Membranes for Hydrocarbon Recovery in Petrochemical, Refinery and Natural Gas Processing Applications


Membrane Technology and Research, Inc.
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Membrane Technology and Research, Inc.

- Company founded in 1982, dedicated to development and commercialization of membrane-based separation technologies.
- Novel technologies based on innovative R&D, funded largely through U.S. government contracts (Department of Energy, Environmental Protection Agency, National Science Foundation, Office of Naval Research, Department of Agriculture).
- Most commercial applications to date involve separations in the gas phase.
- Several liquid phase separation applications are under development.
COMPANY STRUCTURE

- Marketing and Sales
  - Houston and Brussels Sales Offices
- Engineering
- Membrane and Module Manufacturing
- Research and Development
- Finance and Administration

Approximately 40 employees total.
Large installations are constructed by third party fabricators based on MTR engineering packages.
MTR Multilayer Composite Membrane

- Selective Layer
- Microporous Layer
- Support web
Permeation through nonporous polymer film is governed by diffusion and sorption.

Diffusion favors smaller molecules. Sorption favors larger molecules.

Permeation behavior of glassy polymers (diffusion dominates):

$$\text{He} > \text{H}_2 > \text{CO}_2 > \text{O}_2 > \text{CO} > \text{N}_2 > \text{CH}_4 > \text{C}_2\text{H}_6 > \text{C}_3\text{H}_8$$

Permeation behavior of glassy polymers (sorption dominates):

$$\text{C}_3\text{H}_8 > \text{C}_2\text{H}_6 > \text{CO}_2 > \text{CH}_4 > \text{H}_2 > \text{O}_2 > \text{He} > \text{CO} > \text{N}_2$$
MTR’s Spiral-Wound Module

- Module housing
- Feed flow
- Collection pipe
- Feed flow
- Residue flow
- Permeate flow
- Spacer
- Membrane
- Spacer
- Permeate flow after passing through membrane
MTR has achieved a number of world wide “firsts” in commercializing novel and innovative gas separation applications:

1988: First CFC and HCFC Recovery System, 20 membrane systems installed

1992: First VCM Recovery System in PVC Plant, 14 membrane systems installed

1996: First Monomer Recovery System in PP/PE Plant, 25 membrane systems installed, Kirkpatrick Award

1999: First Ethylene Recovery System in Oxidation Reactor Process, 3 systems installed

2001: First Fuel Gas Conditioning System Installed, 3 systems installed

2002: First Natural Gas Nitrogen Removal System Installed
VOC Recovery Capacity of VaporSep Systems Installed in Chemical Processing Industry

Total Amount Recovered Since 1992: 355,000 ton

Annual VOC Recovery Capacity (ton/year)

Year

Energy Savings Capacity of VaporSep Systems Installed in Chemical Processing Industry

Total Energy Saved Since 1992: 19 trillion Btu

Chart showing annual energy savings capacity from 1992 to 2002.
VaporSep Application Example: Recovery of VCM from PVC Manufacturing

• Problem: Loss of VCM through PVC reactor purge gas
  – Lost material = 0.5 to 5 million lb per year
  – Emissions restrictions

• Treatment alternatives:
  – Incineration + HCl scrubber
  – MTR VaporSep\textsuperscript{®} system
Vinyl Chloride Recovery in PVC Plant

Compressor → Condenser → Membrane → Residue
Permeate

99% VCM → 20 - 70% VCM

PVC → Condensed VCM

Fresh VCM

Capital: 10% of Incineration
Payback: less than 1 year
Polyolefin Production Process

- Monomer supply and purification
- Other raw materials supply and purification
- Polymerization reactor
- Resin degassing
- Extrusion/pelleting
- Nitrogen (N₂, C₄, C₃, C₂)
- To flare

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Membrane Recovery of Hydrocarbons in Polyolefin Manufacture: Purge Bin

- Monomer supply and purification
- Other raw materials supply and purification
- Polymerization reactor
- Resin degassing
- Extrusion/pelleting

Recovered C₄, C₃, C₂
Recycled N₂

Membrane system
Propylene Recovery System

- Hydrocarbons in nitrogen
- Compressor
- Refrigerant
- Knock-out
- Nitrogen purge gas
- Purge bin
- Resin
- Polymer product
- Recovered propylene
- Recycle to purge bin (99.9% nitrogen)
Membrane Recovery of Hydrocarbons in Polyolefin Manufacture: Reactor Purge
Reactor Purge Recovery

Recycle Gas:
30% Ethylene in H₂ (6%), C₄ (8%), N₂ (56%)
(800 lb/hr)

Polymerization Reactor

Monomer feed

Polymer discharge

Inert purge

Membrane

Ethylene-depleted stream

Ethylene-enriched stream
### Reactor Purge Recovery

<table>
<thead>
<tr>
<th>Component</th>
<th>Recovery (lb/hr)</th>
<th>Credit ($/lb)</th>
<th>Annual Value ($1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>290</td>
<td>0.20</td>
<td>493</td>
</tr>
<tr>
<td>Butene</td>
<td>284</td>
<td>0.20</td>
<td>483</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td><strong>$ 976</strong></td>
</tr>
</tbody>
</table>

VaporSep system cost: $ 300,000
Power requirement: none
Ethylene Recovery in EDC Production

Inerts to be purged:

Ethane (present in Ethylene feed)
Argon (present in Oxygen feed)
Ethylene Recovery in EDC Production: Recovery Economics

<table>
<thead>
<tr>
<th>Component</th>
<th>Current Losses (lb/hr)</th>
<th>Losses with VaporSep (lb/hr)</th>
<th>Annual Value of recovered Material ($/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>141</td>
<td>13</td>
<td>218,000</td>
</tr>
<tr>
<td>EDC</td>
<td>74</td>
<td>1</td>
<td>93,000</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>$ 311,000</td>
</tr>
</tbody>
</table>

VaporSep system cost: $ 400,000
Power requirement: 50 HP
LIQUID PHASE SEPARATIONS

• Pervaporation
  – Aroma and Flavor recovery
  – Solvent Recovery / Waste Reduction
  – Ethanol Production through Fermentation

• Aqueous Nanofiltration
  – Oil / Water Separation (Bilge and Ballast Water)

• Organic Nanofiltration
  – Separation and Purification of vegetable Oils and Proteins from Extraction Solvents
  – Heterogeneous Catalysis
Polyethylene Purge Bin Application
Chemopetrol Propylene Recovery System

Fabrication

Installed

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Kemya Propylene Recovery System