Application of Barrier Membrane Technology to Catalytic Cracker Recycle Gas Hydrogen Separations

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Inorganic Membrane Technology Laboratory
(IMTL, Bechtel-Jacobs LLC, Oak Ridge, TN)

Phillips Petroleum
ChevronTexaco

Background

- Refineries use many high pressure hydrogenation processes
- ~ 20% of the hydrogen used is purged (ultimately used as fuel)
- Recycle, purification and reuse will conserve hydrogen (and $$)
- Inorganic membranes offer the possibility of
  - Corrosion resistance (custom materials)
  - Higher operating temperatures, pressures and throughput
- Separation performed at temperatures and pressures closer to process conditions offers considerable savings

History

- Inorganic membranes have been used by the US Government for gas separation (uranium isotopes) on a vast scale for over 50 years
- Inorganic membranes designed for H_2 / HC separation are being developed by the Inorganic Membrane Technology Laboratory (IMTL) in Oak Ridge, TN.
- Commercialization of similar membranes for other applications is underway via Pall Corp
- Successful application to petroleum refining is the question.

Statement of Problem

- Determine the effectiveness of custom inorganic membranes for separation of hydrogen from hydrocarbons in high pressure mixtures simulating refinery gas streams.

- Effectiveness encompasses a variety of performance factors
  - Separation efficiency
  - Throughput
  - Optimum temperatures and pressures
  - Allowable temperatures and pressures
  - Longevity in process environment

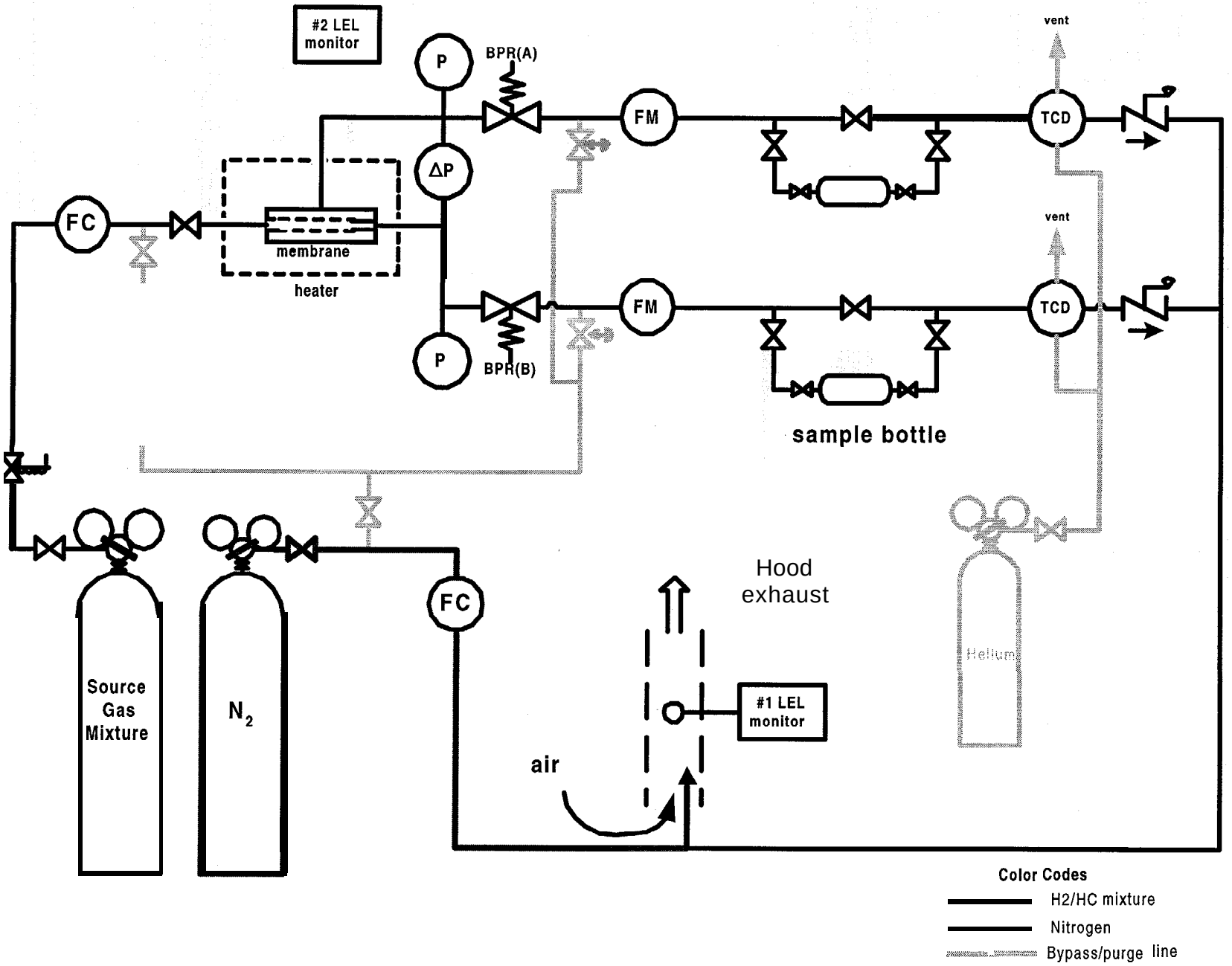
- This project was funded in early June 2001

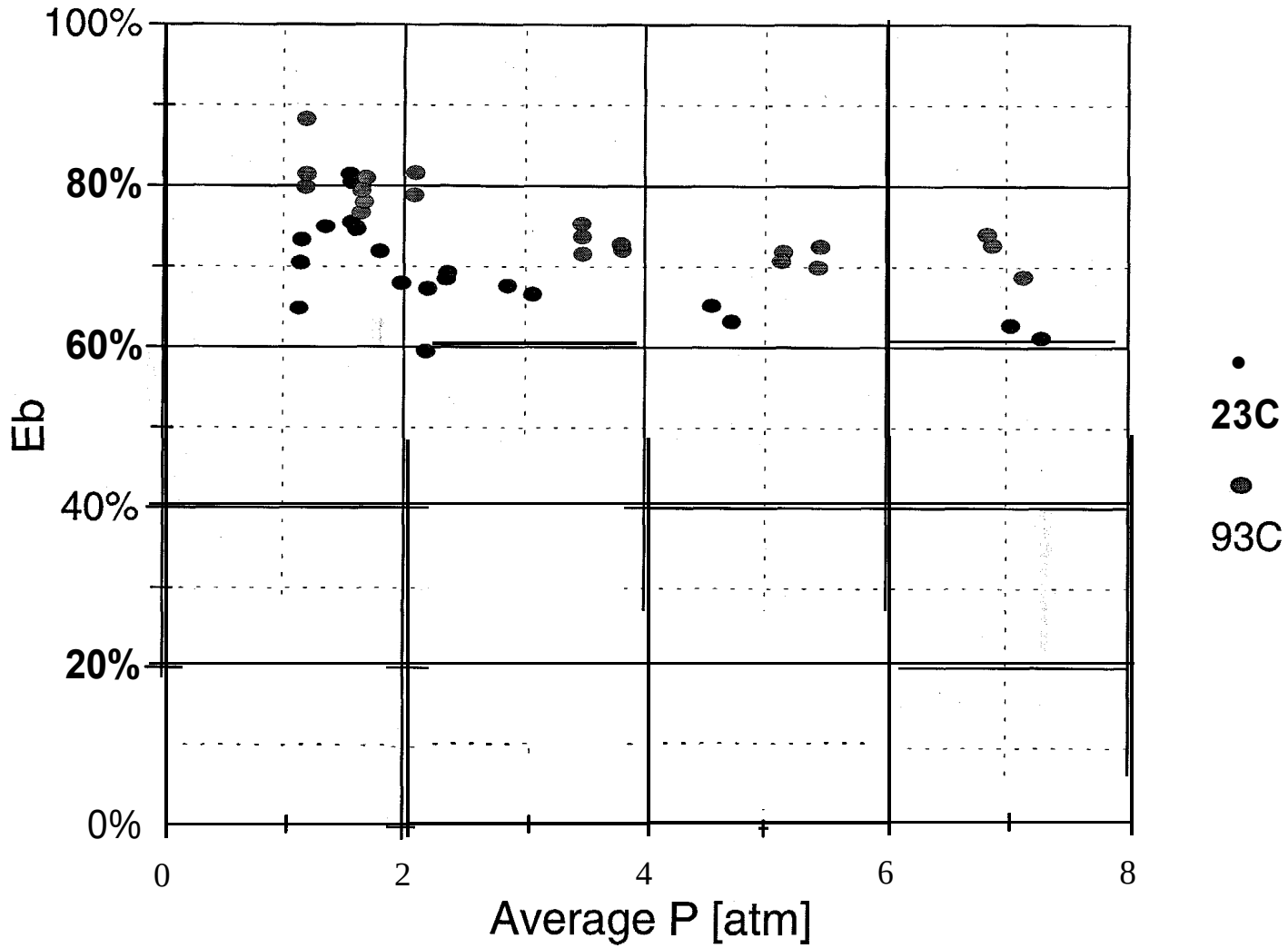
Accomplishment – Summary

- Completed construction and testing of separation apparatus
- Initial testing is on an IMTL Knudsen membrane
- Separation testing
  - Physical Property Ranges examined so far:
    - Temperature: 23 to 140°C
    - Pressures: 1 to 8 atm
    - Flows: up to 100 sccm / cm^2
  - Binary gas mixtures examined:

    H_2 / CH_4 — He / CO_2
    H_2 / C_2H_6 — He / Ar
    H_2 / C_3H_8
  - Data Analysis: Comparison of observed to ideal separation factors after correcting for known effects (back pressure; cut; mixing)

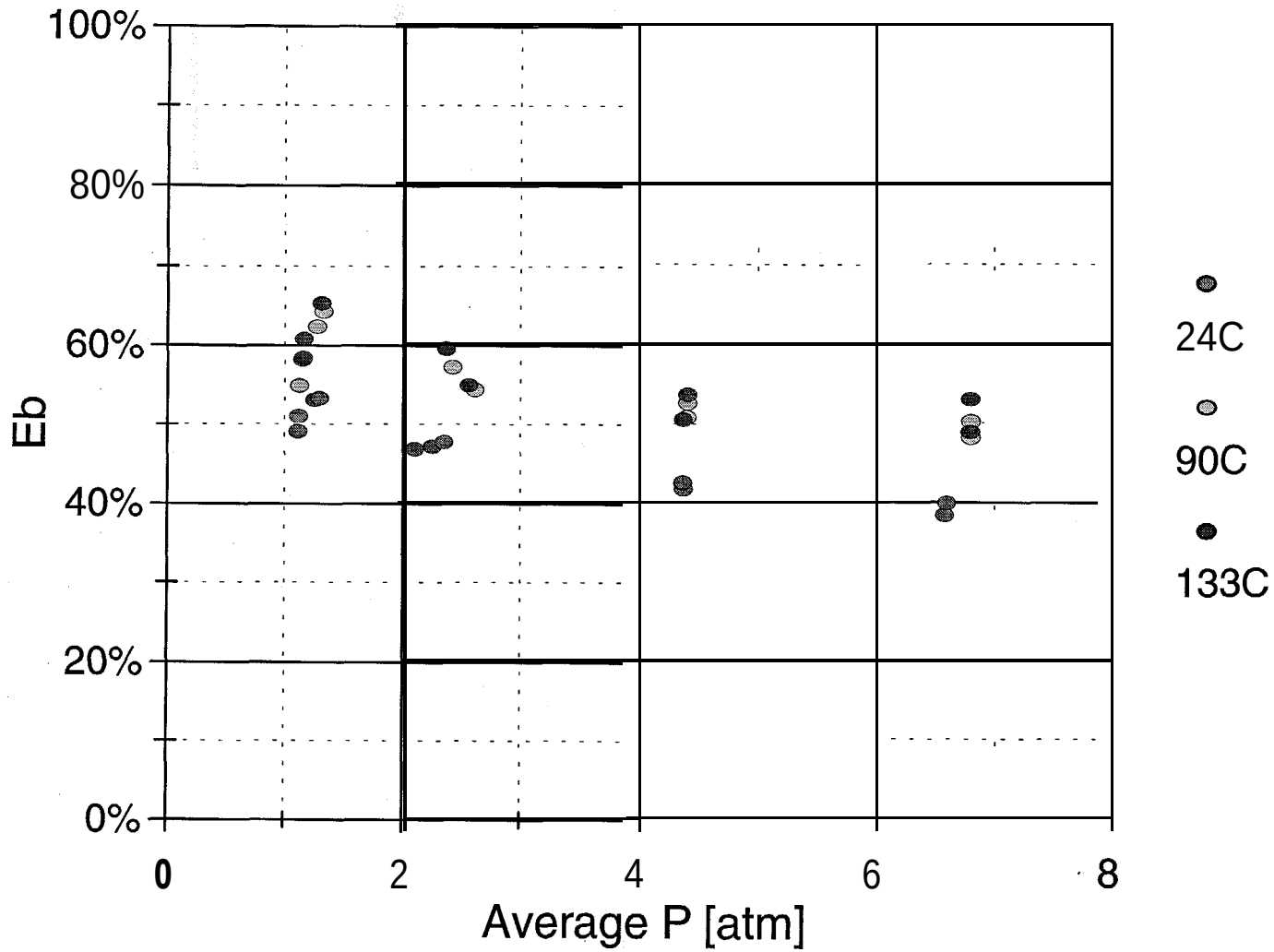
Apparatus Schematic





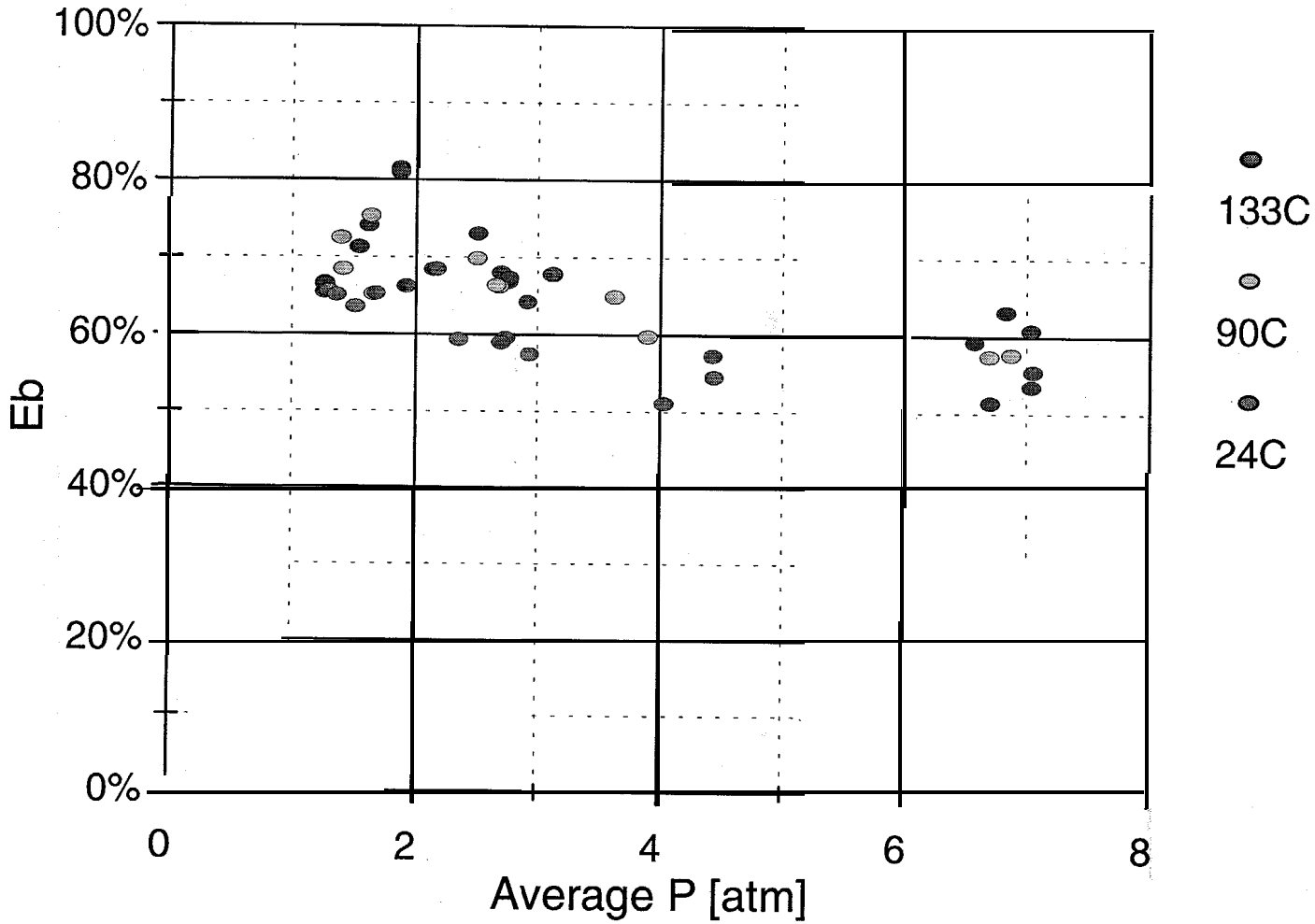
75% H_2 / 25% CH, separation at 23 **and 93°C** (IMTL Knudsen Membrane 12266784 -1)
E_b = barrier efficiency: Observed separation factor is corrected for back pressure, cut, and mixing efficiency. When pressures and flows are optimum for separation,

$$(a-1) = (\alpha^* - 1)\, E_b$$



75% **H_2 / 25% C_3H_8 separation at** 24 **to 133°C** (IMTL Knudsen Membrane 1226678-1-l)
E_b = barrier efficiency: Observed separation factor is corrected for back pressure, cut, and mixing efficiency. When pressures and flows are optimum for separation,

$$(a - l) = (\alpha^* - 1) E_b$$



75% H_2 / 25% C_2H_6 separation at 24 to 133°C (IMTL Knudsen Membrane 1226678-1-1)
E_b = barrier efficiency: Observed separation factor is corrected for back pressure, cut, and mixing efficiency. When pressures and flows are optimum for separation,

$$(\alpha - 1) = (\alpha^* - 1)\, E_b$$

Observations
(Knudsen Membrane)

- Most gas mixtures behaved similarly, as expected for a Knudsen membrane.

- The typical mixtures showed efficiencies of 80%+ at lower pressures (trending higher as pressures decrease). Efficiencies declined to 70% or lower at higher pressures.

- Separation factors for mixtures with more condensable gases (i.e., CO, and C_3H_8) were measurably lower, especially at low temperatures, suggesting enhanced surface flow of the heavier compound.

Planned Work

FY2002

- Complete remaining separation tests using Knudsen membrane (higher temperature; > 200°C)
- Obtain and install surface flow membrane; determine separation factors for binary hydrogen hydrocarbon gas mixtures
- Performance testing on promising additional membrane designs
- Adapt apparatus for multi-component feed gas separation testing

FY2003

- Obtain lab-scale micro-catalytic bed unit (or fluid catalytic cracking unit or hydrotreater) from industrial partner.
- Performance testing using simulated cat-cracker recycle gas using most promising membrane

A Word on Membrane Designs

- Knudsen membrane - Effusive (molecular) gas flow
  - H_2 separates to low pressure side of membrane
  - Best performance at higher temperatures

- Surface Flow - small pores size and surface composition encourage some species to adsorb and transport by surface flow.
  - Heavier components preferentially adsorb
  - Each compound is likely to have an optimum temperature
  - Increased surface flow must overcome higher H_2 effusive flow
  - *If if does* then H_2 will separate to high pressure side of membrane

- Sieve - pores physically screen larger molecules.
  - Potential for very high separation factors
  - Potential for high temperature operation
  - H_2 preferentially separates to low pressure side of membrane

Conclusions

- The separation apparatus has proven capable of determining separation efficiency with reasonable accuracy for the relatively low separation factors that a Knudsen membrane
- It should thus have no difficulty with the higher separation factors anticipated for surface flow or sieve membrane designs

Funding Table

Participants	FY2001 (actual)	FY2002 (req.)	FY2003 (req.)
ORNL	120k	290k	300k
Univ	—	—	—
Total DOE	120k	290k	300k
Industry (in kind)	20k	75k	75k

BACKUP SLIDES

- Separation factor a is defined as:

$$\alpha = X_{LO}(1 - X_{HI}) / X_{HI}(1 - X_{LO})$$

X are mole fractions on high or low pressure side of membrane

- For a Knudsen membrane, the ideal separation factor a* is

$$a^* = (M_{HEAVY} / M_{LIGHT})^{1/2}$$

- Separation Efficiency - the effective separation factor is influenced by several known efficiency effects

$$(\alpha - 1) = E_P E_M E_C E_B (\alpha^* - 1)$$

- E_P: Back-Pressure efficiency accounts for flow from low to high pressure side of membrane

$$E_P = (1 - P_{LO}/P_{HI})$$

- **E_M, Mixing Efficiency**, accounts for depletion of the separated component at tube wall. For "well developed" flow in a tube,

$$E_M = \exp - [\ (2 / f)\ (\eta / D \rho)\ (v / V)\ ]$$

D = diffusivity
η = viscosity ,
ρ = density

v = radial bulk gas velocity
V = axial bulk gas velocity
f = friction factor

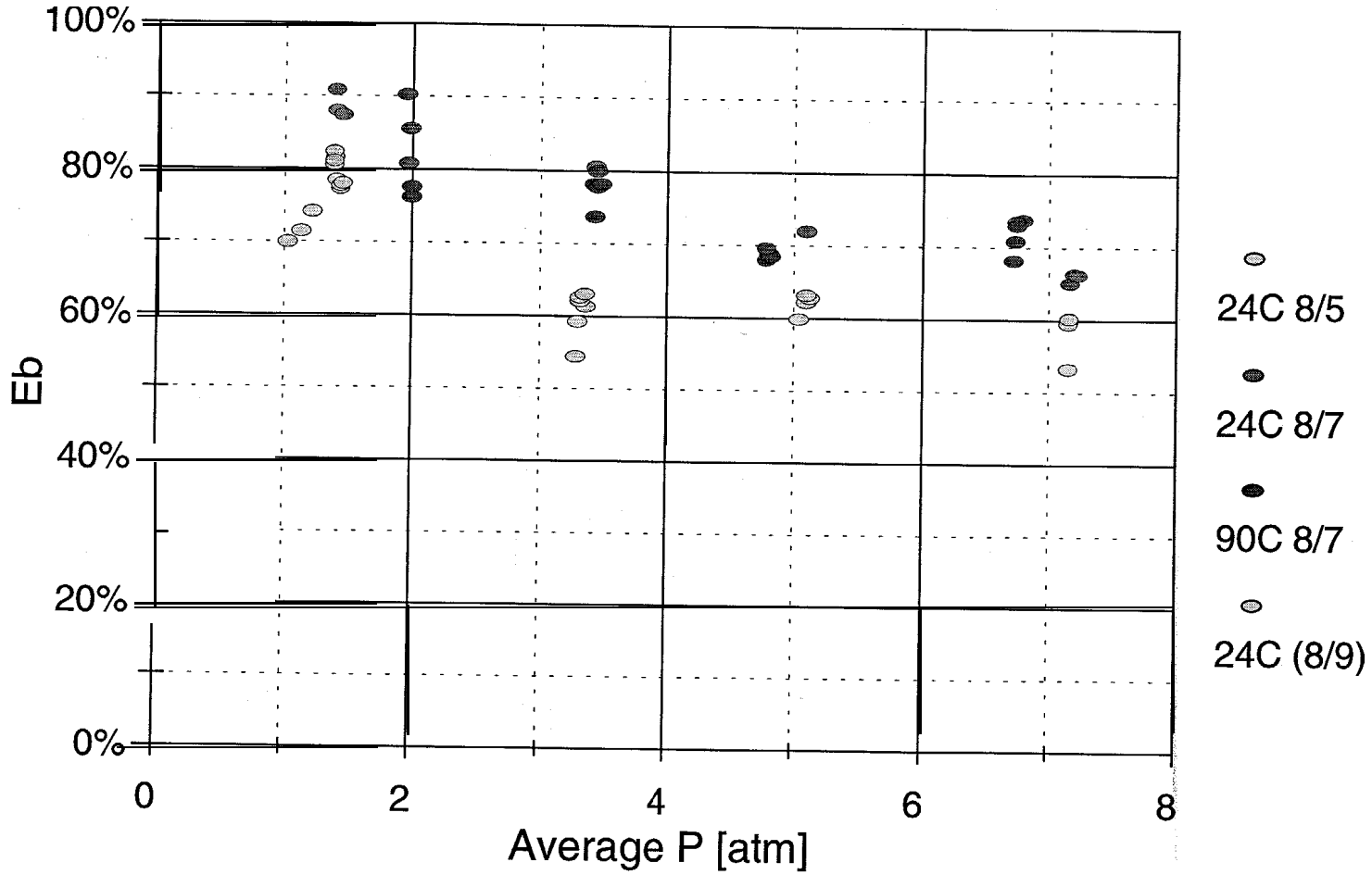
- **E_C, Cut Correction**, accounts for depletion of separated component along axis of the tube

$$E_C = 1/\theta \ \ln [1/(1- \theta)]$$

$$\theta = \text{Flow(LO)} / \text{Flow(IN)}$$

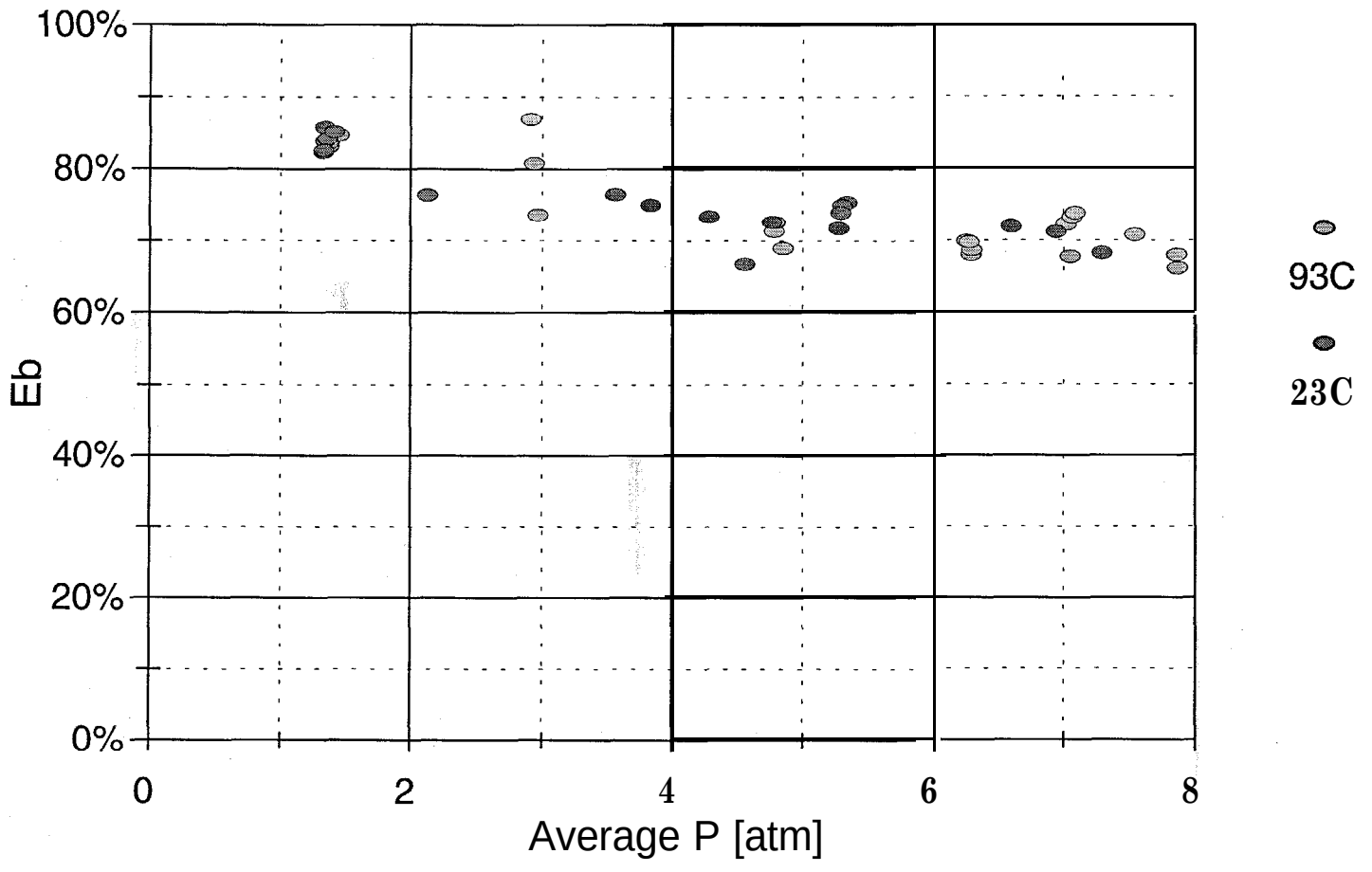
- **E_B, Barrier efficiency,** is the efficiency of the membrane relative to an ideal Knudsen membrane. At the limit of $P_{LO} = 0$ and $\theta = 0$,

$$E_B = (\alpha - 1)/(\alpha^* - 1)$$



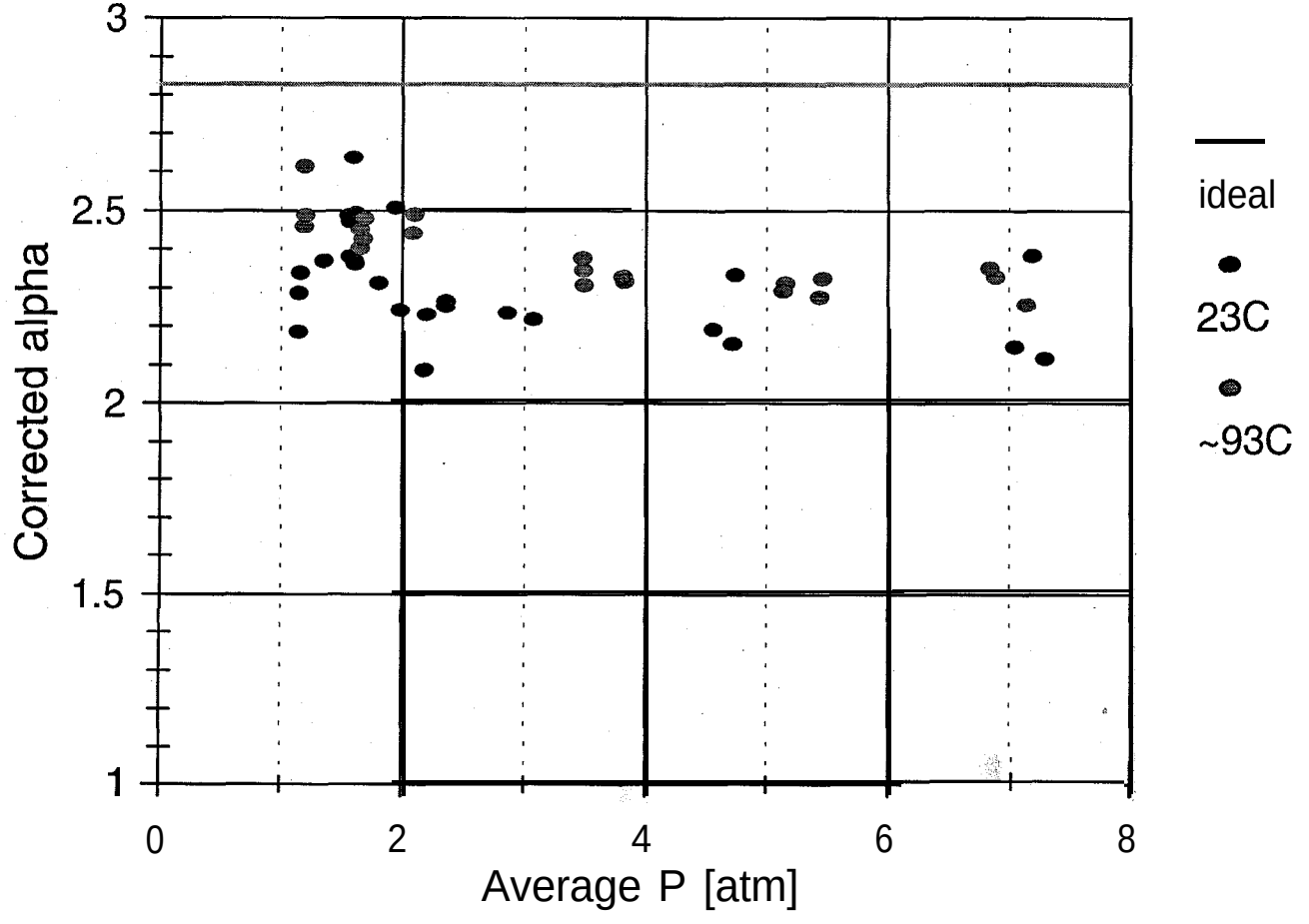
75% He / 25% CO_2 separation at 24 to 90°C (IMTL Knudsen Membrane 1226678-1-1)
E_b = barrier efficiency: Observed separation factor is corrected for back pressure, cut, and mixing efficiency. When pressures and flows are optimum for separation,

$$(\alpha - 1) = (\alpha^* - 1)\, E_b$$



75% He / 25% Ar separation at 23 **and 93°C** (IMTL Knudsen Membrane 1226678-l -1)
E_b = barrier efficiency: Observed separation factor is corrected for back pressure, cut, and mixing efficiency. When pressures and flows are optimum for separation,

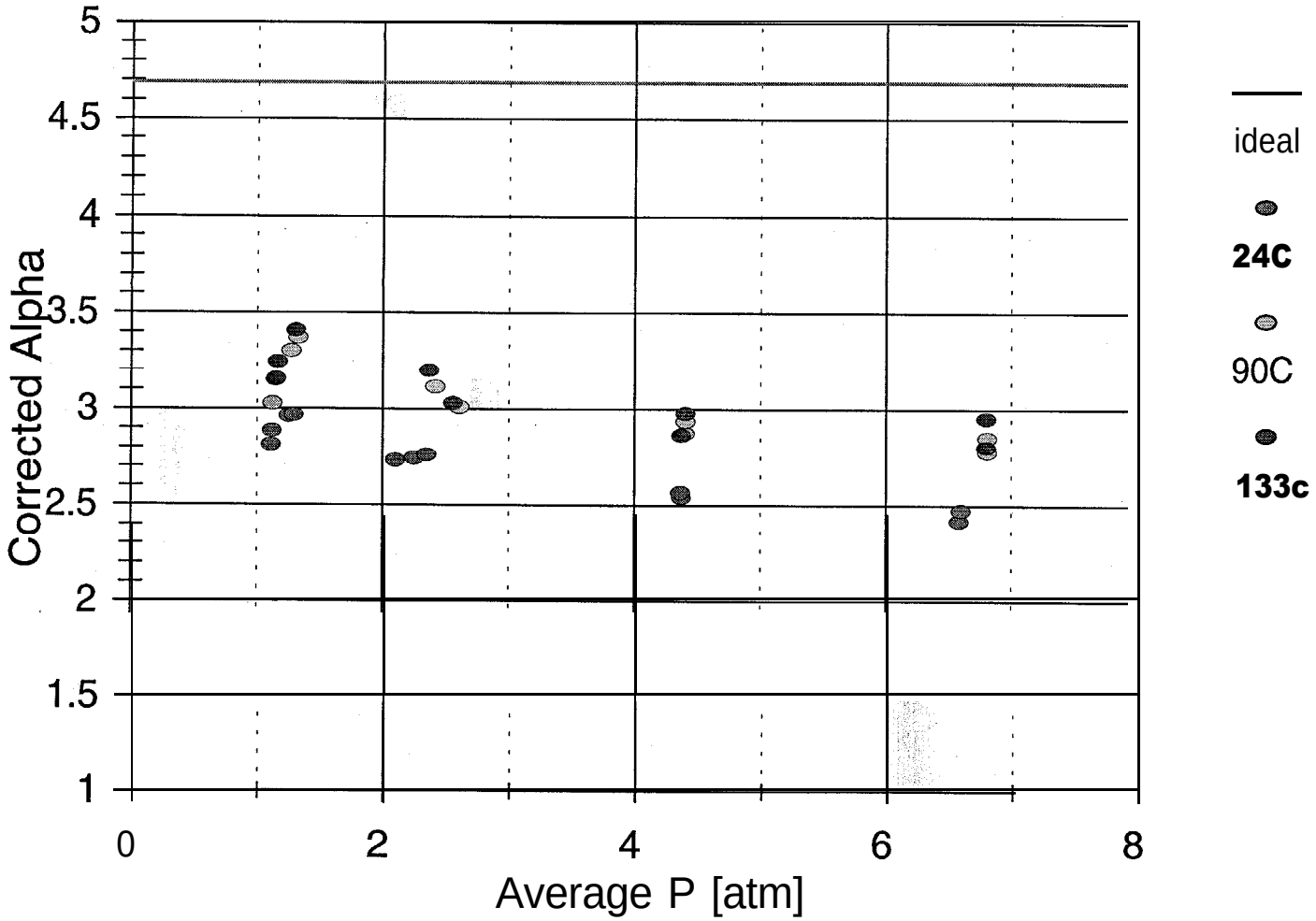
$$(a - l) = (\alpha^* - 1) E_b$$



75% H_2 / 25% CH_4 separation at 23 and 93°C (IMTL Knudsen Membrane 1226678-l -1)
Observed separation factor corrected for back pressure, cut, and mixing efficiency, ratioed to ideal separation factor, per

$$(a - l) = (\alpha^* - 1)\, E_P\, E_C\, E_M\, E_b$$

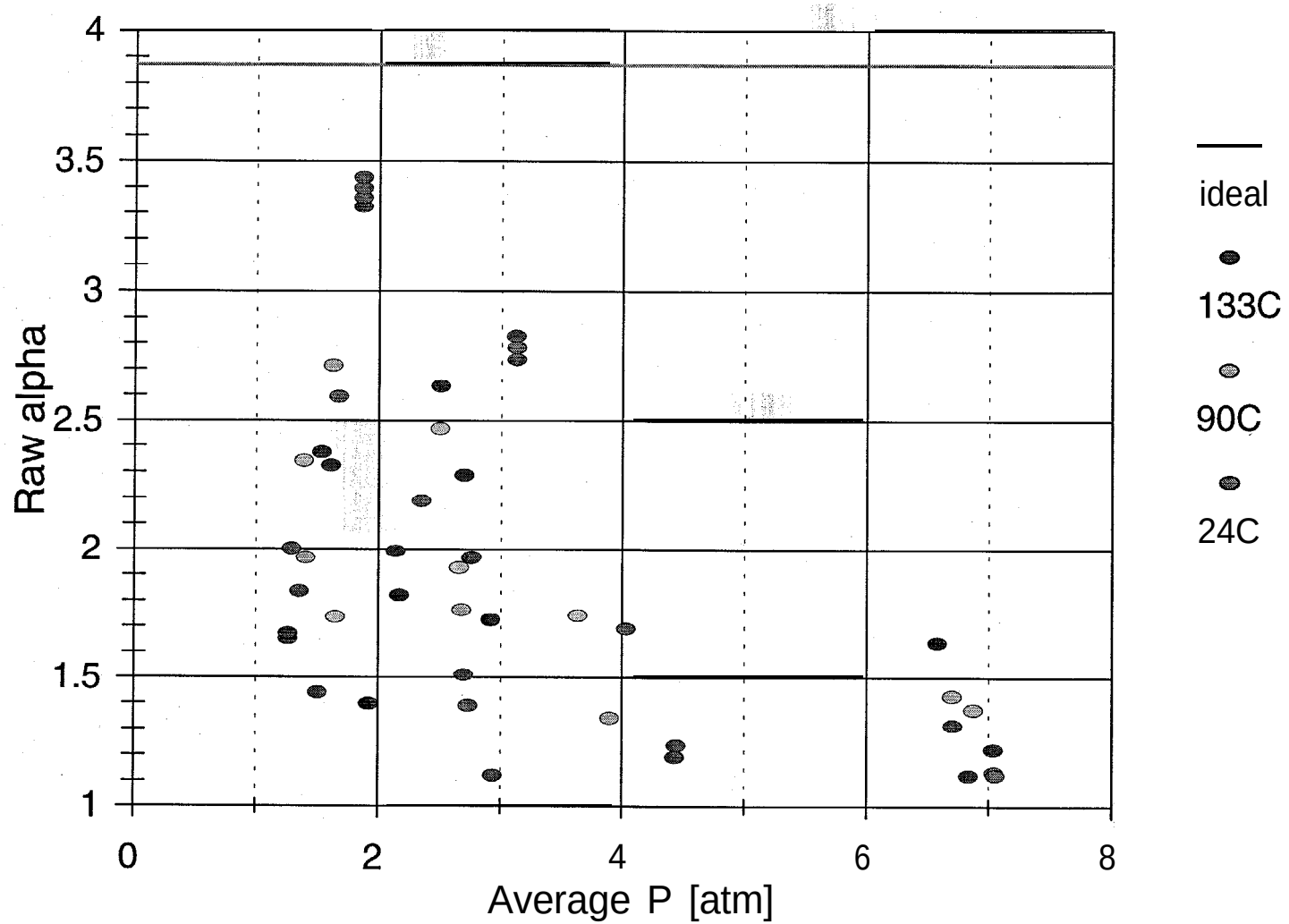
- $a_{corrected}$ is essentially the separation factor expected at optimum flows and pressures.



75% H_2 / 25% C_3H_8 separation at 23 **to 133°C** (IMTL Knudsen Membrane 1226678-l -1)
Observed separation factor corrected for back pressure, cut, and mixing efficiency, ratioed to ideal separation factor, per

$$(a - l) = (\alpha^* - 1)\, E_P\, E_C\, E_M\, E_b$$

$a_{corrected}$ is essentially the separation factor expected at optimum flows and pressures.



75% H_2 / 25% C_2H_6 separation at 23 to 133°C (IMTL Knudsen Membrane 1226678-1-I)
Observed separation factor, a. No corrections have been applied for known effects of back pressure, cut, or mixing efficiency.

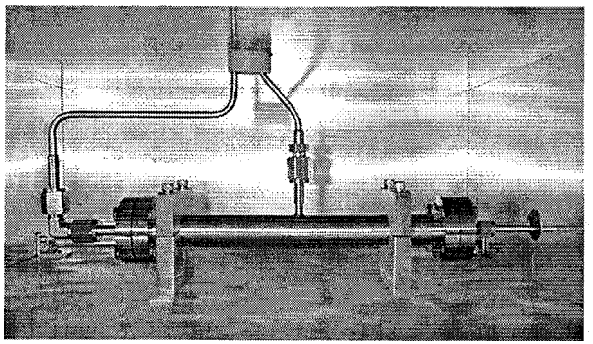
Conclusions

- Inorganic membranes have potential to allow gas separations with high separation factors, reasonable throughput, at high temperatures and pressures.

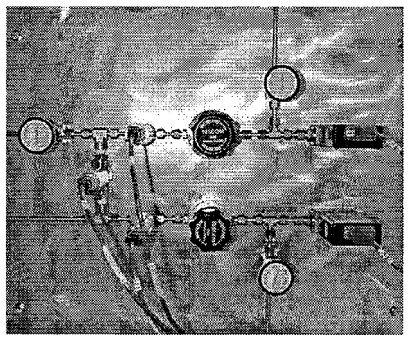
- Scaleup can be done (the historic example of gaseous diffusion illustrates this well beyond the scales needed in refining)

- Spinoffs (beyond the targeted application) might include other hydrogen separations (such as syn-gas applications) or other gas separations (such as H_2S).

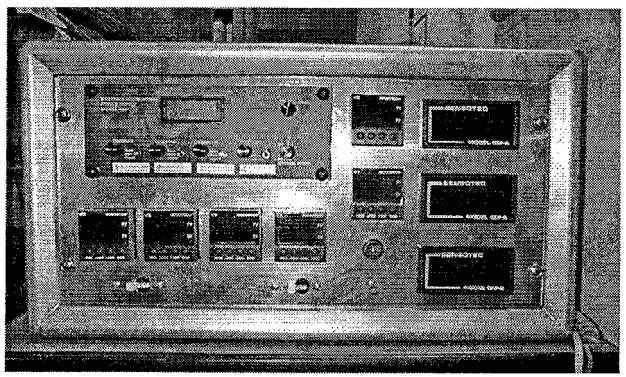
- The issue is one of demonstrating the promised effectiveness at lab scale and then larger scales and determining economics



Membrane module



Pressure / Flow Panel



Instrument Panel