CASE STUDY

PRISM® PB6050 Membrane Separators for hydrogen separation in glycol manufacturing

tell me more

“Our relationship with the petrochemical industry is growing stronger as we adapt technology to meet the demands of modern business.”

Shawn Smith, Sales Account Executive, Air Products
Economical Alternatives


When Xinjiang Tianye Group approached the engineers at Permea China, they issued a challenge. Remove the buildup of hydrogen from the glycol manufacturing process. Make it efficient. Figure out how to do it economically.

Our engineers delivered. The teams at Permea China collaborated with the Air Products engineers in North America and synthesized a solution. Utilizing a new membrane separator, which is designed for small process gas and biomethane applications, our engineers designed a hydrogen-rejection membrane system that operates at low pressures more economically than other technologies.
Glycol Production

Glycols, in their various forms, are used in a number of different industrial and commercial applications, as a heat transfer fluid for cooling systems to primary material used in the manufacture of various polyesters.

The process is evolving away from using reactants like sodium hydroxide and sulfuric acids, which are very corrosive and somewhat dangerous to use, to more environmentally friendly options. These manufacturing processes involve reacting dimethyl oxalate (DMO) and carbon monoxide (CO) over a catalyst to create the synthesis compounds required to produce glycol.

The process begins with the generation of carbon monoxide in the tail gas of a calcium carbide furnace. The tail gas contains 75–90% carbon monoxide with hydrogen molecules and other impurities. Typically, these systems use a palladium catalyst reaction to remove hydrogen from the tail gas stream. In the presence of a catalyst (palladium which is very expensive) the hydrogen ions will be removed but there are secondary reactions that cause a buildup of carbon dioxide (CO$_2$). The buildup of byproducts slows down the reaction rate and additional equipment is required in the downstream process; dehydration and a carbon bed are required to remove the CO$_2$ and the water molecules. The reaction chamber and downstream equipment makes this option 1.5 to 2 times more expensive than the membrane-based system. The reduction of hydrogen molecules is essential to ensure that DMO production is optimized.
System Design

The treatment array consists of 104 of the PRISM PB6050-P3 membrane separators each processing approximately 230 Nm³ of feed gas per hour. The system configuration is a single stage with feed gas passing through the bore of the membranes. This setup facilitates very large flow volumes making the system compact and the low pressure requirements minimize the compression, making the process economical to operate. The gas flow through the PB6050-P3 membrane separator is directed through the bore of the hollow fibers, compared to the shell-side feeds of the larger Single End (SE) membrane separators, making the molecular diffusion more efficient. The SE membrane separators are designed for use in facilities with systems that operate up to 200 BARG.

“Using the PB6050 membrane separator makes sense in this processing facility. The low pressure, large gas flow volumes, and economic considerations all made this product and configuration the clear choice to meet all of the customer’s requirements.”

Don Henry – Senior Engineer, Air Products
The P0 fiber has a thick wall and small inner diameter which makes it very durable for high-pressure, shell side feeds up to 200 BARG. This flow forces the hydrogen molecules into the small bore of the hollow fiber. The P3 fiber has thinner walls and an inner diameter that is more than twice as large as the P0, making a bore-feed flow more efficient. The P3 fiber operates at much lower pressure and permeates the hydrogen molecules to the outside of the hollow fiber.

The PB6050-P3 membrane separators are designed for flammable gas processing, like biogas to biomethane which requires secondary containment. The shell design is PED Class-3 rated so it does not require a secondary containment pressure vessel. This design eliminates extra fabrication costs and makes installation, service, and replacement very efficient. Each membrane separator is piped directly into the distribution manifold.

The PB6050-P3 separator weighs 27.4 kg, which makes installing and field service manageable without employing lift assist equipment.

**System Performance**

The total flow of product gas treated by the PB6050-P3 membrane separators is 22,062 Nm³ per hour. The processed carbon monoxide gas exits a PSA with a hydrogen concentration at 1000 ppm and the carbon dioxide concentration around 300 ppm. After membrane separation, the hydrogen concentration is reduced to 239 ppm and the carbon dioxide concentration is reduced, by about 45% in the product gas, to 169 ppm. The carbon monoxide concentration remains essentially the same at 99.5 mol% in the feed and product streams. The treated stream then enters the reaction chamber for CO/DMO coupling before glycol synthesis.
Processing the feed gas through the PB6050-P3 membrane separators, the hydrogen concentration is reduced by a factor of approximately 4x (in this example, from 1000 ppm to 239 ppm) and the carbon monoxide concentration is relatively unchanged. For safety reasons, it is important to control the hydrogen concentration to less than 300 ppm in the ethylene glycol product.

### Hydrogen reduction glycol manufacturing

<table>
<thead>
<tr>
<th>Composition</th>
<th>Feed Gas</th>
<th>Pre-heat feed gas</th>
<th>Post-heat feed gas</th>
<th>&quot;Product gas&quot;</th>
<th>Permeate gas</th>
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<tr>
<td>H₂</td>
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<td>1,000</td>
<td>1,000</td>
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<td>100</td>
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<td>Total Flow kmol/hr</td>
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<td>1,070.7</td>
<td>1,070.7</td>
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<td>Total Flow Nm³/hr</td>
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<td>24,000</td>
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<td>28.0</td>
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Options and Economics

The Xinjiang Tianye system generates 24,000 Nm$^3$/hour of carbon monoxide feed gas, a relative large volume, which creates options for separating the unwanted hydrogen molecules in the process reaction stream.

Traditionally, these applications will use a catalytic process to achieve the 200 ppm hydrogen concentrations at these high volumes. A cryogenic process is viable in this flow range but the cost of constructing a distillation column is quite high and the maintenance of the system can be complex.

Very large hydrogen (SE) separators are capable of processing this volume of gas using a shell-side feed configuration. In a shell-side feed, or in an axially-wound membrane configuration, the process is constrained by physical limitations due to flow design of the gas over the hollow fiber membranes. This generally requires a great deal of compression power to facilitate the separation process.

There are economic advantages realized by utilizing low pressure separation with the PB6050-P3 membrane units. Operating cost is reduced since the secondary compression power is not required. Capital expenditures are reduced by approximately $500,000 over the SE membrane separator system and $700,000 over the catalytic process.
Permea China, Ltd. is the exclusive distributor of gas separation products manufactured by Air Products PRISM Membranes. Permea China, Ltd. sells membrane separators in China and most of Asia through a distribution network of value-added-resellers that are called "Preferred Partners".

Permea China, Ltd. provides engineering and fabrication of high-specification systems for EPC companies that supply treatment systems for petrochemical and refinery applications. For more information about product applications and capabilities, visit www.Permea.com.cn.

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