

UPDATE FOR HYDROCARBON and NITROGEN RECOVERY SYSTEMS

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- ABSTRACT:** Increasing oil and energy costs emphasize the importance of maximizing raw materials utilization in polyolefin plants. Manufacturers and technology licensors should reconsider improved recovery systems for retrofits at existing plants, and for designs of new grassroots facilities. By recovering valuable olefins, solvents, and nitrogen, producers can reduce production costs by as much as \$10/MT (metric ton), and avoid unnecessary flaring that results in emissions of NOx, VOC'S (including HRVOC'S), CO, and CO2. Air Products' recovery systems achieve essentially complete recovery for valued hydrocarbons and nitrogen. The improved performance delivers millions of dollars per year improvements to the producers' bottom line. Air Products has sold one system for a new grassroots HDPE plant that started in June 2003, and a second system for a major PP plant that started in March 2004. Both units meet or exceed all design and operating goals. A third recovery system, for a North America polypropylene producer, will start in early 2006.

For more information about Air Products' gas separation solutions and technologies click on <http://www.airproducts.com/hydrocarbon>, or contact

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INTRODUCTION

Value Statement

With energy prices hovering around \$60/bbl for oil and \$9.0/MMBTU (26.1 Euro/MWH) for natural gas, polyolefin producers should take a hard look at vent streams as a source of cost savings. A typical 300,000 Metric Ton per year (MTPA) polyethylene plant with 1.014 monomer utilization is losing more than \$3.0 MM/yr of ethylene at today's prices. Add purchased nitrogen for degassing polymer, and fuel gas, potentially needed for proper flaring, and that number is even higher.

Air Products provides recovery systems for processing purge streams from Polyethylene (PE) plants and Polypropylene (PP) plants. The systems combine Pressure Swing Adsorption (PSA) and partial condensation technology, reclaiming essentially 100% of the materials for reuse. With a high performance recovery unit, owners can achieve the lowest costs for their polymer degassing operations, and near zero emissions rates.

Off-gas Sources

Off-gas sources in PE and PP plants include direct reactor section purging, polymer degassing operation vents, vents from solids transfer operations, and miscellaneous vents from feed drier regeneration, catalyst preparation, etc.

Reactor section purges:

In some processes, a direct purge from the reactor section removes light inert materials. The inert materials carry valued monomer and perhaps other raw materials. In the past, reactor vents were sent to flare, or maybe, processed to achieve 50 to 60% recovery of the hydrocarbons. With today's feedstock costs complete recovery systems should be considered.

Polymer Degassing

Many polyolefin plants use a degassing step to remove un-reacted olefin, additives and solvents from the raw polymer before entering downstream extrusion operations. Nitrogen is commonly used as the stripping gas. The operation produces a low pressure vent containing nitrogen and values materials.

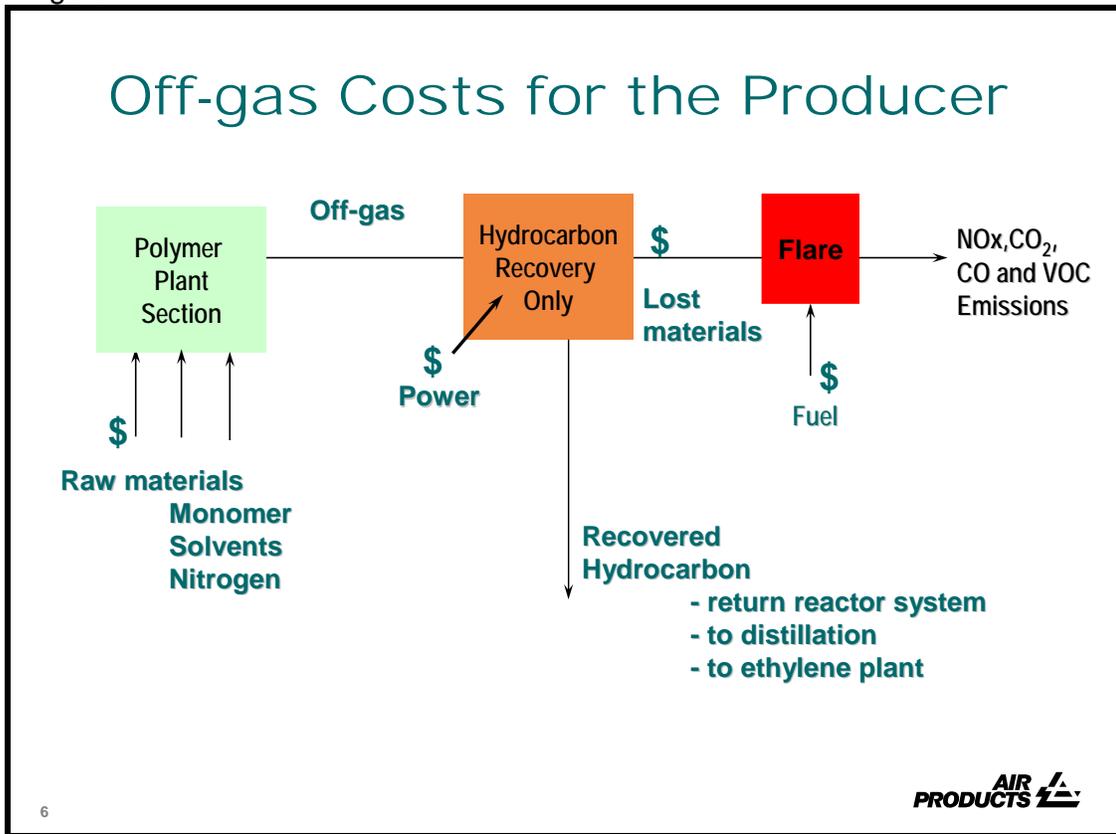
Other vents:

Other vent streams can include nitrogen used for polymer transfer and downstream processing, or vents from drier regeneration or catalyst preparation areas.

All these operations produce off-gases (most at low pressure) containing N₂ and valuable hydrocarbons. Directly disposing of these streams in a flare, or processing for only partial recovery of the hydrocarbons results in lost value, and unnecessary emissions of highly reactive volatile organic compounds (HRVOC'S), NO_x, CO, and CO₂.

Air Products has developed a model that quantifies the direct costs and the emissions associated with the reactor purge, polymer degassing and flaring steps. Figure 1 shows the costs the producers should consider are: costs for: un-recovered valued hydrocarbons and nitrogen, power for running the recovery system, and purchased fuel for flaring. We have demonstrated that significant savings in operating costs are realized by using an Air Products high recovery system. Partial recovery systems, ones that recover hydrocarbons only, may reduce degassing system costs compared to simple flaring, but the costs are still significant, and the problem of emissions remains.

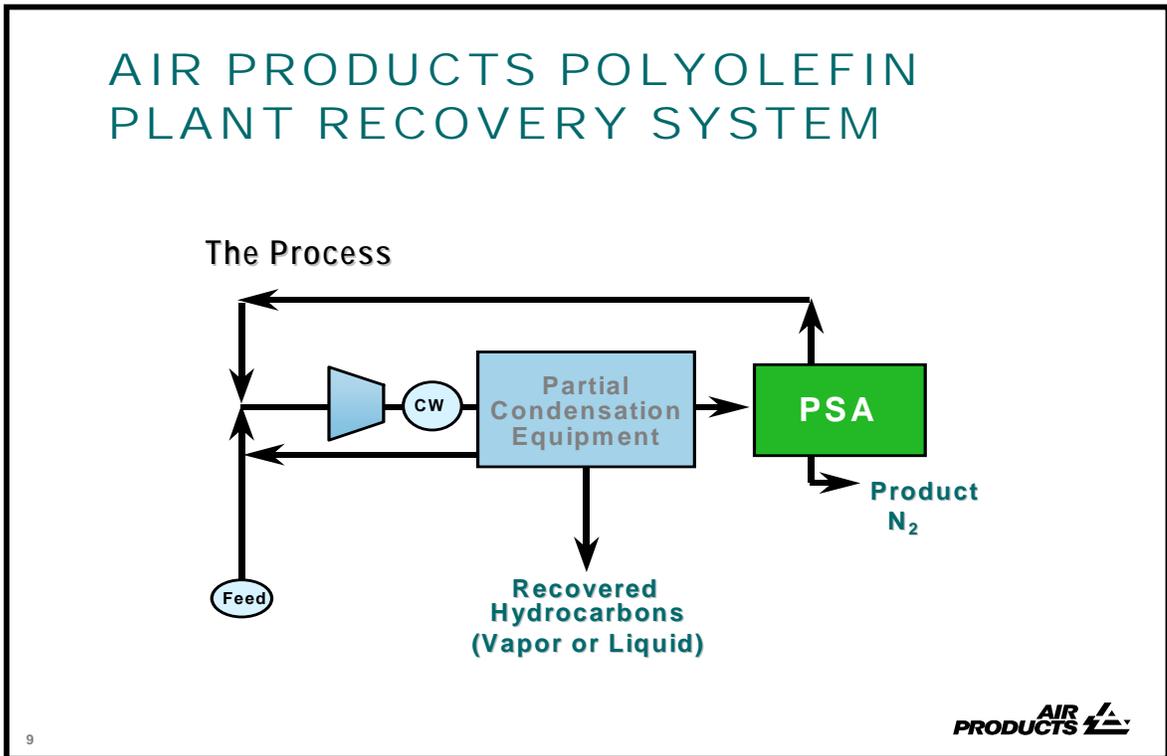
Figure 1:



AIR PRODUCTS HYBRID PSA PROCESS

Air Products' hybrid process uses partial condensation and Pressure Swing Adsorption (PSA) (See Figure 2). The process delivers two product streams - recovered hydrocarbons for making more polymer, and nitrogen for reuse in the degassing step. The distinguishing features for this recovery system are the essentially 100% recoveries achieved, and the high purities for both the nitrogen and recovered hydrocarbons products.

Figure 2:



Process Description

An off-gas or combination of off-gases is compressed and cooled in the partial condensation section. Recovery units that contain water in the feed operate at temperatures above 0 °C, avoiding water freezing, and the formation of hydrides. On a single pass, most of the hydrocarbons are liquefied in the condensation unit and separated. The uncondensed hydrocarbons flow with the nitrogen to the PSA unit.

The PSA step produces a high purity N₂ product, with C₂+ impurities limited to between 50 to 1000 ppm (by weight). All hydrocarbons recovered in the PSA are recycled in a low-pressure tail gas stream to the feed compressor.

The hybrid process achieves essentially 100% recovery of both the nitrogen and hydrocarbons. No gas is sent to flare. This performance translates into significant cost savings and reduced environmental impact with today's focus on eliminating highly reactive volatile organic compounds (HRVOC's), nitrogen oxides (NO_x), carbon monoxide (CO) and carbon dioxide (CO₂). The only utilities required by the hybrid process are cooling water and electric power for the compressor.

The PSA section uses multiple beds arranged in parallel. Each bed operates in a cyclic mode, alternating between the adsorption and desorption steps. The PSA unit performs as a continuous flow process by staggering the cycles imposed on the parallel beds.

The key feature of the PSA based process is the very high recoveries of both nitrogen and hydrocarbons. The recovered N₂ is suitable for reuse in polymer degassing operations. Some producers could even evaluate releasing N₂ directly to the atmosphere, if site conditions prevent full use of recoverable N₂ (still more cost effective than flaring).

EXPERIENCE IN COMMERCIAL OPERATION

1. Recovery System for a 320 MTPA PE PLANT - USA - 2003

Figure 3 is a photo of Air Products first recovery system started in June 2003 as part of a 320,000 Metric Tons Per Annum HDPE grassroots plant in the United States. This recovery unit was included in the new design for the licensors HDPE technology.

Figure 3:



2. Recovery System for a 1MM MTPA Polypropylene Facility - USA – 2004

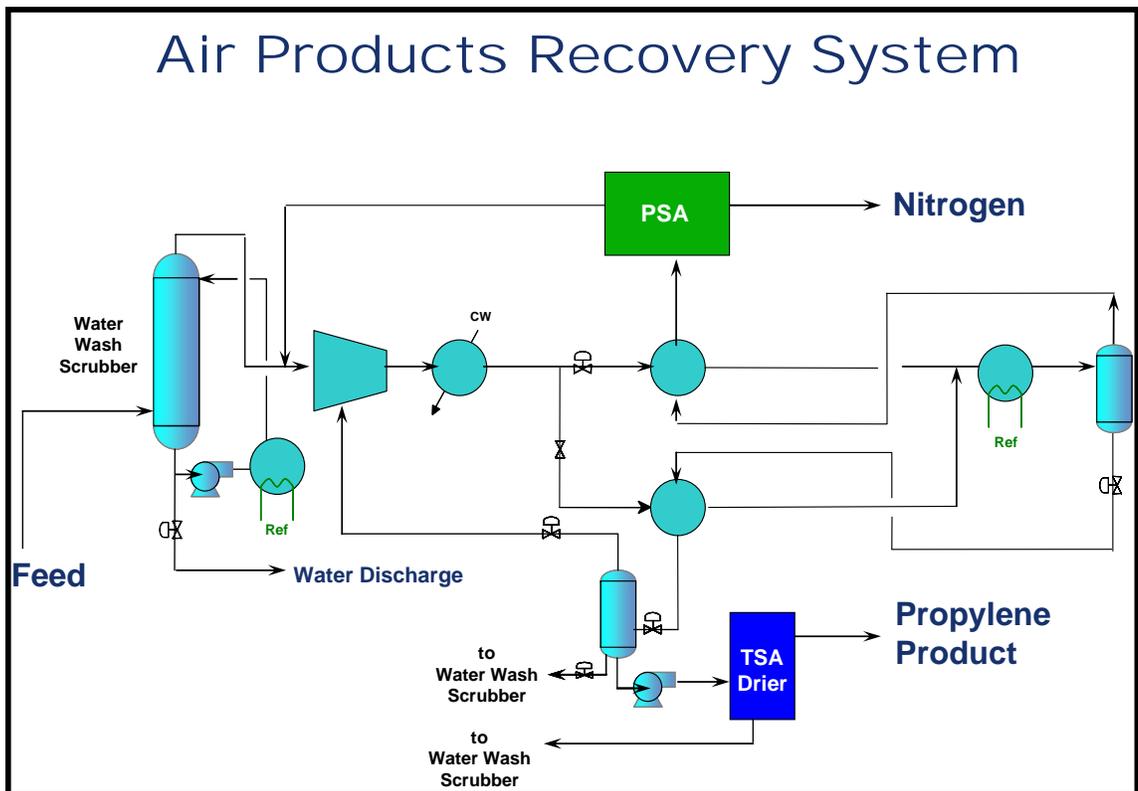
Air Products' second commercial monomer recovery system is a retrofit at an existing polypropylene (PP) facility with total PP capacity over 1 million MTPA. One Air Products recovery system processes vent streams from multiple production lines. It recovers propylene and nitrogen valued at more than \$5.5MM /yr (Air Products estimates).

Air Products technology was selected because it readily handles fluctuations in flow and composition for gases from the multiple units, and in part, because it achieved essentially 100% for both hydrocarbon and nitrogen recoveries. The high purity products are recycled directly to the facility's processing units.

Propylene Nitrogen Recovery Process:

Figure 5 is a simple process flow diagram (PFD) for the propylene nitrogen recovery unit (PNRU). All equipment shown was included in Air Products scope of supply.

Figure 5



Partial Condensation Section:

The feed gas enters the process and contacts chilled water in the scrub column to remove the bulk of the moisture in the feed. An oil-flooded screw compressor compresses the cooled feed with PSA tail gas. The compressed gas cools against cooling water, returning process streams, and externally supplied refrigeration.

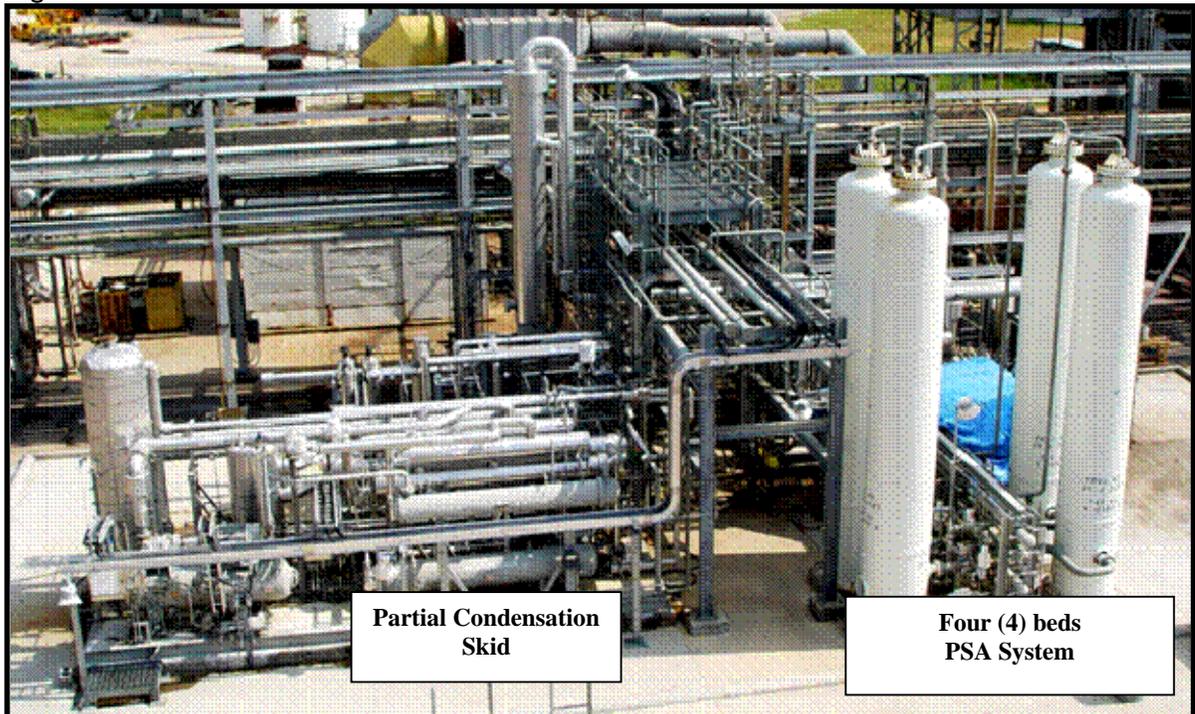
Condensed liquid from the PSA Feed Separator warms against part of the compressor discharge flow and flashes to an intermediate pressure in the HC Product separator. This flash step removes dissolved nitrogen from the liquid to meet customer specifications. The vapor from the HC Product separator recycles back to the compressor. A pump raises the liquid hydrocarbon product to the required delivery pressure. The final step before returning the liquid to the polypropylene production unit is removing any remaining dissolved water from the hydrocarbon in the liquid-phase product drier.

PSA Section:

The N₂-rich vapor from the PSA feed separator warms against part of the compressor discharge flow and then flows to the PSA for further purification. The PSA extracts the remaining hydrocarbons from the gas producing a N₂ product with less than 50 ppmw of C₃+ hydrocarbons. The hydrocarbons return to the feed compressor in a low-pressure tail gas stream from the PSA.

Figure 6 is a photo showing the PSA skid and Process skid.

Figure 6



PNRU Operations Assessment

The PNRU recovery system started in spring 2004. The recovery system has achieved the project objectives:

- No vents to flare – all HC and N2 reused
- N2 Product purity better than design
- Demonstrated Operational Flexibility
- Valuable Recovered Products
- More stable polypropylene degassing operations

PNRU Flexibility and Benefits

The PNRU handles purge gas from multiple PP units at site. It has run smoothly through design and all turndown conditions. The operator is quite pleased with the unit's steady performance when processing variations or swings in feed composition (feeds leaner than design to feeds richer than design).

The project simple payback was less than 24 months, using propylene and nitrogen values from 2003. The PP producer realizes much higher returns with today's feedstock and energy costs. In addition, the project better positions the producer for tighter HRVOC emission regulations in the US.

3. Third System – North American PP Producer

Air Products has sold our third recovery system. This is another retrofit project for a North American polypropylene producer. The expected PNRU startup date is early 2006.

SCOPE OF SUPPLY

Air Products offering for the recovery equipment includes design and packaging of the skidded equipment modules for cost effective installation. Air Products can supply the skidded equipment for others to install. Alternatively, we can offer "turnkey" systems, where Air Products will handle all aspects of the project. We provide mechanical warranties and process performance guarantees for product recoveries, and utilities consumption.

CONCLUSIONS

- Air Products has successfully commercialized improved polyolefin plant vent gas recovery systems using PSA and partial condensation technology. The first unit, for a grassroots PE plant, started in June 2003. The unit meets or exceeds operation goals. It is a good example of how a technology licensor optimized the overall plant design using Air Products system's complete recovery performance.
- Our second unit started in March 2004. It is a retrofit project at a world scale PP facility. The unit processes purge gas from multiple PP lines, and has met or exceeded all design goals for performance and operation.
- Air Products developed a benefits model so producers can assess major operating costs for off-gas treating, including polymer degassing vents, and the gas flaring steps. It also quantifies emissions resulting from flaring.
- Full recovery systems deliver the lowest operating costs and the most environmentally benign operations. They capture valued materials for re-use, and avoid unnecessary flaring.
- Air Products' commercial experience show the improved recovery technology is appropriate for new, world scale, grassroots plants, and for site-wide vent gas processing.