

Improve monomer recovery from polyolefin resin degassing

Case histories highlight how to recover and recycle ethylene and propylene from polymer waste-gas streams

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Recovering volatile organic compounds (VOCs) from vent gases with membrane systems is an attractive alternative to flaring. The systems are based on membranes that selectively permeate organic compounds from air or nitrogen. Most systems installed have the basic design illustrated in Fig. 1, which consists of two steps. First, the feed gas is compressed and passed to a condenser where it is cooled; a portion of the organic vapor condenses and is directed to a storage tank for recycling or reuse.

In the second step, the noncondensed portion of the feed gas, which still contains a significant fraction of organic compounds, passes across the surface of an organic-selective membrane. The membrane separates the gas into two streams: a permeate enriched in organic vapor and a residue stream of purified air or nitrogen. The organic-rich permeate is recycled back to the compressor's inlet; the organic-depleted gas is vented. Such systems typically achieve greater than 99% removal of VOC from the feed gas, and reduce the VOC content of the vented gas to 100 parts per million (ppm) or less.¹

In most membrane system applications, high-value organic vapors such as vinyl chloride monomer, methyl chloride and methyl formate are recovered from process streams. Carbon adsorption may be a better treatment option for low-VOC-concentration (5,000 ppm or less) air streams, but membrane systems are competitive with carbon adsorption or condensation for more concentrated streams, especially if high VOC recovery is required.

Polyolefin plant vents.

Recently, a new application of membrane technology has been recognized: recovery of ethylene or propylene monomers from resin degassing vent streams in polyolefin plants. The source of such a vent stream is shown in Fig. 2.²

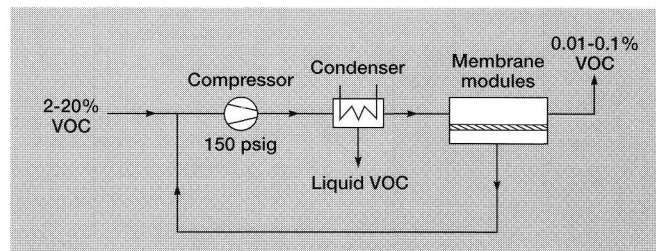


Fig. 1. A typical compression-condensation membrane system generally achieves 95–99% VOC recovery. The process is most commonly used to recover high-value VOCs such as vinyl chloride monomer, methyl chloride and methyl formate.

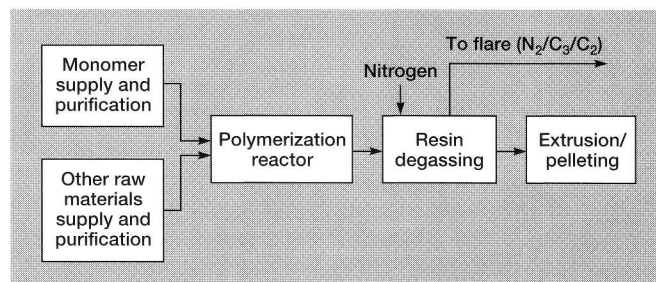


Fig. 2. In a typical polyolefin plant, the vent stream currently flared can be treated by a membrane system to recover nitrogen and valuable monomer.

In a typical olefin polymerization process, monomer plus catalyst, various comonomers, solvents and stabilizers are contacted at high pressure in a polymerization reactor. The polymerization reaction may be in the gas phase or in a slurry phase using an organic solvent such as butane or hexane. The raw polymer product (in powder form) contains significant amounts of sorbed unreacted monomer, comonomers

and processing solvents. These components must be removed before the polymer can be used. The raw polymer is passed to large resin purge bins, where nitrogen removes absorbed monomer and process solvents. End users are increasingly requiring very low levels of residuals in the final polymer, so nitrogen usage in this step is increasing. The composition and volume of the vent gas from the degassing step vary widely, depending on

Membrane separation benefits

More than 100 polyolefin manufacturing plants are operating in the United States.³ Waste gases from these plants represent a considerable recycle and recovery opportunity. The vent gas from a typical resin purge bin contains 500 to 1,000 lb/hr of recoverable monomer and processing solvent, and 1,000 to 2,000 lb/hr of recoverable nitrogen. At current monomer costs of \$0.20–0.30/lb, compared to nitrogen costs of \$0.01–0.02/lb, the recovery value lies mainly in the monomer fraction. But taken together, the total recovery opportunity is about \$1 million/year.

The membrane equipment required to perform this separation is designed as a complete skid-mounted package. Installation is simple, requiring only power, cooling water and process piping connections. Capital costs of the membrane systems will depend on the nature of the feed stream, but based on installed costs, payback times can be as short as 12 months.

Table 1. Composition of the resin purge-bin vent stream

Process	Purge-bin vent stream composition, vol %	Flowrate, scfm [lb/hr]
Gas phase, polypropylene	85% nitrogen, 10% propylene, 3% propane, 1% ethylene/ethane	700 [3,500]
Slurry-diluent, polypropylene	74% nitrogen, 6% propylene, 18% butane	700 [4,000]
Gas phase, polyethylene	87% nitrogen, 11% ethylene, 3% hexane, methane, hydrogen	750 [3,700]

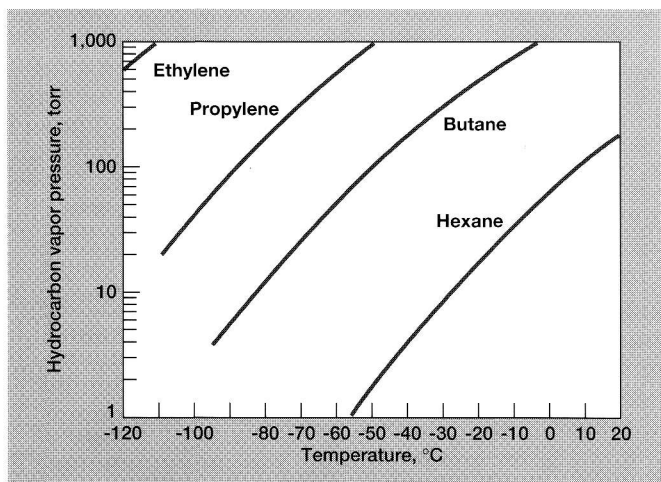


Fig. 3. Vapor pressure of light hydrocarbons found in olefin purge-bin gases as a function of condenser temperature. Because of the volatility of these gases, cryogenic temperatures are required to achieve good recoveries by simple condensation.

the size of the plant, the product polymer (polyethylene or polypropylene) and the polymerization process. Representative stream compositions are listed in Table 1.

In most plants, the vent gas is flared and the monomer content is lost. The value of these potentially recoverable monomers is very high: about \$1 million dollars annually, representing a considerable resource-recovery opportunity. Until the development of membrane technology, no appropriate recovery technology existed, however. The streams are not good candidates for pressure swing adsorption treatment, which generally only recovers the heavier components of the gas. Condensation can be used, but very low temperatures are required to sufficiently remove the volatile gases ethylene and propylene. Vapor pressure curves for common vent gas components are shown in Fig. 3. Even at -120°C , the offgas from a low-temperature condenser will never contain less than 50% ethylene or 2% propylene. Such modest recovery does not generally justify the cost of a cryogenic system.

Application of a membrane system to resource recovery from the purge-bin vent is shown in its simplest form in Fig. 4. The membrane unit fractionates the vent gas into two streams—a monomer/solvent-rich stream that is recycled to monomer supply and purification, and a nitrogen stream that is recycled to the resin purge bin.

A number of membrane process designs can be considered, depending on the composition of the purge-bin vent gas and the specific plant requirements for the recycled materials.

Two-stage membrane system. If plant design does not require complete nitrogen removal from the recycled

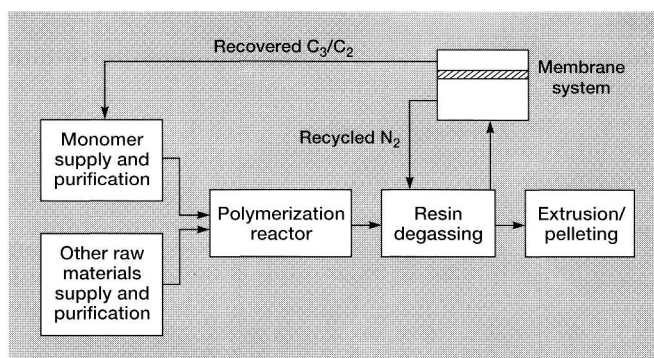


Fig. 4. A membrane separation system recovers monomer, solvents and nitrogen from the resin degassing operation.

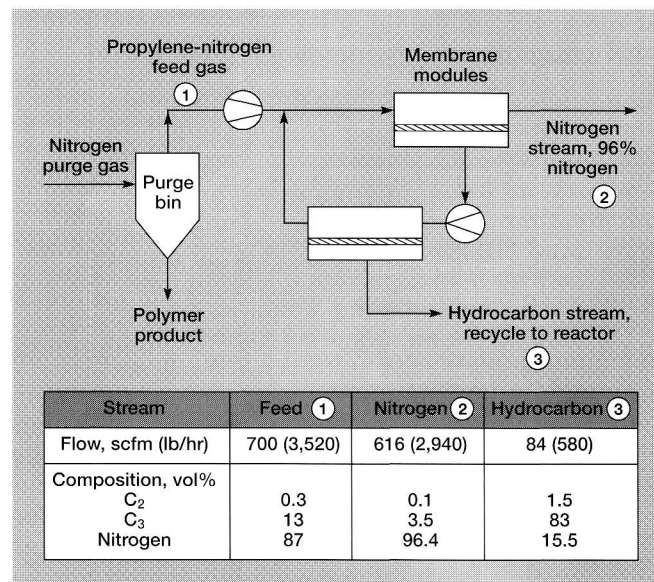


Fig. 5. Two-stage membrane separation process fractionates non-condensable organics from nitrogen. A plant of this general design is currently being constructed for a new polypropylene facility in Europe.

monomer, a two-stage membrane system is the most efficient design. A typical system is shown in Fig. 5. The purge-bin vent gas is first compressed and sent to the main membrane separation step. This step produces a residue gas containing 96% nitrogen that can be recycled to the purge bin. The hydrocarbon-rich permeate from this step cannot be sent directly to the olefin plant because it contains too much nitrogen; therefore, the stream is recompressed and concentrated further in a second membrane stage. This stage produces a nitrogen-rich gas, which is recycled to the feed gas line, and a monomer stream containing 85 vol% (91 wt%) hydrocarbon, which is recirculated to the reactor.

The nitrogen stream produced in the design in Fig. 5 still contains about 4 vol% hydrocarbon, which may make it unsuitable for direct reuse in the resin purge bin. Flaring this gas would be a loss of nitrogen and valuable monomer. However, because the gas is under pressure, a second nitrogen clean-up step can be added to the system (Fig. 6). This second step produces relatively pure nitrogen ($> 99\%$) and a stream containing 10–15% hydrocarbon. The nitrogen stream is now pure enough to be recycled to the plant, but the hydrocarbon stream is too dilute to mix with the hydrocarbon-rich concentrate going to the olefin plant. The hydrocarbon stream can be flared or, better, recycled to the main compressor.

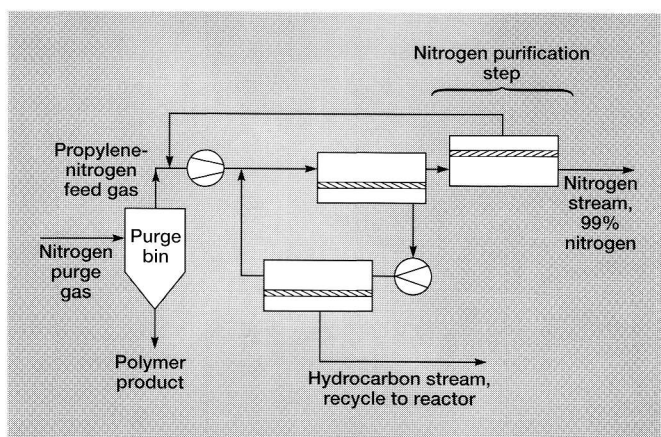


Fig. 6. Using a second nitrogen purification step to remove the last few percent of hydrocarbon from the nitrogen stream facilitates reuse of this nitrogen. The permeate contains 10–15% hydrocarbon and can be flared or, as shown, mixed with feed gas from the purge bin.

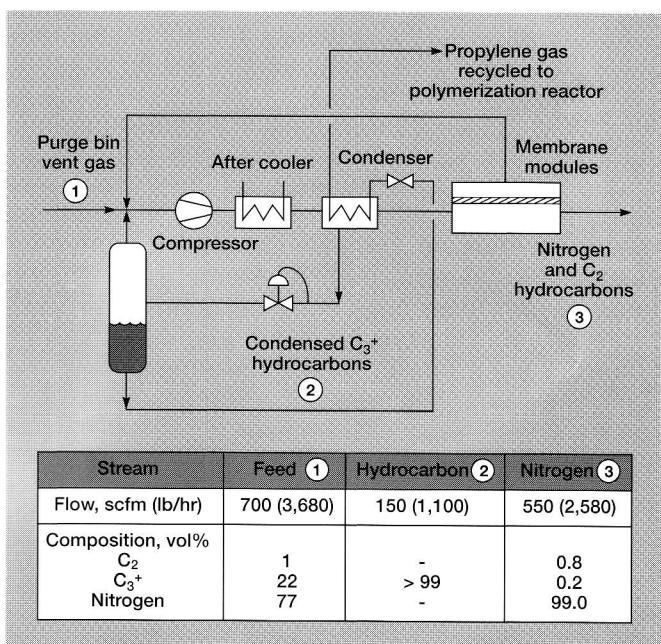


Fig. 7. A compression-condensation membrane system to recover pure nitrogen-free propylene from a purge-bin vent gas. In this design, most of required refrigeration is provided by evaporation of the recovered propylene liquid.

Compression-condensation membrane system. If better removal of nitrogen from the recycled organic stream is required, a compression-condensation design is the optimum process. A system designed to treat a concentrated

propylene/nitrogen stream is shown in Fig. 7.

After compression and cooling, most of the propylene and some of the ethylene and nitrogen are removed as a condensed liquid. This C₃⁺ hydrocarbon condensate is first flashed at low pressure to remove dissolved nitrogen and most of the dissolved ethylene. These gases are returned to the inlet of the compressor for treatment. The nitrogen-free condensed C₃⁺ hydrocarbon stream (stream 2, Fig. 7) is then ready to be recycled to the polymerization reactor. The remaining uncondensed fraction of the propylene is removed from the condenser offgas by the membrane step. The residue gas, which is essentially free of all C₃⁺ hydrocarbons and contains only nitrogen and ethylene, is recycled to the purge bin (stream 3, Fig. 7).

The main design disadvantage is the refrigeration required to cool the incoming feed gas to -20° to -30°C. However, by using the recovered liquid propylene as a refrigeration medium to unload the condenser, as shown in Fig. 7, the external refrigeration requirement can be reduced up to 60%.

LITERATURE CITED

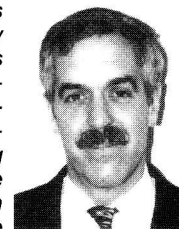
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