Hydrocarbon Recovery in Polymer Production Using Membrane Technology

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Menlo Park, CA

Process Optimization Conference

Marriott Westside Hotel
Houston, Texas

March 24, 25, & 26, 1998

Organized by
Gulf Publishing Company
and
Hydrocarbon Processing
**Introduction**

Efficient use of utilities, catalysts, and particularly feedstocks is one of the major goals of chemical process optimization. The costs for inefficient use of feedstocks can be large. For example, monomer losses in vent streams from polyolefin plants typically range from 1 to 2 percent of the total plant feed stock. With more than 300 polyolefin plants worldwide, and total capacity in excess of 60 million tons per year, worldwide monomer losses represent a loss of almost one half billion dollars per year. This amount represents a significant opportunity for recycle and recovery.

There are many places in a chemical plant where raw materials are lost. Figure 1 indicates that a typical chemical plant can be divided into three process sections: raw material purification and preparation, chemical reaction, and product purification and finishing. Each section provides opportunities for more efficient material use. MTR has developed a novel, membrane-based technology called VaporSep® for recovering monomers, solvents, and other hydrocarbon vapors from chemical plant vents. The enabling technology of VaporSep is a membrane that selectively permeates hydrocarbon vapors over nitrogen and other noncondensable gases. This paper describes how VaporSep is applied to chemical plant vent streams to optimize the use of chemical feedstocks. Examples will be provided from each of the three process sections.

![Figure 1. Three Process Sections in a Typical Chemical Plant](image_url)

The heart of the VaporSep process is a high-flux composite membrane that is 10 to 100 times more permeable to hydrocarbon compounds than to nitrogen. The membrane, illustrated in
Figure 2, consists of an ultrathin, selective, rubbery top layer, a microporous support layer, and a nonwoven support web. The top layer performs the separation; the porous support provides mechanical strength. The support web serves as a substrate.

![Thin Film Composite Membrane](image)

Figure 2. Thin Film Composite Membrane

The membranes are packaged into spiral-wound modules of the type illustrated in Figure 3. As the feed gas enters the module and flows between the membrane leaves, the hydrocarbon vapor preferentially permeates the membrane and spirals inward to a central permeate collection pipe. The nitrogen flows across the membrane surface and exits as the residue. To meet the capacity and separation requirements of a particular application, modules are connected in series and parallel flow arrangements.

**Application of VaporSep in the Raw Material Purification Section**

The first step in many chemical plants after receipt of raw materials is purification of the raw materials. This step is very common because raw materials often are not available at the required purities, and because having the capability to use low quality feedstocks lowers overall production costs and provides greater operating flexibility. One opportunity for feedstock recovery is in the Raw Material Purification Section of a chemical plant during the production of polypropylene.
In the production of polypropylene, propylene supply and purity are very important aspects of production. At polymer plants where an olefin plant is on-site, propylene purification is accomplished in a propylene-propane splitter column within the olefin process train. However, many polypropylene plants are stand-alone and receive feedstocks from refineries or other sources by pipeline. Feedstock purity ranges from 85% for refinery grade, 95% for chemical grade, and 99.5% for polymer grade. To be able to accept lower quality feedstocks, most stand-alone polypropylene plants have their own propylene-propane splitter columns. When nitrogen is present in the feed, it builds up in the overhead of the column and must be vented. This vent stream also contains a significant amount of propylene, which in a typical plant is valued at more than $500,000 year.

A VaporSep system for the Raw Material Purification Section is shown in Figure 4. The objective of the unit is to remove a fixed amount of nitrogen and to recycle the enriched propylene back into the column. Since the stream is at 250 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 a propylene-enriched permeate and a propylene-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 1. Similar applications can be found in the production of polyethylene and many other chemical products.
Application of VaporSep in the Reaction Section

In a large number of reaction processes, only a fraction of the feed actually reacts during a single pass through the reactor to form the desired product. After separation from the product, the unreacted reactants are recycled to the reactor. Ideally this results in no losses of reactants. In reality, however, reactants usually contain some inert compounds. For example, oxygen is normally 99.5% pure with the impurity being argon, ethylene is normally 99.9% pure with the impurity being ethane, and propylene is normally 99.5% pure with the impurity being propane. These inert compounds are recycled along with the unreacted reactants and will eventually build up to unacceptable levels. To avoid this build up, a purge stream is vented from the reactor.
section to remove the inerts. Unfortunately, a portion of the unreacted reactants are also lost in
this inert purge stream. VaporSep can be used to separate the reactants from the inerts, and
recycle them to the reactor, eliminating as much as 90% of reactant losses through the purge
vent.

In the production of some types of polyethylene, two inerts, ethane and nitrogen, require
purging. Nitrogen is added to the reactor to control reactant partial pressures; ethane is an
impurity in the ethylene feed. Both of these inerts must be purged from the reactor, taking a
substantial quantity of ethylene and other hydrocarbons. 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. Inerts plus ethylene exit the
reactor at high pressure and temperature. The objective of the VaporSep unit is to remove fixed
amounts of nitrogen and ethane, and to recycle the enriched ethylene 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 (containing the inerts) is
sent to the flare. The performance is summarized in Table 2. The first unit for ethylene recovery
has been in service for six months, and two additional units are under construction. Besides
polyethylene, VaporSep has been applied for similar applications in the production of polyvinyl
chloride, ethylene dichloride, and vinyl acetate, and other chemicals.
**Application of VaporSep in the Purification and Finishing Section**

After products are produced in the reaction section, they usually require some purification and finishing steps. The products must be separated from unreacted reactants and from reaction byproducts. In polymer production, hydrocarbons dissolved in the polymer product must be
removed prior to the extrusion step. In the production of polypropylene, the raw polymer product (in powder form) contains significant amounts of unreacted hydrocarbons. Before the polymer 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.

The process is illustrated in Figure 6. The hydrocarbon/nitrogen feed stream is compressed to a pressure of approximately 200 psia and then fed into a molecular-sieve adsorbent dryer to remove moisture. The gas then enters a shell and tube condenser and is cooled down to approximately -30 °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) 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 while the permeate from the second stage is sent to flare. The liquid stream from the separator is pumped to the propylene-propane splitter column for purification. The performance of the system is summarized in Table 3. The VaporSep unit recovers approximately 90% of the propylene and 75% of the nitrogen in the vent stream. Two VaporSep units are in operation to treat resin degassing streams in polypropylene plants, with three additional units under construction. Resin degassing applications also exist in polyethylene production, and the first VaporSep unit for a polyethylene application is now under construction.
15% propylene in nitrogen

Resin

Nitrogen purge gas

Polymer product

Compressor

Dryer

Refrigerant

Membrane

Knock-out

Recovered propylene

Recycle to purge bin (99% nitrogen)

Figure 6. VaporSep System for Resin Degassing Applications in PP Plants

TABLE 3 - SYSTEM PERFORMANCE
Purification and Finishing Section

<table>
<thead>
<tr>
<th>Feed Flow Rate</th>
<th>(#/hr)</th>
<th>5,500 lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Composition</td>
<td>(volume %)</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>84.4</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbon Recovery</td>
<td>(%)</td>
<td>91</td>
</tr>
<tr>
<td>(#/hr)</td>
<td>1,000</td>
<td></td>
</tr>
<tr>
<td>Nitrogen Recovery</td>
<td>(%)</td>
<td>50</td>
</tr>
<tr>
<td>(#/hr)</td>
<td>2,000</td>
<td></td>
</tr>
<tr>
<td>Nitrogen Purity</td>
<td>(volume %)</td>
<td>99</td>
</tr>
<tr>
<td>Power Consumption</td>
<td>(Hp)</td>
<td>850</td>
</tr>
<tr>
<td>Value of Recovered Nitrogen ($000/yr)*</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>Value of Recovered HC ($000/yr)*</td>
<td>1,700</td>
<td></td>
</tr>
<tr>
<td>Capital Cost</td>
<td>($000)**</td>
<td>2,400</td>
</tr>
</tbody>
</table>

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

VaporSep is a cost-effective solution for recovering monomers, other hydrocarbons, and nitrogen from the Raw Materials Purification, Reaction, and Product Purification and Finishing sections of many chemical plants. The VaporSep unit is supplied as a complete skid-mounted package with only one piece of rotating machinery. For many applications the equipment required is even simpler, containing no moving parts at all. Payback times, based on installed costs, range from 12 to 24 months. The first VaporSep unit has been in service since 1990. Since then more than 40 units have been installed with a cumulative operating experience of more than 50 years.