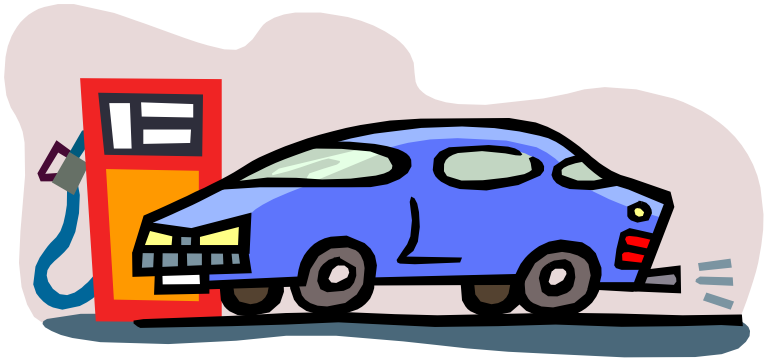
Perfluoropolymer Membranes for Gasoline Vapor Emissions Reduction

John Bowser, Sudip Majumdar
Compact Membrane Systems, Inc.



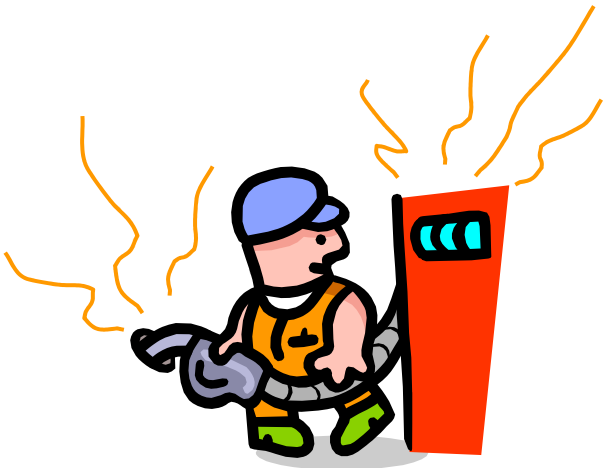
Presentation

- Reducing Gasoline Emissions at Service Stations
- Glassy vs Rubbery Membranes
- Advantages of Perfluoropolymer Membranes over Hydrocarbon-based Glassy Membranes
- Practical Use in a Vapor Processor

Motivation for this Work

A typical gas station operating without vapor controls emits 200 – 1000 liquid gallons of gasoline to the atmosphere in vapor form each month.

- These vapors are transformed into smog, a recognized health hazard.
- Non-renewable energy from oil is lost, and the station has an unnecessary cost.



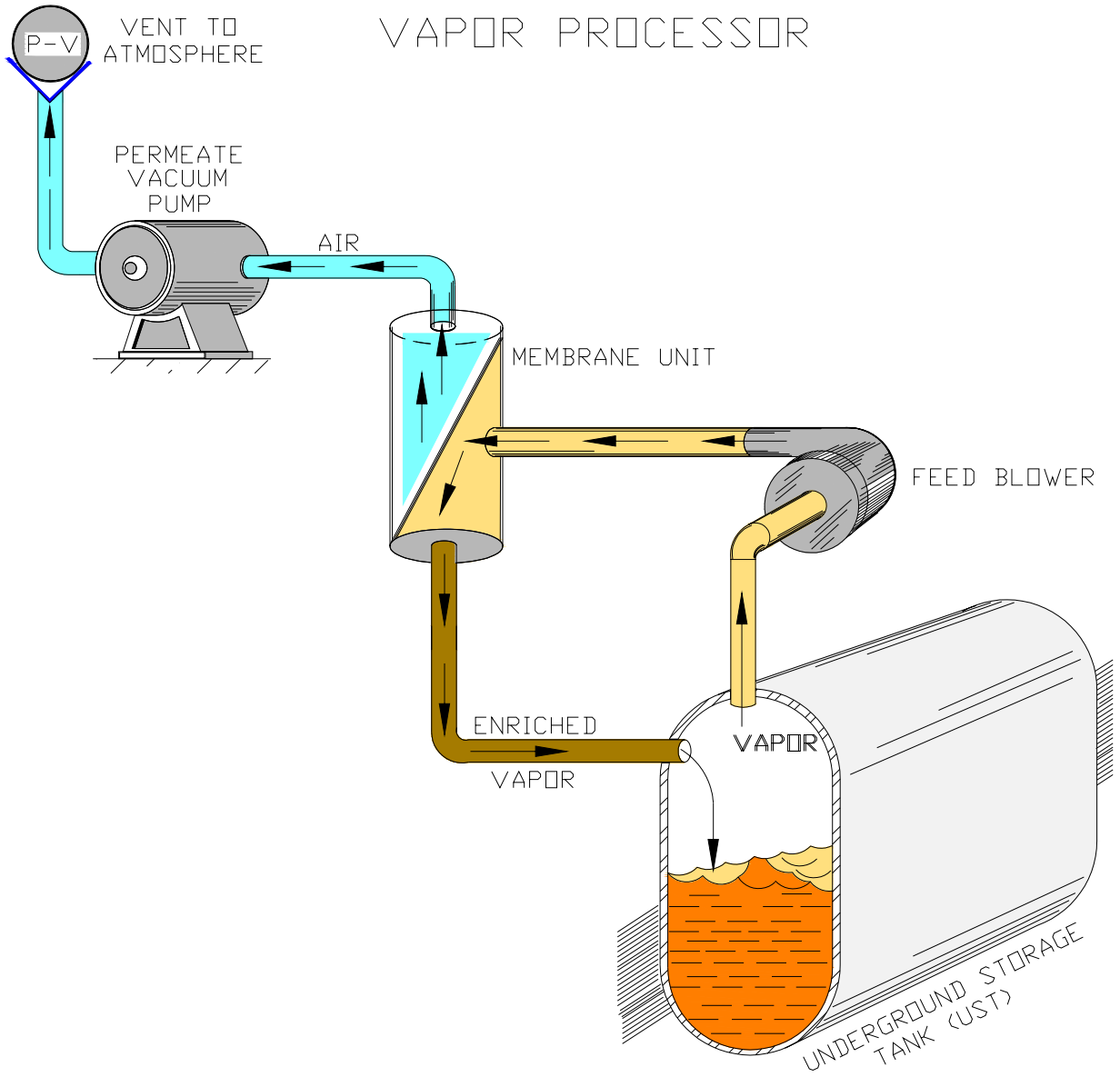
New California Air Quality Regulation

13,000 service stations in California must install Enhanced Vapor Recovery (EVR) equipment by April, 2009.

CMS Technology is Certified as Effective for EVR by CARB

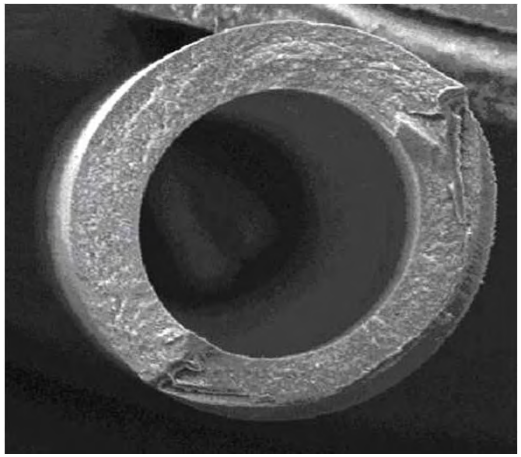
- 90% of CA stations are the “bellows” type.
- The CMS membrane based system is the only equipment certified for EVR use with this type.

Vapor Processor Design

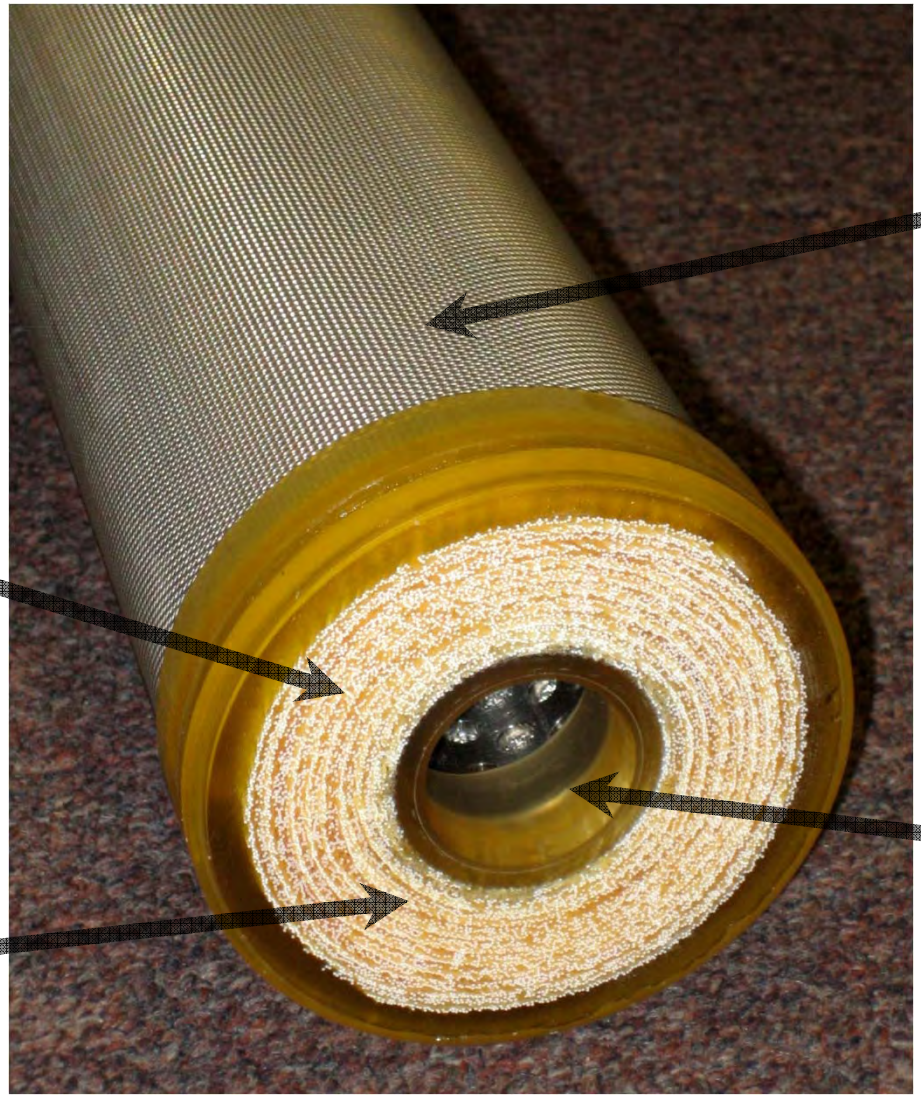


Vapor Processor

Membrane Cartridge



Composite Hollow Fiber Membranes



Dilute Vapor Enters Here

Port for Concentrated Vapor Return

Air Exits Here

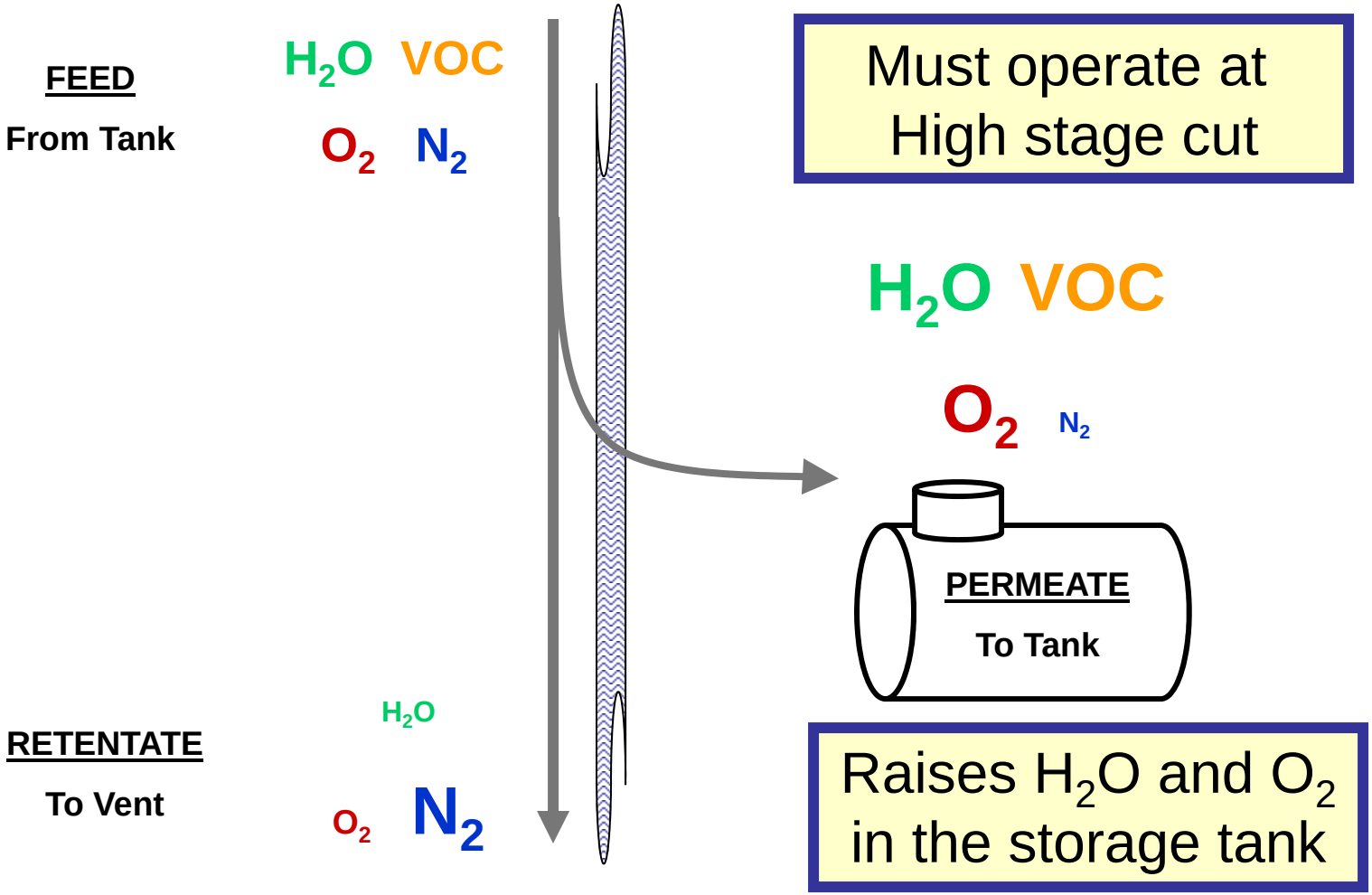
Typical Site

Tank Vents

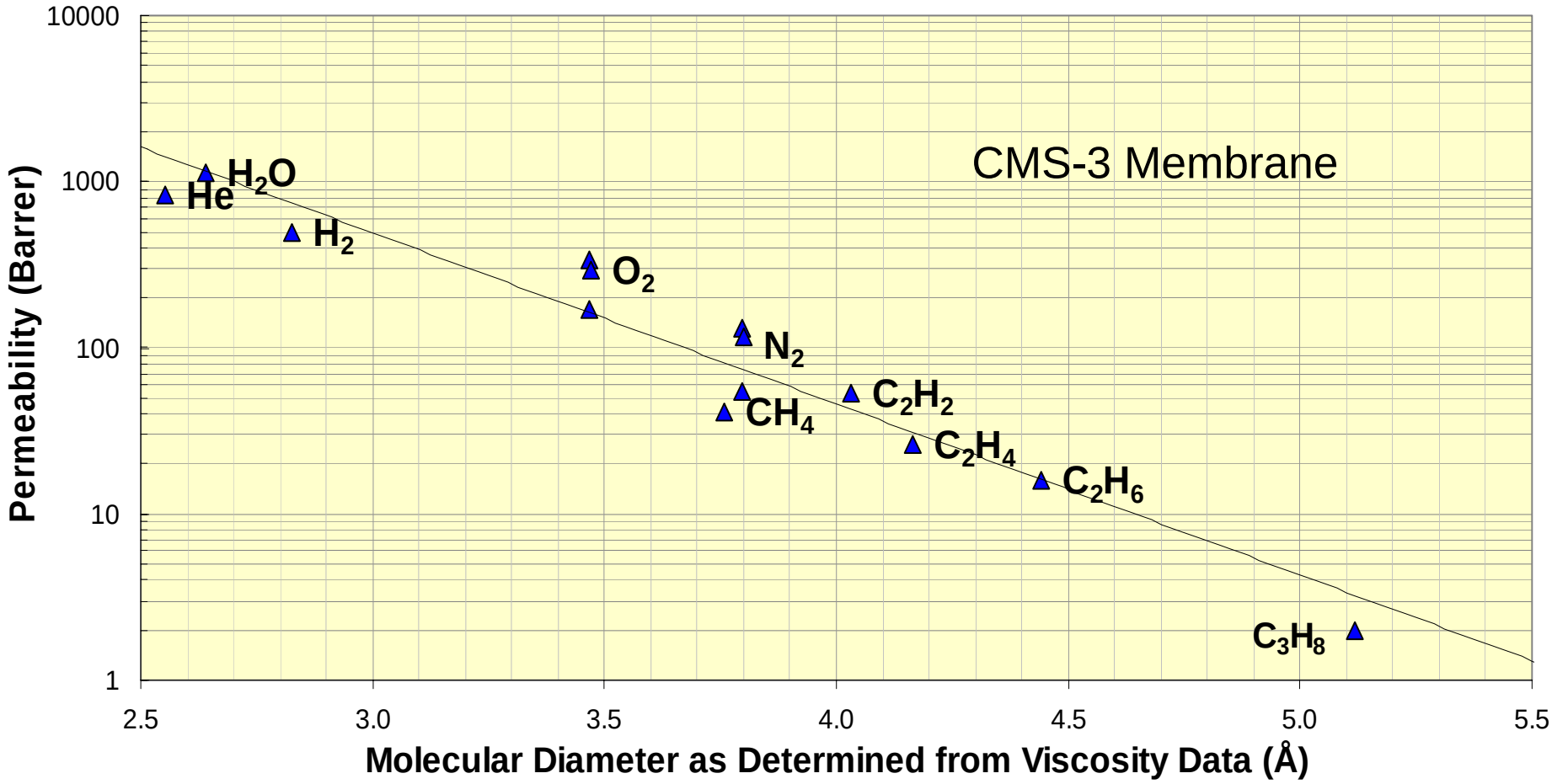
Vapor Processor

Performance 99% Efficiency
(CARB Requirement 95%)

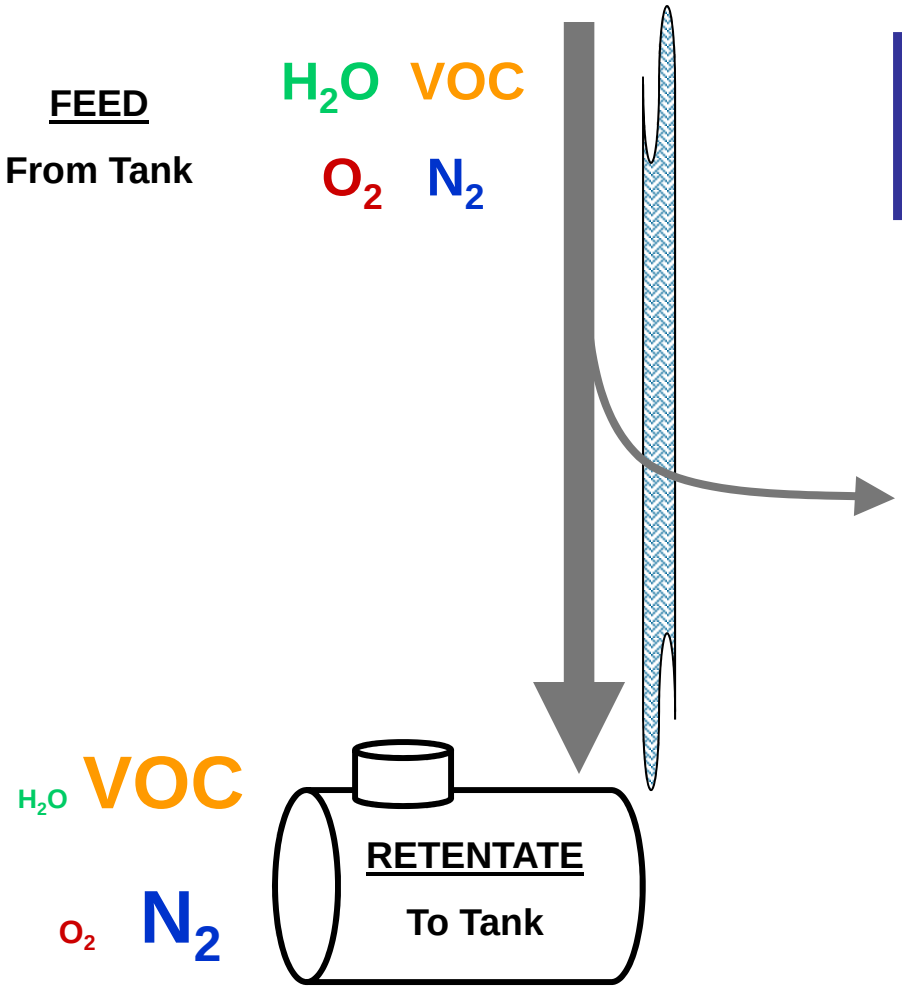
Gasoline Vapor Separation with a Rubbery Membrane



Permeability Decreases with Diameter of Many Gases in Glassy Polymers



Vapor Separation with a Glassy Membrane



Operates at low stage cut

H_2O

O_2 N_2

PERMEATE

To Vent

Lowers H_2O and O_2 in the storage tank

Amorphous Perfluoropolymers

Perfluoropolymer ≡ Fully Fluorinated

Examples:

- Teflon® AF – DuPont
  - Copolymer of TFE and perfluoro-2,2-dimethyl-1,3-dioxole
- Hyflon® AD - Solvay Solexis
  - Copolymer of TFE and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole
- Cytop™- Asahi Glass
  - Cyclopolymerized perfluoro(alkeynyl vinyl ether)

Commercial Amorphous Perfluoropolymer Applications

- Late 1980's – Developed for opto-electronics
- Early 1990's – Porous oleophobic membrane vents and contactors
- Late 1990's – Nonporous membrane contactors
- Today – Nonporous gas and vapor separation membranes

Why Choose a Perfluoropolymer Over a Hydrocarbon Polymer?

Membrane selectivity:

$$\alpha_{xy} = \frac{P_x}{P_y} = \frac{D_x}{D_y} \times \frac{S_x}{S_y}$$

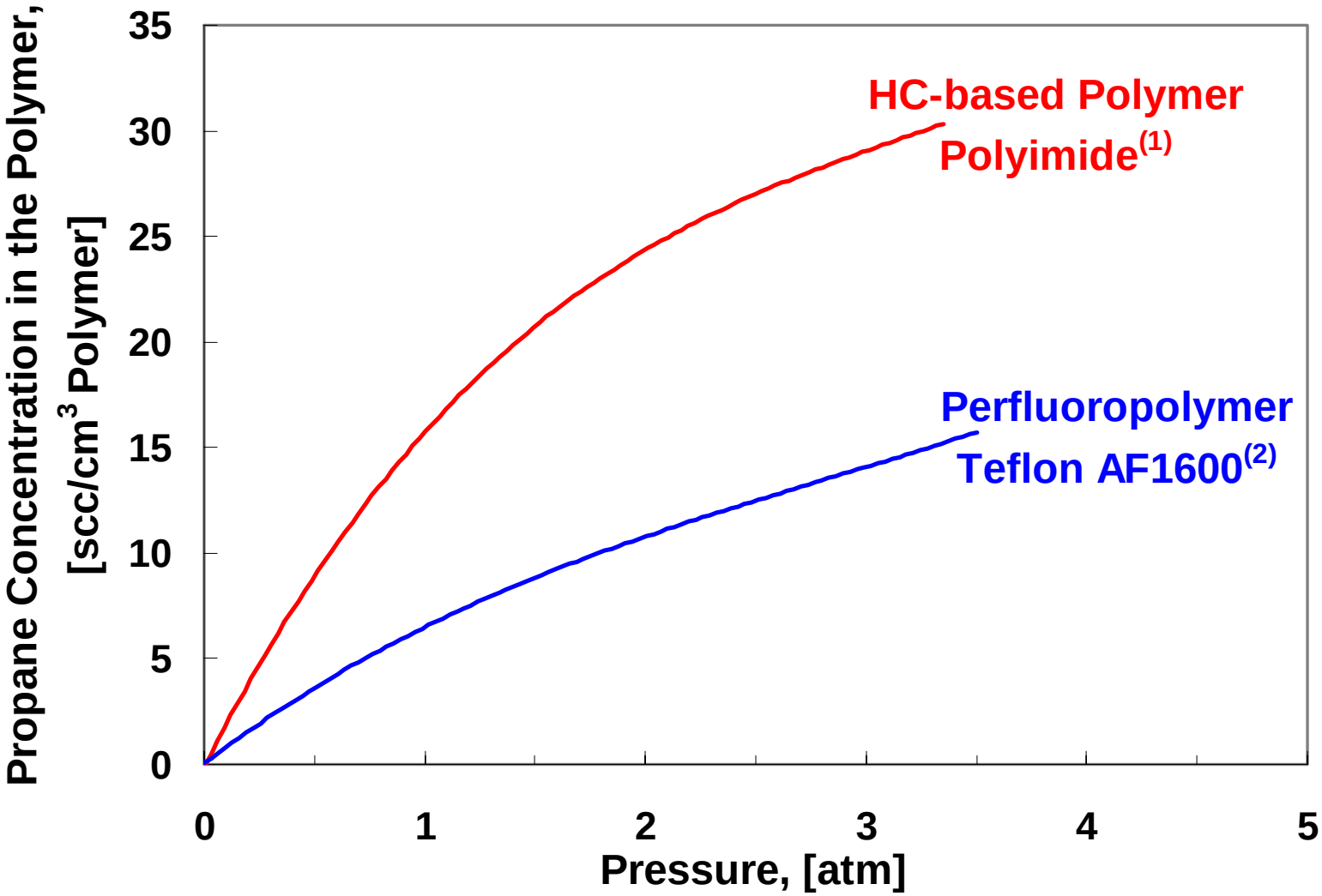
Diffusivity Ratio

Solubility Ratio

For permanent gas (x) – hydrocarbon vapor (y) separation with 'size-sieving' membrane

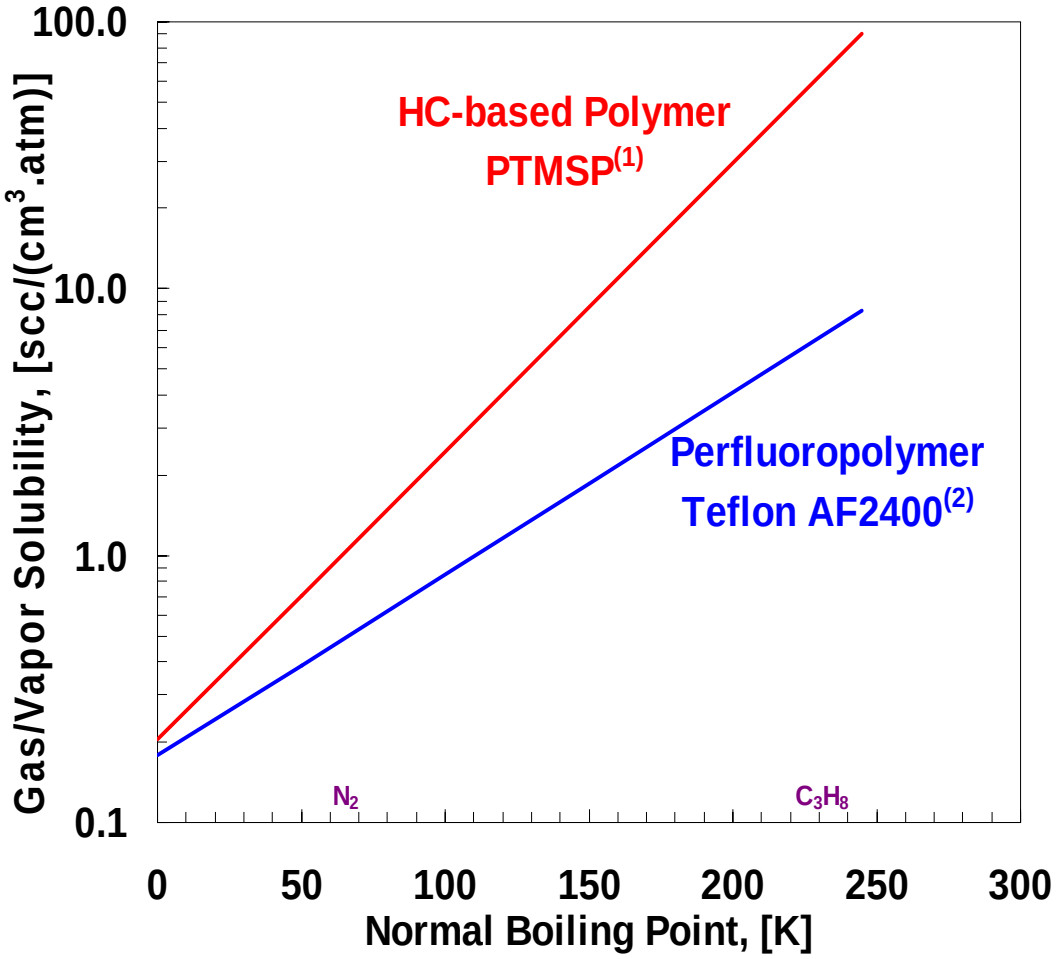
$$\frac{D_x}{D_y} \gg 1 ; \quad \frac{S_x}{S_y} < 1$$

Sorption of Hydrocarbon Vapor in Hydrocarbon vs Perfluoropolymer Membranes



(1) Staudt-Bickel and Koros, *JMS*, **170**, 205 (2000); (2) Alentiev et al., *Macromolecule*, **35**, 9513 (2002)

Gas and Vapor Solubility in Hydrocarbon and Perfluoropolymer Membranes



Permanent Gas/Hydrocarbon Solubility Ratio:

$$\left[\frac{S_{N_2}}{S_{C_3H_8}}\right]_{HC} < \left[\frac{S_{N_2}}{S_{C_3H_8}}\right]_{PF} < 1$$

(1) Merkel et al., *J Polym Sci*, **38**, 273 (2000); (2) Merkel et al., *Macromolecule*, **32**, 8427 (1999)

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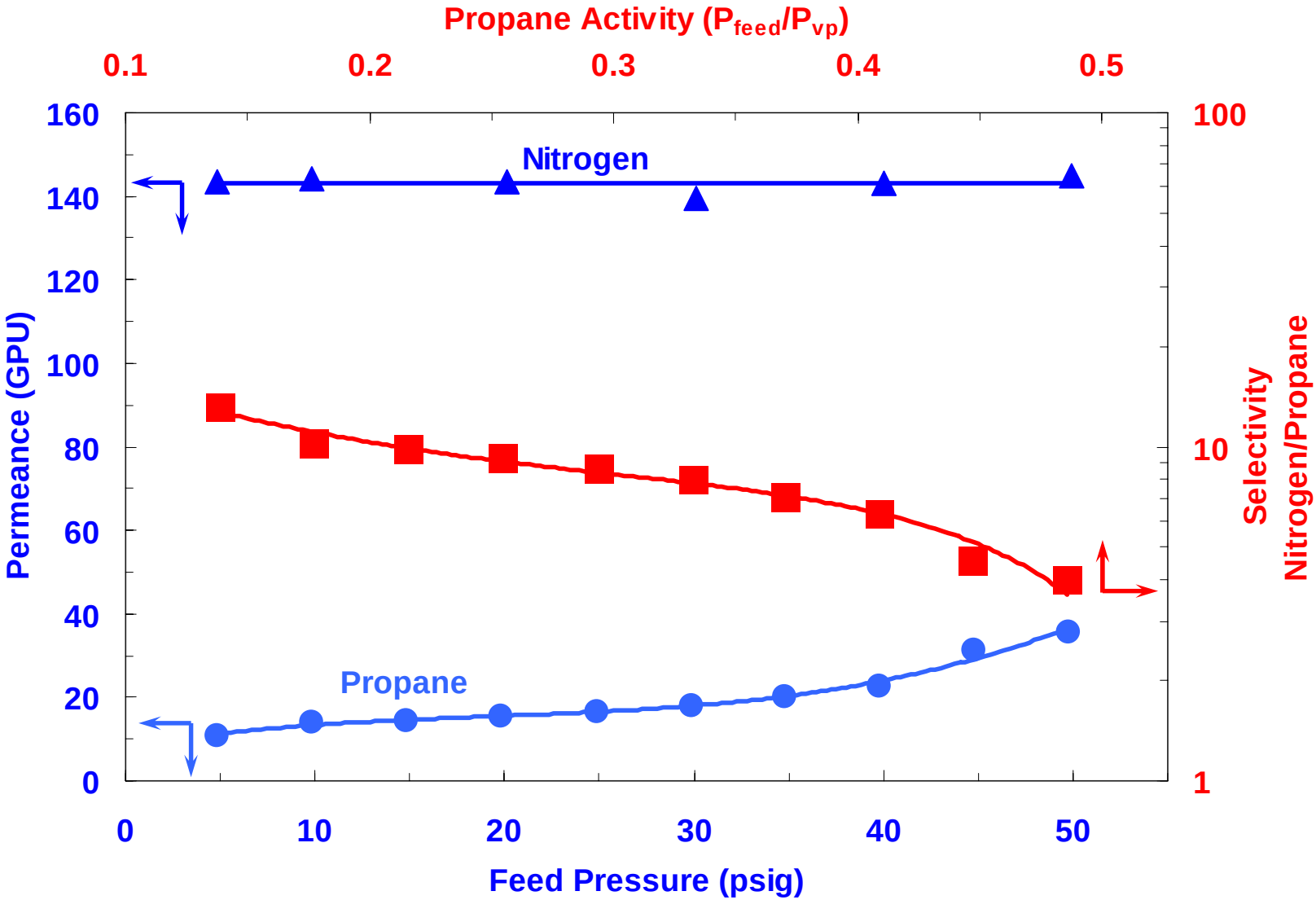
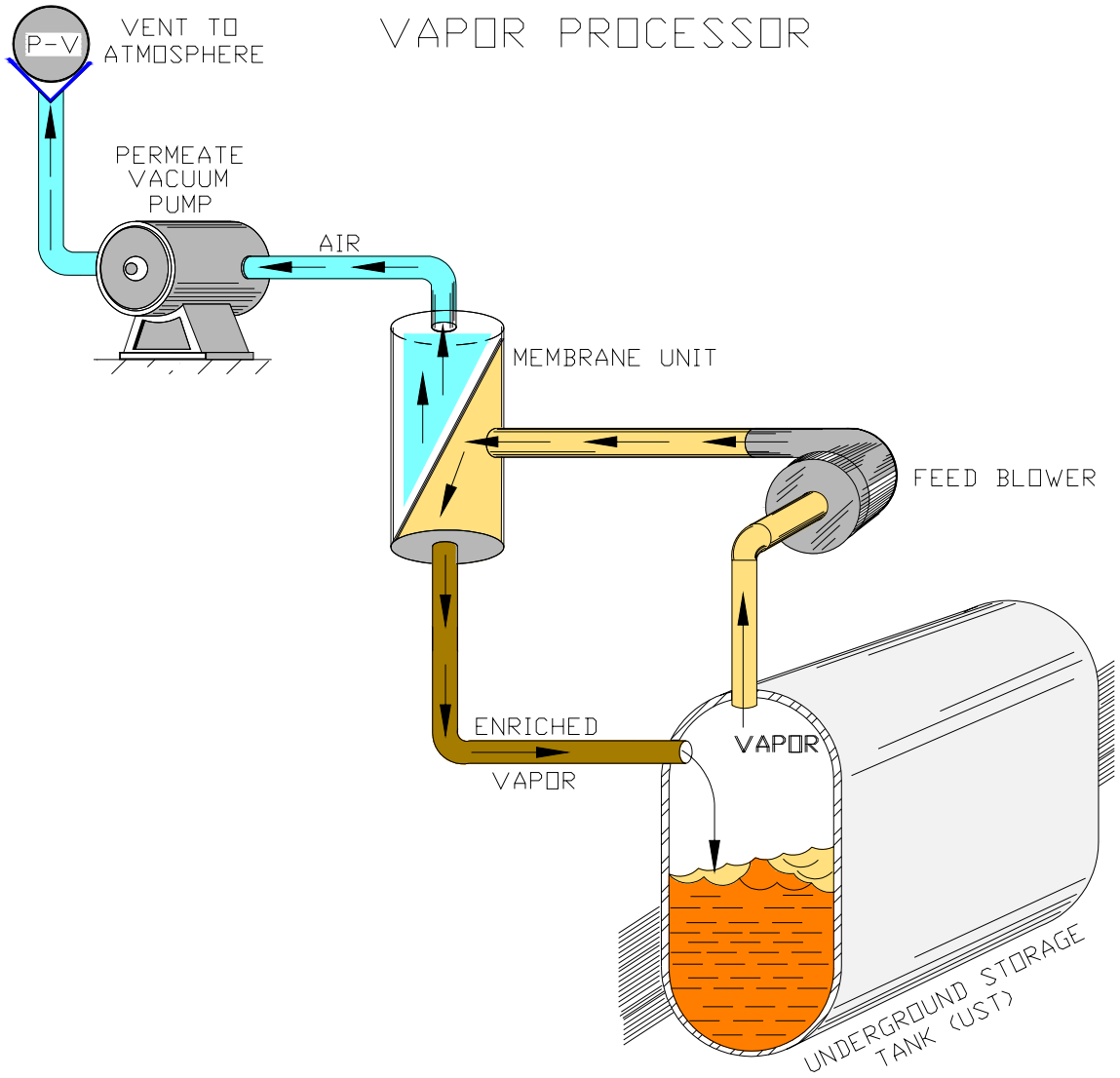
Perfluoropolymer vs Hydrocarbon-based Membranes

- Perfluoropolymers in general exhibit low hydrocarbon vapor solubility. As a result they resist polymer plasticization and thus loss of membrane selectivity with time.
- Permanent gas/hydrocarbon vapor solubility ratios for perfluoropolymers are larger than those of hydrocarbon-based polymers and work in favor of overall selectivity.

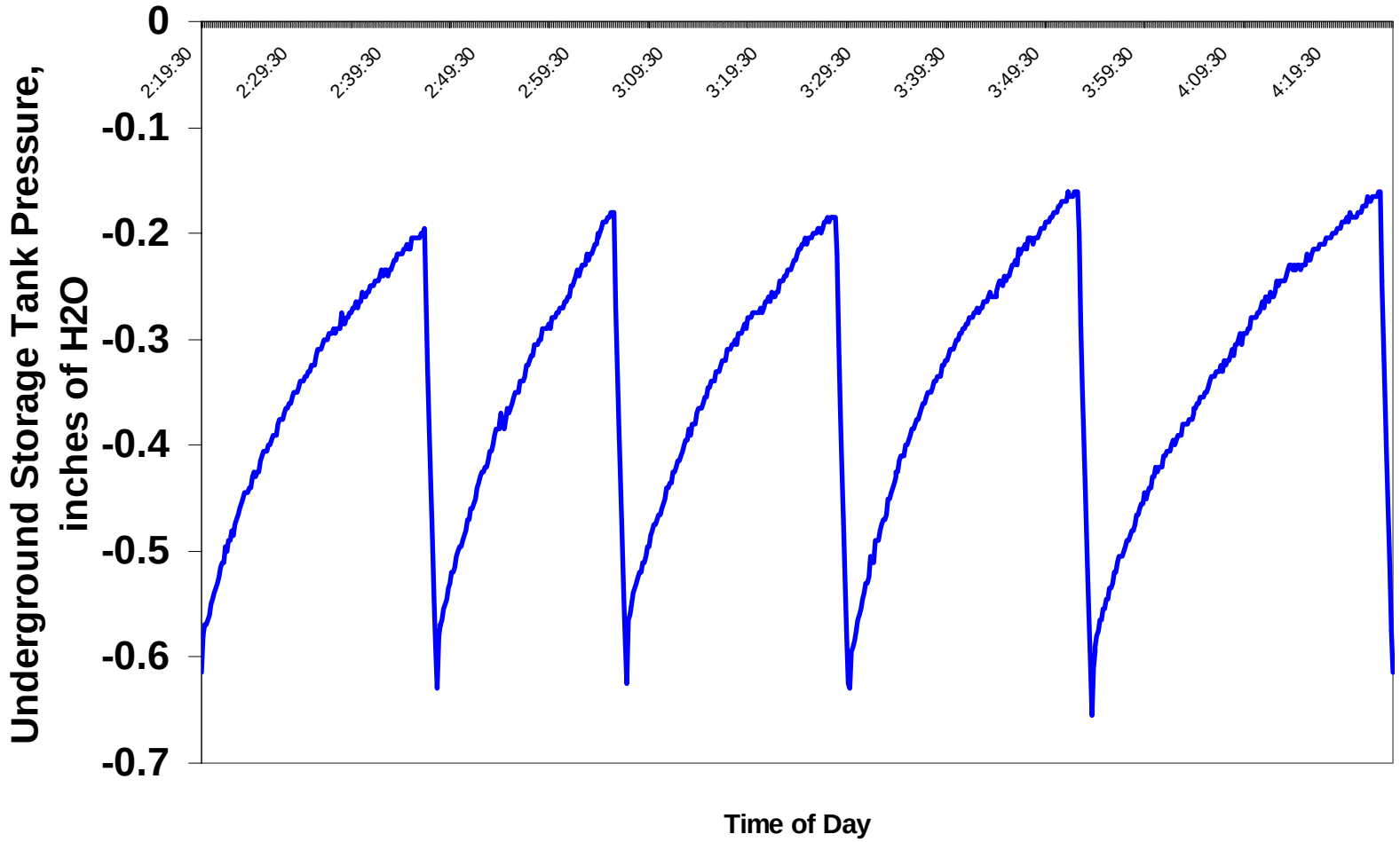
Plasticization Resistant doesn't mean Plasticization Proof



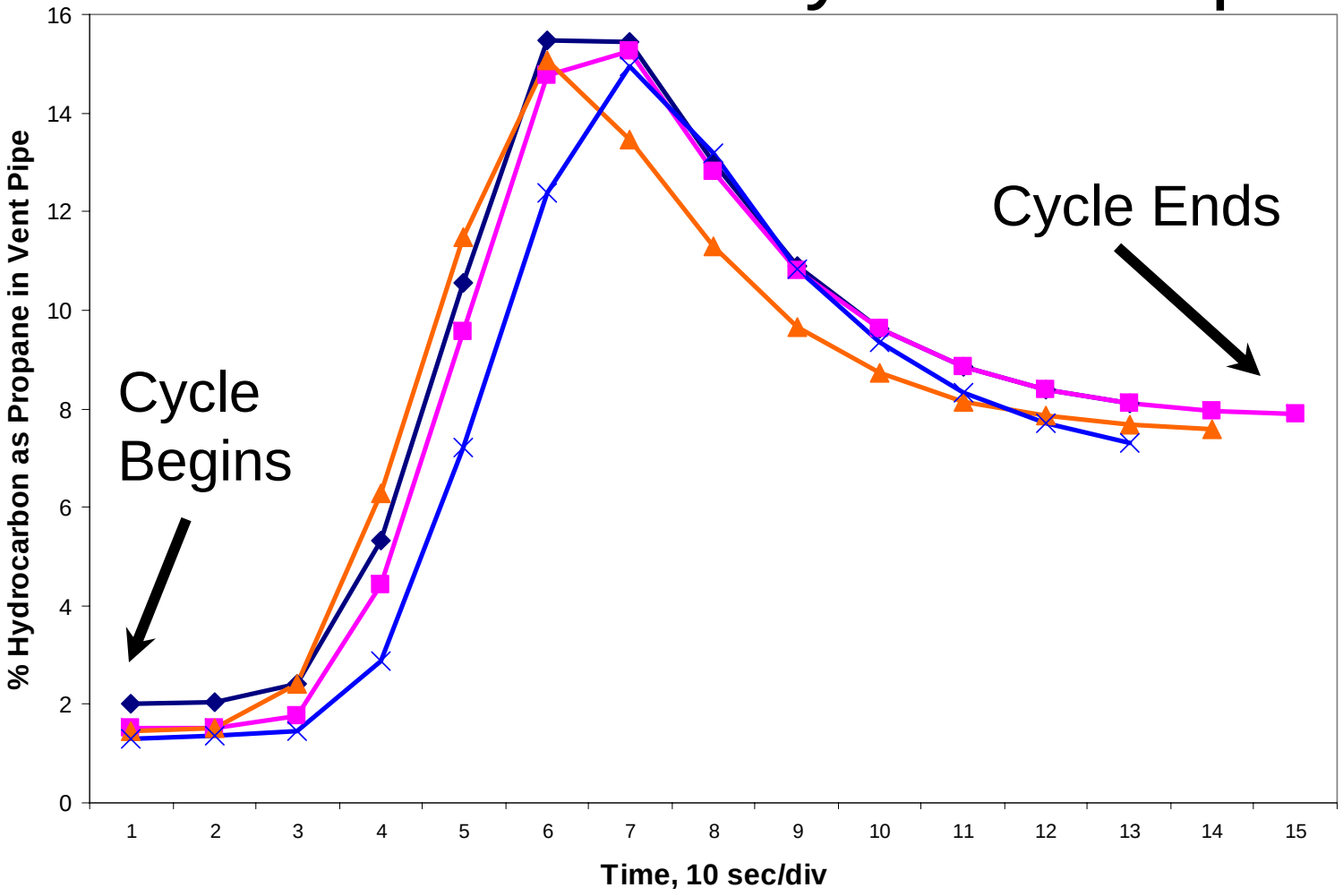
Practical Use of Perfluoropolymer Membranes in a Vapor Processor



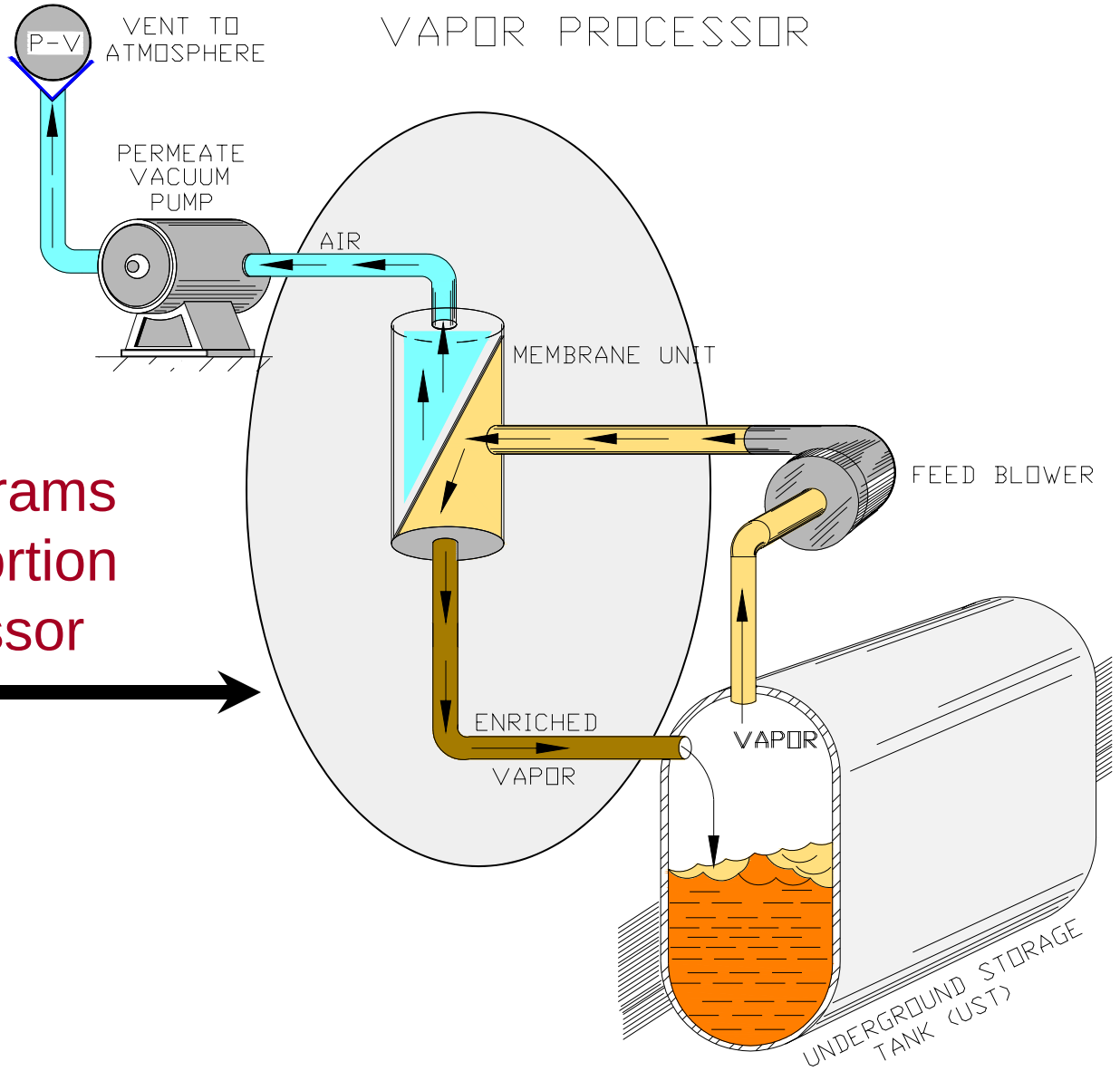
Storage Tank Head Space is Held Below Atmospheric Pressure



Vented VOC Surge on Processor Cycle Startup

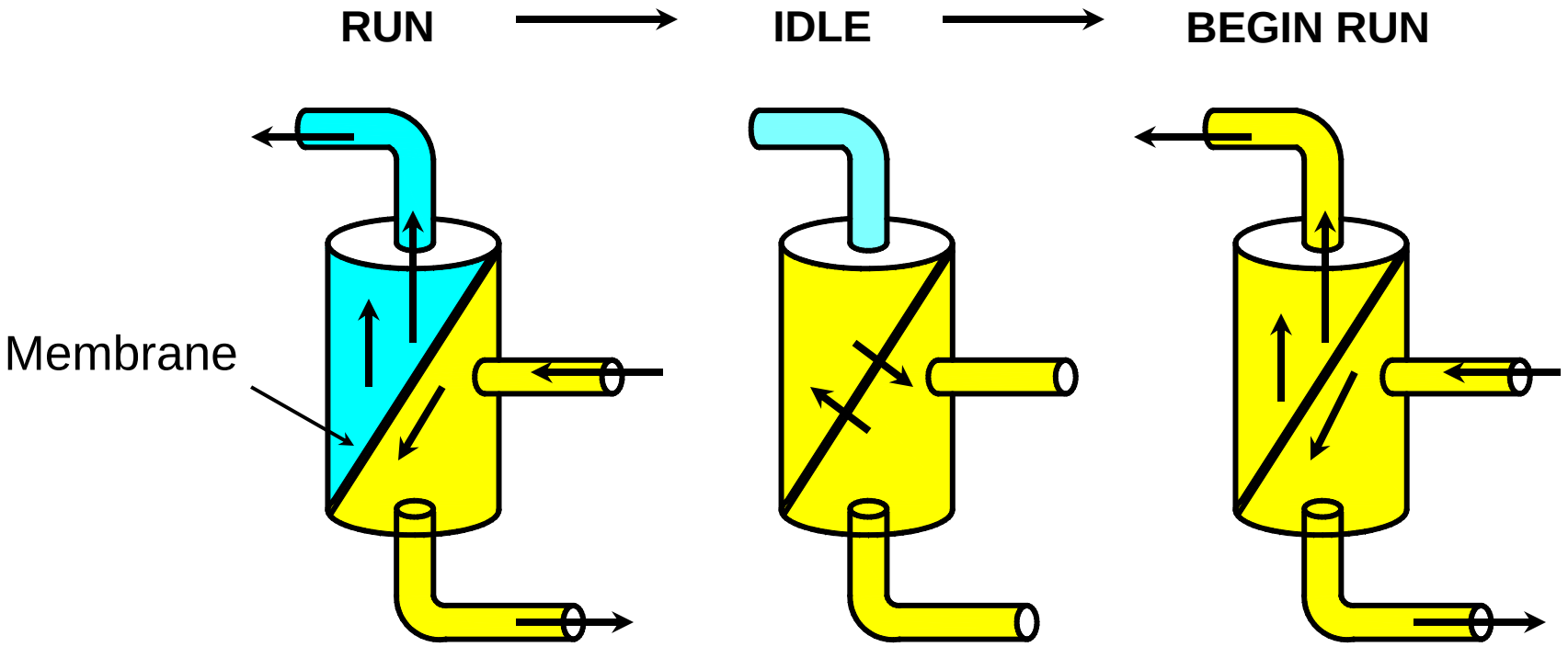


Vapor Processor Design

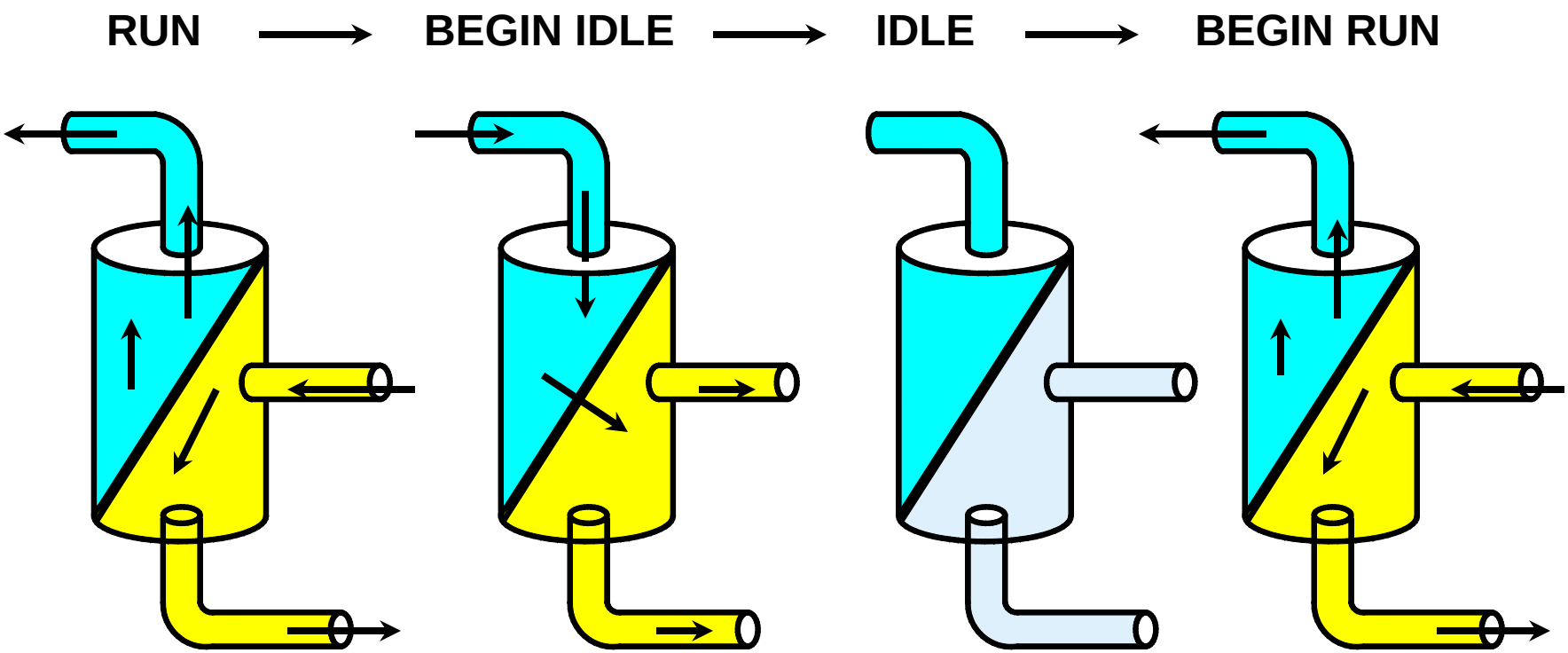


Next few diagrams refer to this portion of the processor

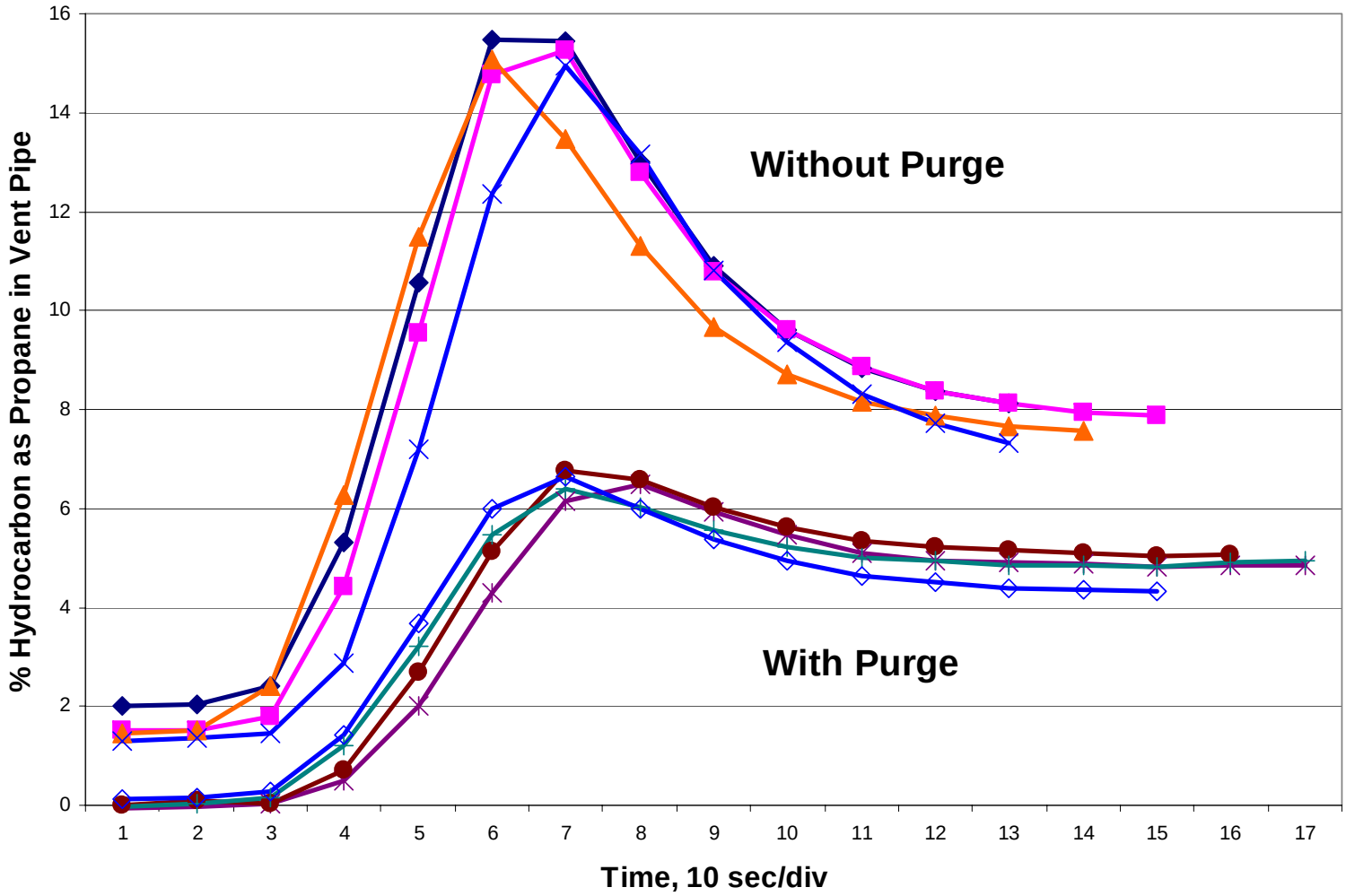
Why the VOC Surge Occurs



A Remedy for the VOC Surge? Briefly purge the module with air.



Vented VOC Profile with Module Purge



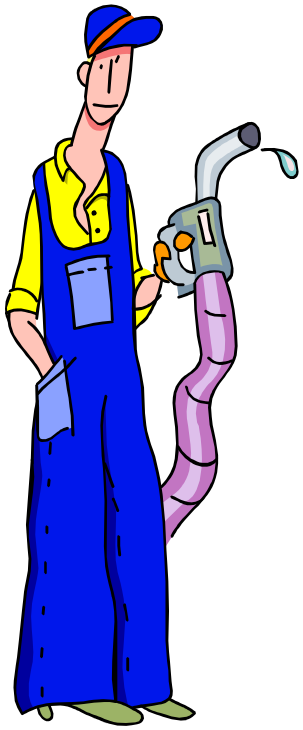
To Sum Up…

- Amorphous perfluoropolymer membranes have advantages for vapor separation
  - High permeance of atmospheric gasses
  - Relatively low plasticization by hydrocarbons
  - Can remove O_2 and H_2O from the hydrocarbon stream returning to the storage tank
- These are the heart of a vapor processor system currently being installed in California gas stations

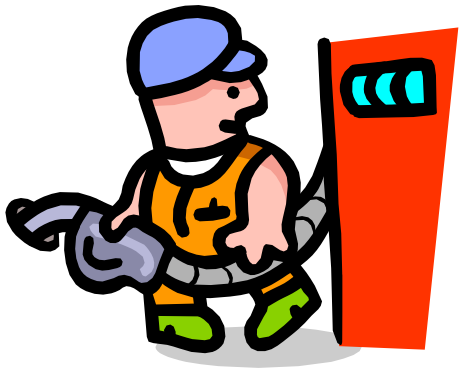
Acknowledgement

The authors gratefully appreciate the support of the US **Department of Energy** and the **Environmental Protection Agency** through SBIR Grants.

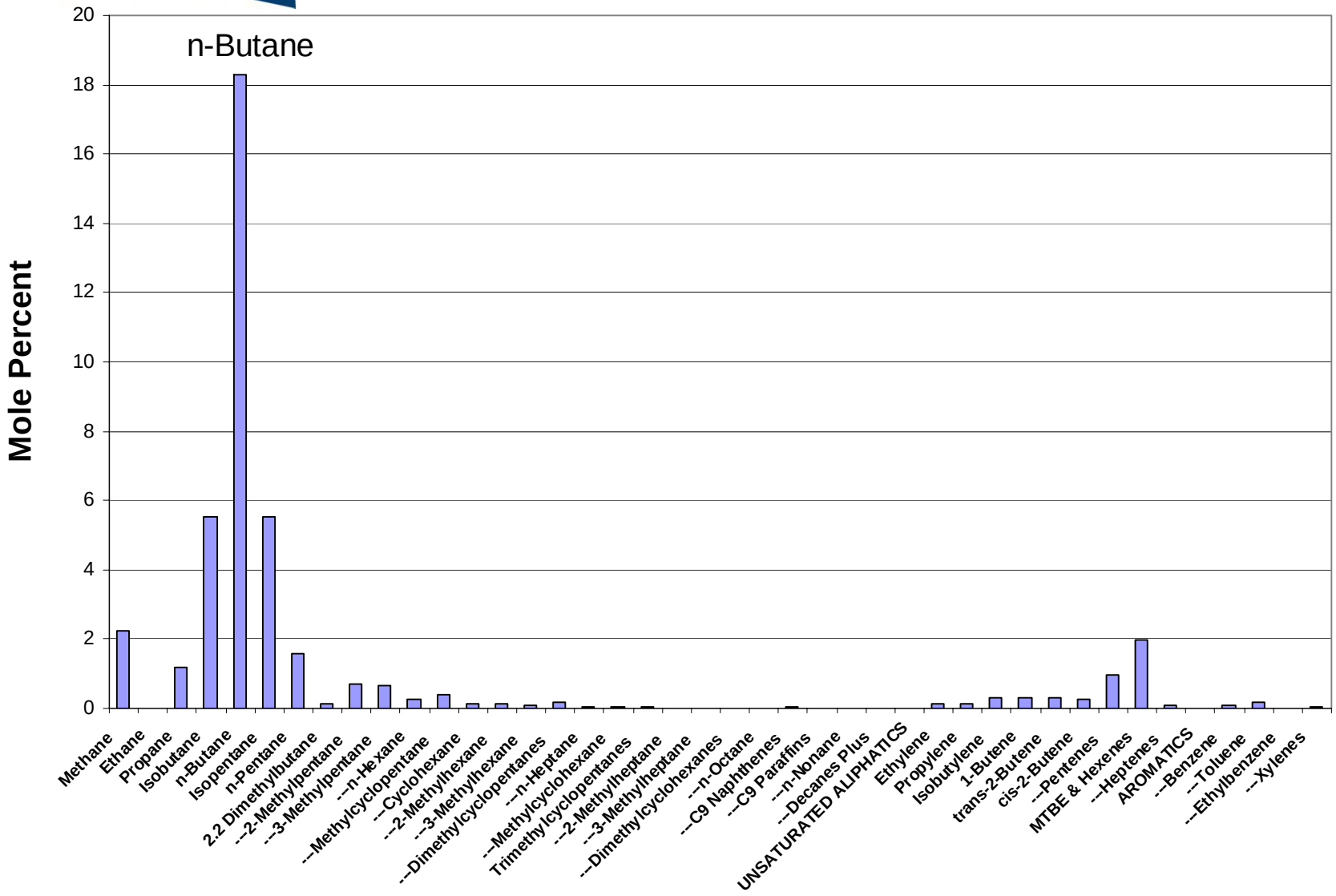
Mahalo!



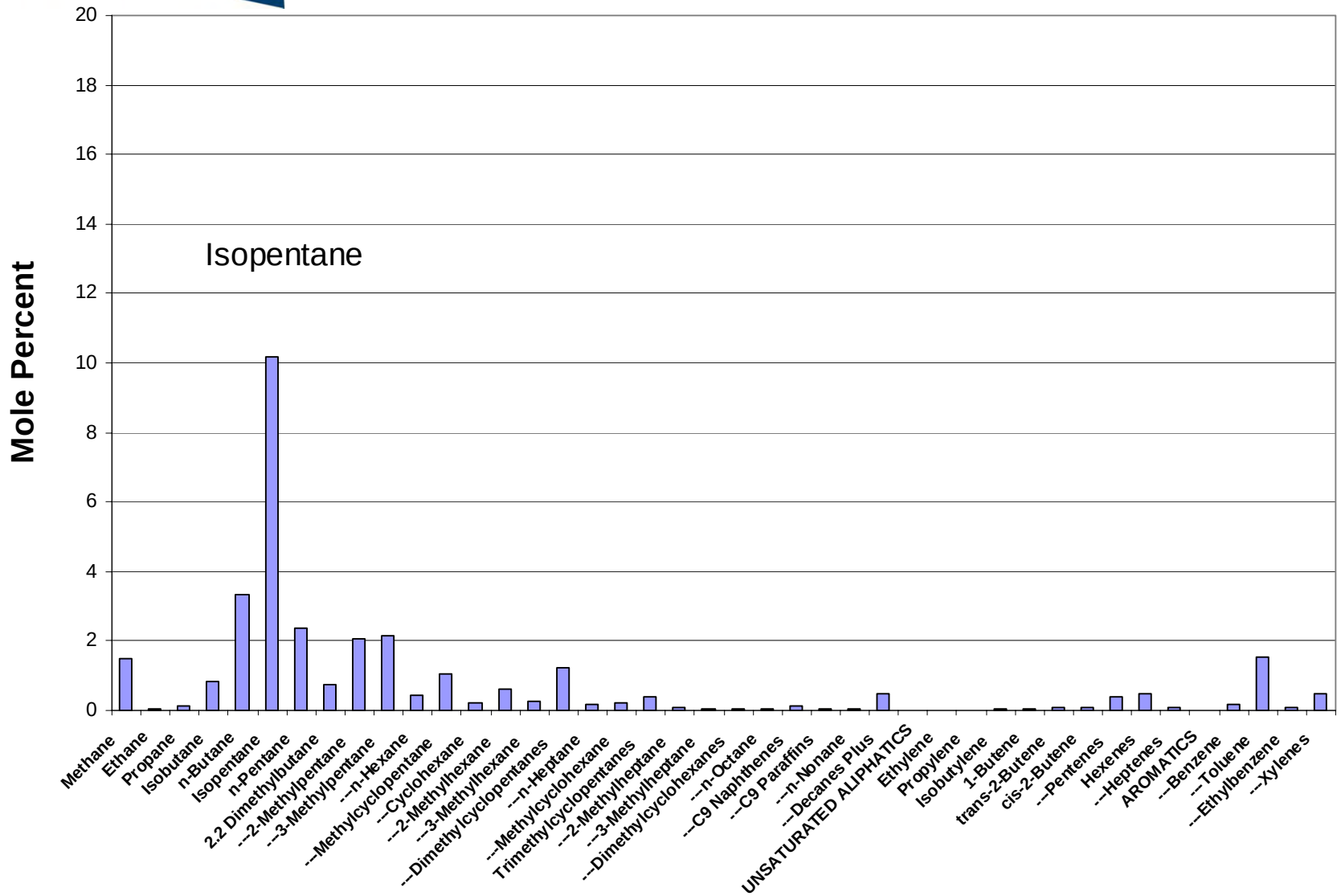
Extra Slides Follow



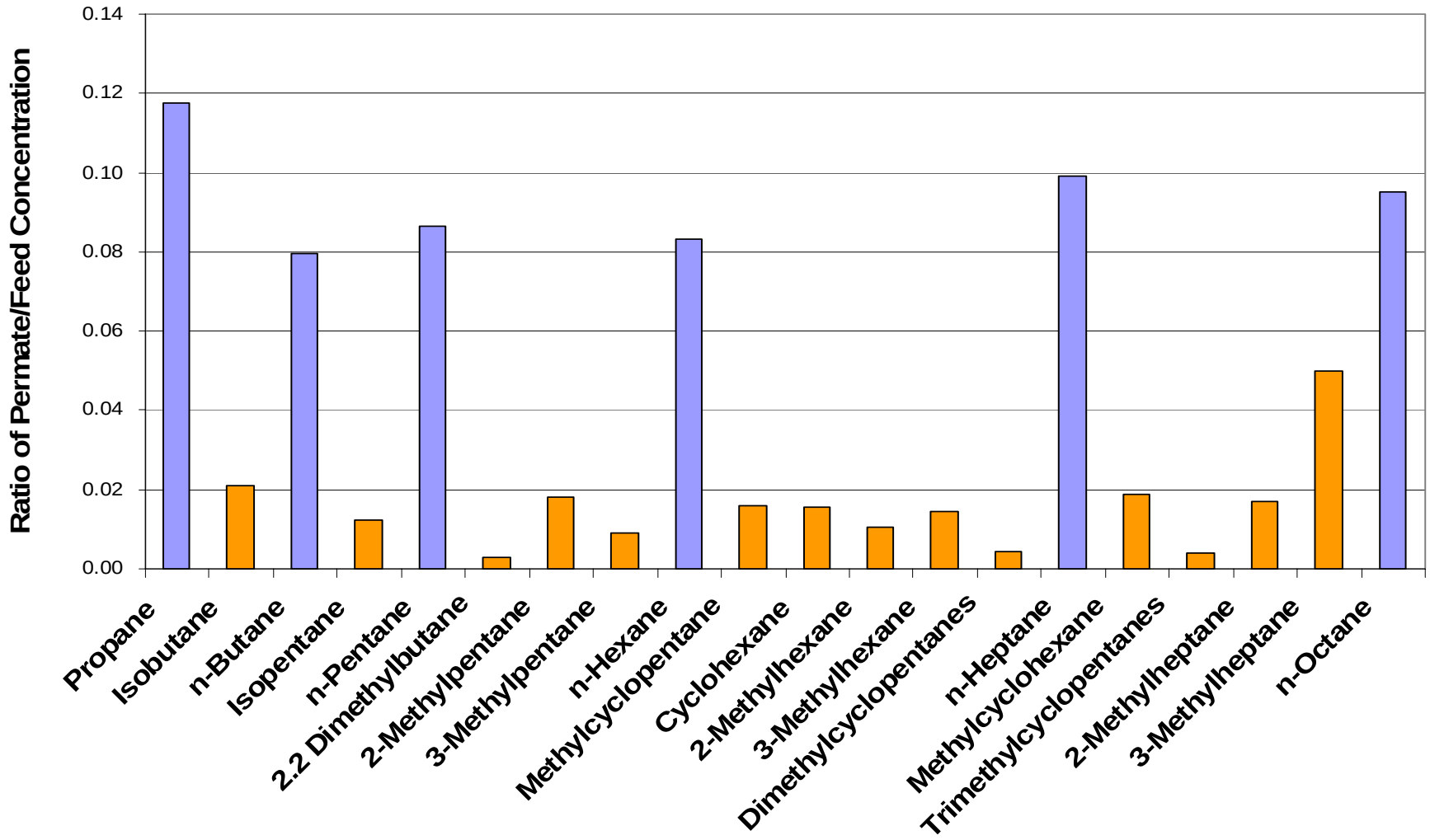
Winter Fuel Vapor Components



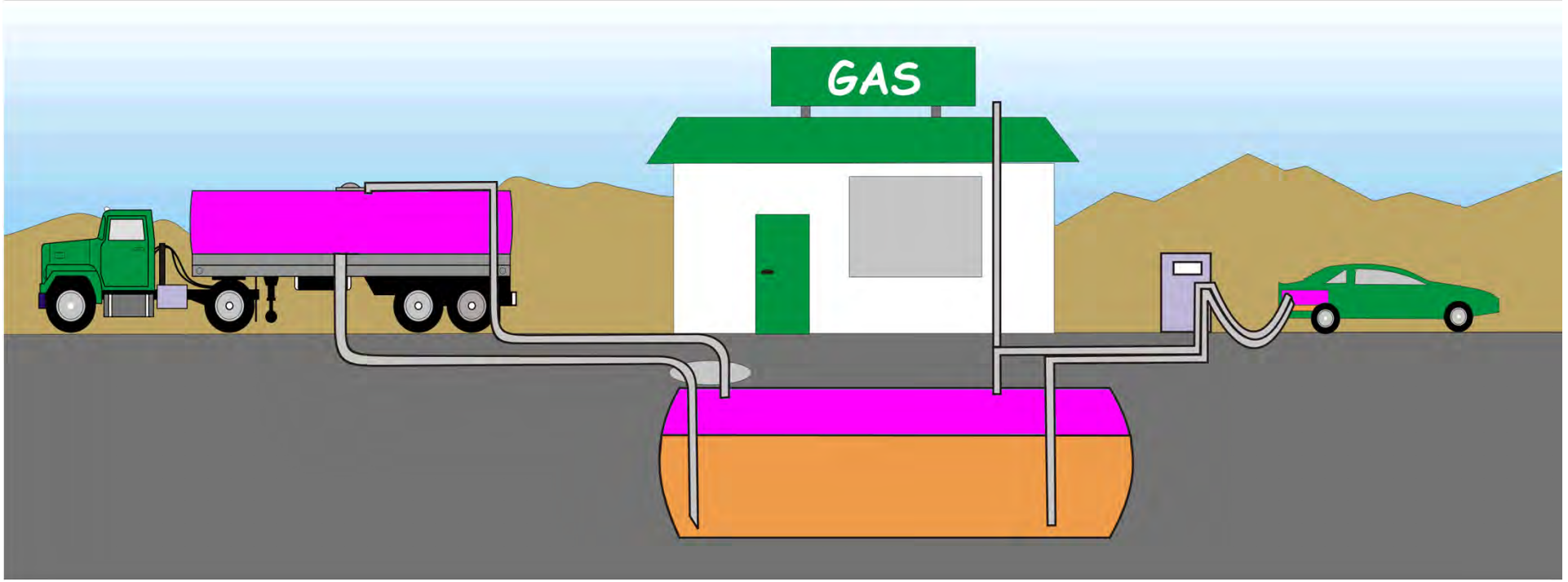
Summer Fuel Vapor Components



Processor Reduction Ratio for Selected Gasoline Components



Vapor Recovery at Service Stations



Phase I

Diagram courtesy of California Air Resources Board

Phase II

Source of Vented Gasoline Vapor

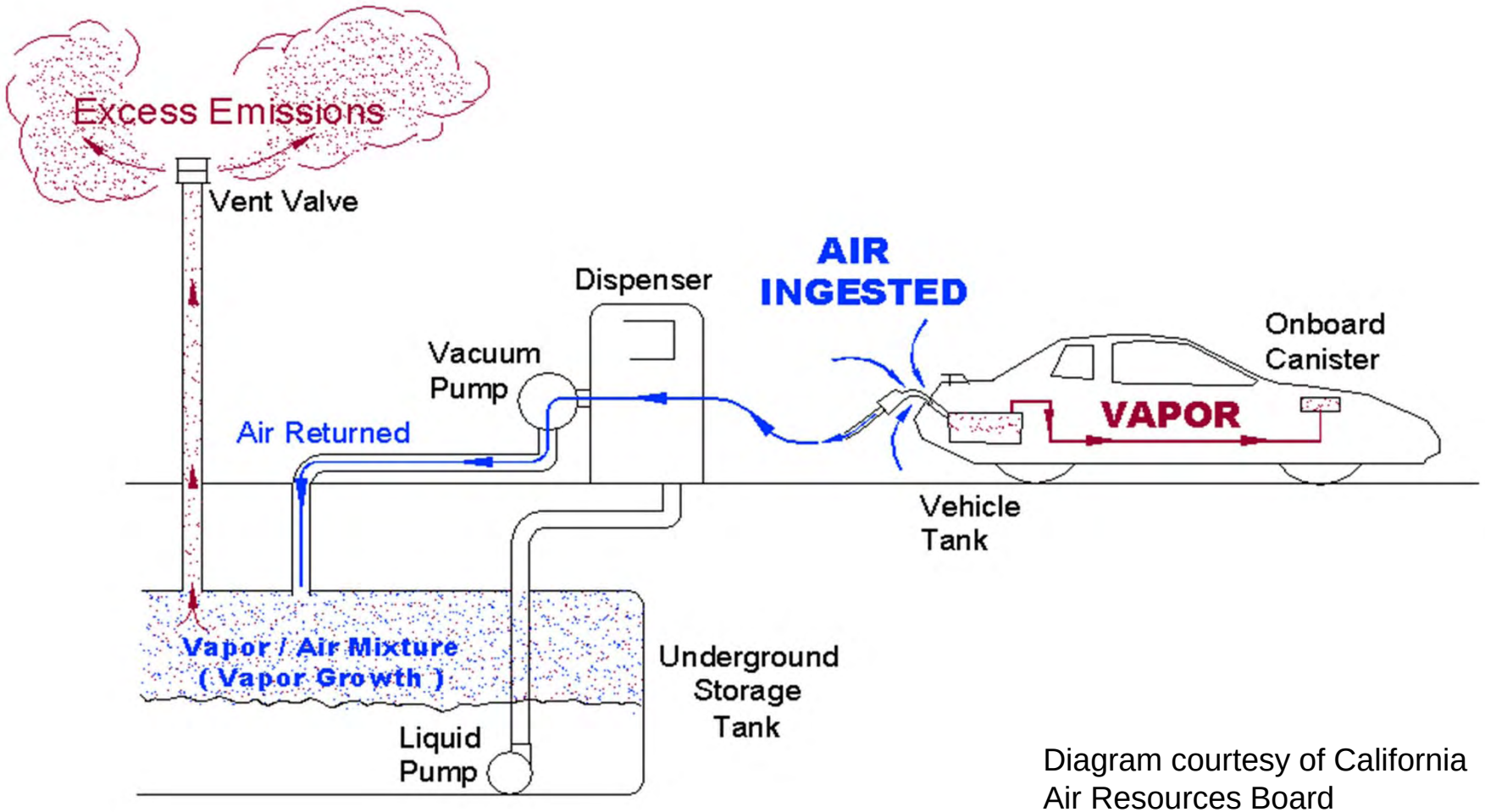
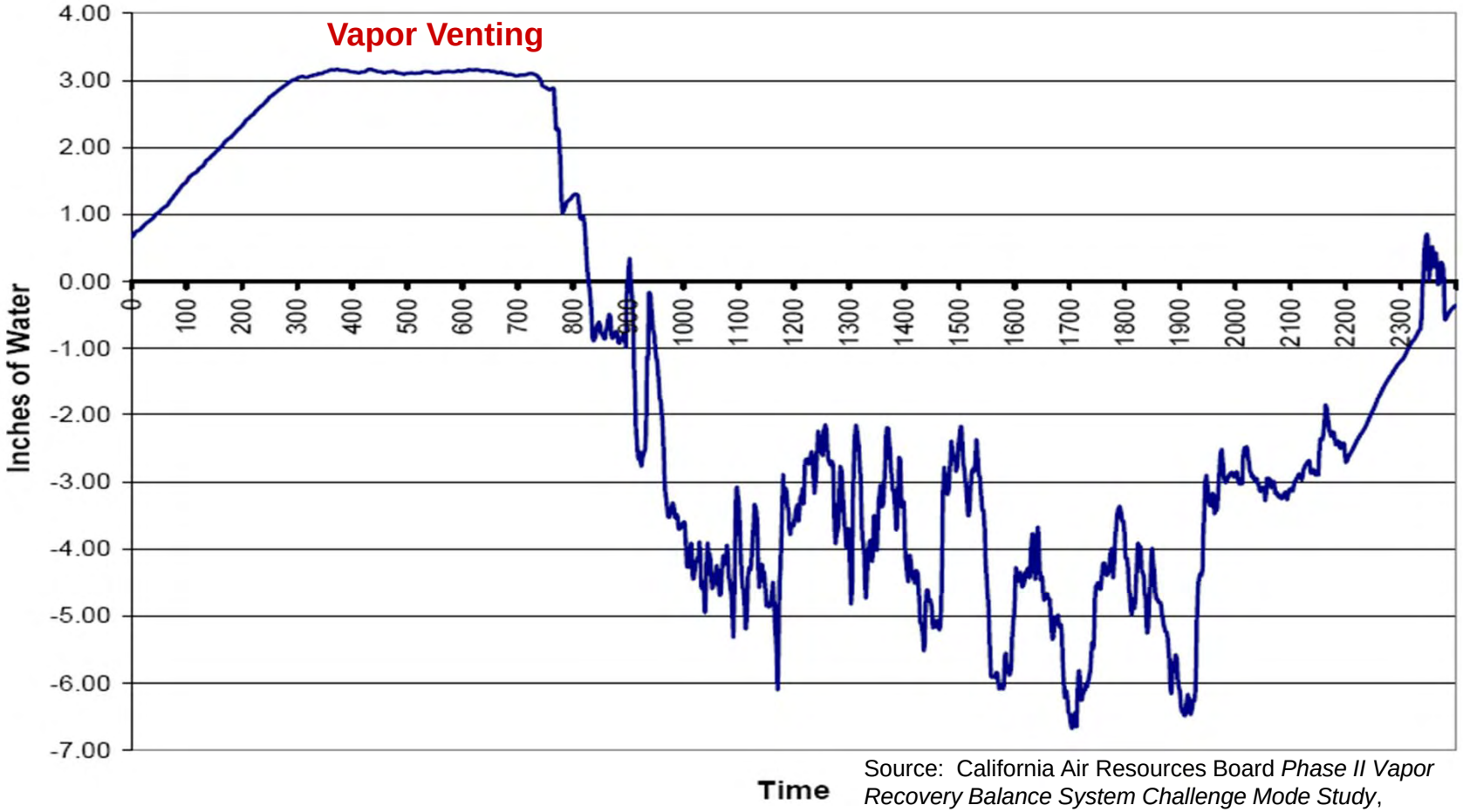


Diagram courtesy of California Air Resources Board

Gasoline Vapor Emissions due to Vapor Growth in Storage Tank

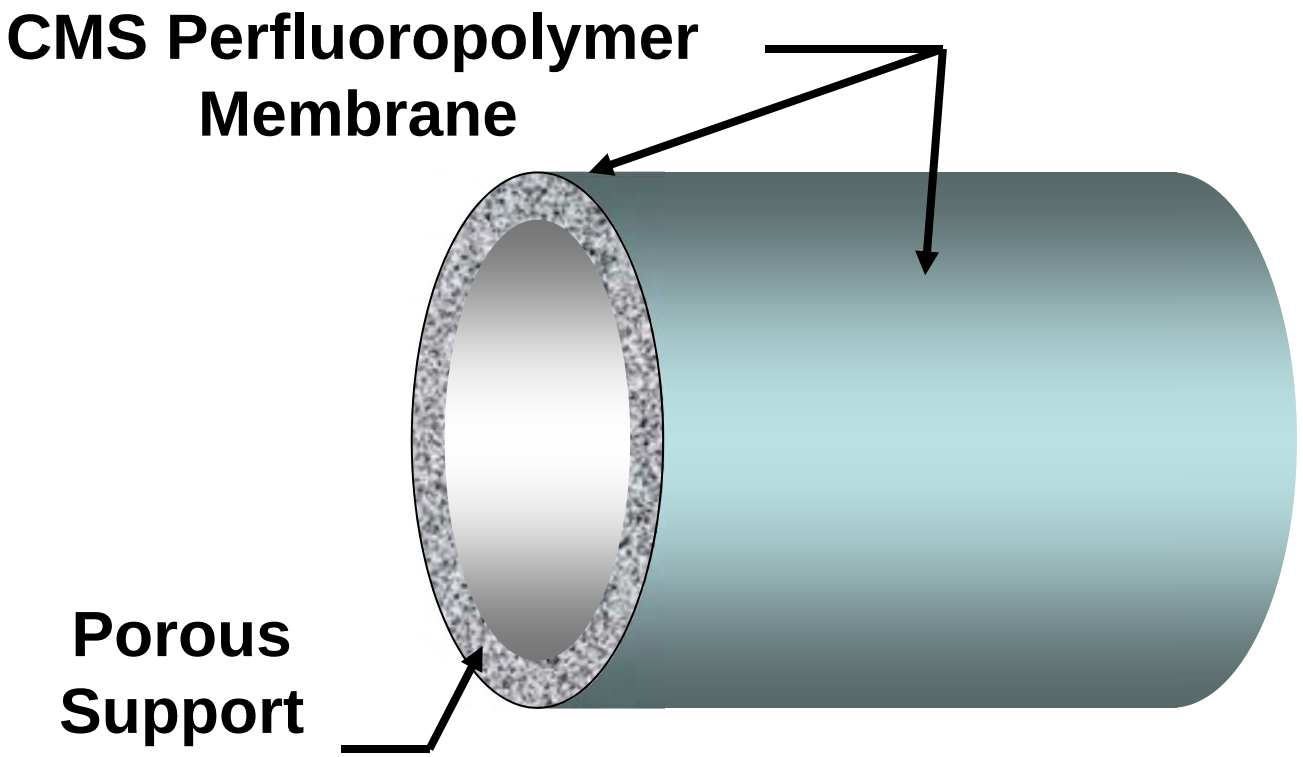


Source: California Air Resources Board *Phase II Vapor Recovery Balance System Challenge Mode Study*, October 25, 2006.

More on Amorphous Perfluoropolymer Membranes

Merkel, Pinnau, Prabhakar and Freeman, "Gas and Vapor Transport Properties of Perfluoropolymers," Chapter 9 of *Materials Science of Membranes for Gas and Vapor Separation,* Yampolskii, Pinnau and Freeman, (Eds.), J Wiley & Sons, inc., New York (2006).

Composite Hollow Fiber



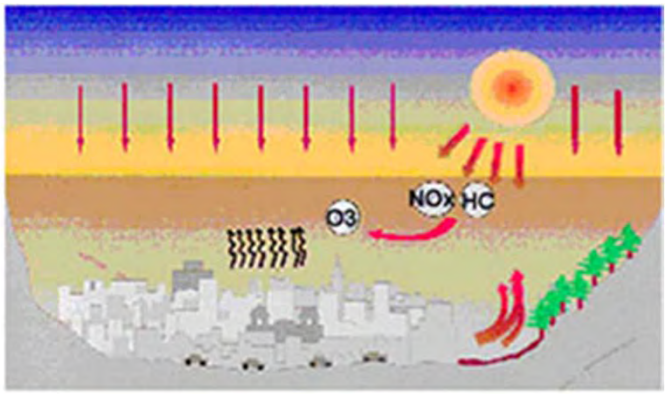
Beijing Smog

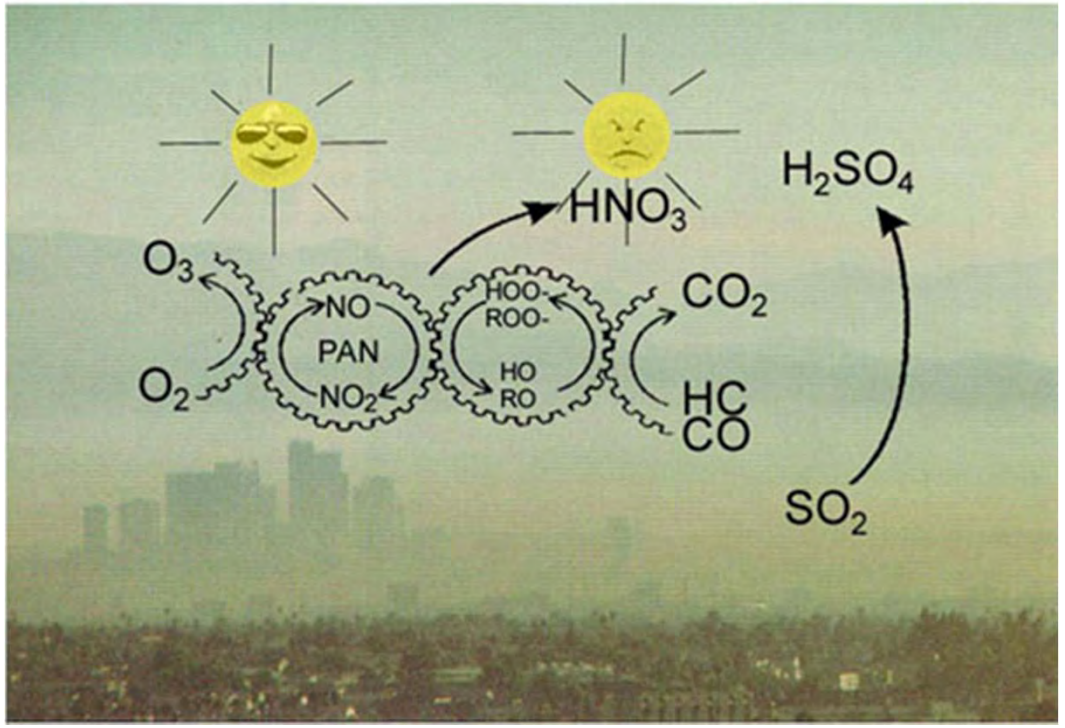
After a Rain Shower

On a Normal Day

Smog Formation

The Smogmachine



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