDPE	
Feed Composition (#/hr)	
Hydrogen	5
Nitrogen	172
Ethylene	328
Ethane	7
1-Butene	288
Total	800
Hydrocarbons Recovered (#/hr)	
Ethylene	290
1-Butene	284
Hydrocarbon Recovery (%)	
Ethylene	88
1-Butene	98
Value of Recovered HC* ($000/yr)	700
Capital Cost ($000)	300

*Ethylene and Butene valued at $300/ton

Application of VaporSep in the Product Purification and Finishing Section

After the polyolefin products are produced, they must be further purified before they are ready to be shipped to the customer. Raw polyolefin product, which is produced as a powder, 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 6. The feed stream is compressed to 200 Psig 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 III.

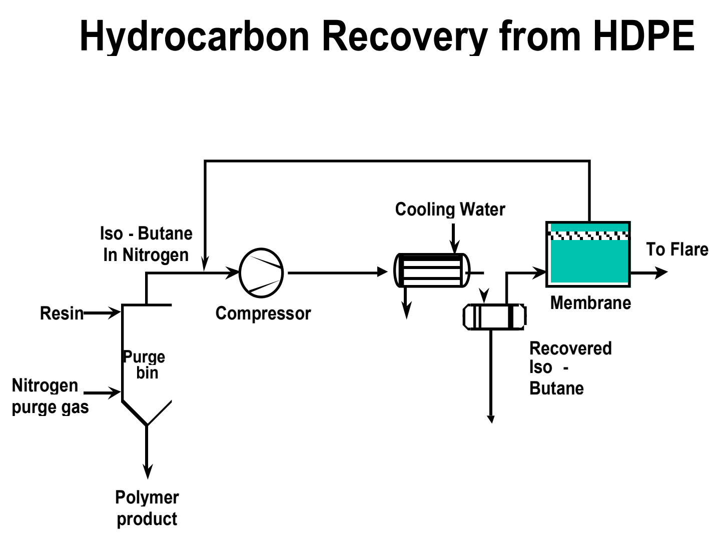

Figure 6

Table III - System Performance Product Purification - HDPE	
Feed Composition (#/hr)	
Nitrogen	1,620
Carbon Dioxide and Oxygen	100
Iso-butane	2,370
Water	10
Total	4,100
Iso-butane Recovered (#/hr)	2,325
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/ton

Three Propylene Recovery Units (PRU) are in operation to recover propylene in polypropylene plants, with five additional units under construction. The process design which was used for several of these PRU is illustrated in Figure 7. The hydrocarbon/nitrogen feed stream is compressed by an oil-flooded, screw compressor to a pressure of approximately 200 Psia 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) flows back through the 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. 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 used 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 IV.

Propylene Recovery Unit

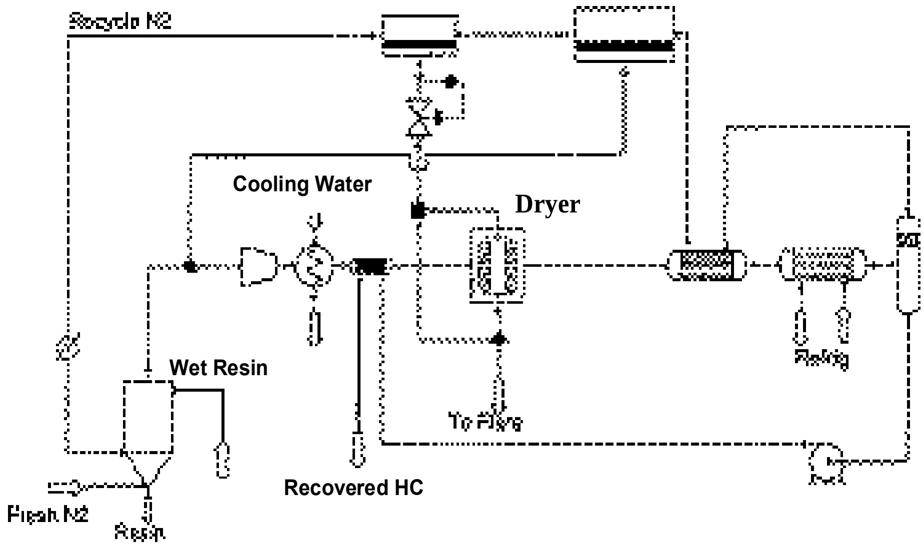

Figure 7

Table IV - System Performance Product Purification - PP	
Feed Flow Rate (#/hr)	6,000
Feed Composition (volume %)	
Hydrogen	1.0
Nitrogen	84.4
Propane	0.3
Propylene	14.0
Water	0.3
Hydrocarbons Recovered (#/hr)	1,000
Hydrocarbon Recovery (%)	91
Nitrogen Recovered (#/hr)	2,000
Nitrogen Recovery (%)	50
Nitrogen Purity (volume %)	99
Power Consumption (kw)	630
Coolant Requirements (MMBtu/hr)	0.2
Value of Recovered Nitrogen ($000/yr)*	600
Value of Recovered HC ($000/yr)*	1,700
Capital Cost ($000)**	2,400

* Propylene valued at $400/ton; nitrogen valued at $75/ton

** Includes the low temperature refrigeration unit

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 twenty four months. Five systems are in the pre-commissioning phase with a 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 distillation column vents (raw material purification section), reactor vents (reaction section), and resin degassing streams (product purification section) in polyolefin plants.