Ionic Liquid Membranes for Carbon Dioxide Separation

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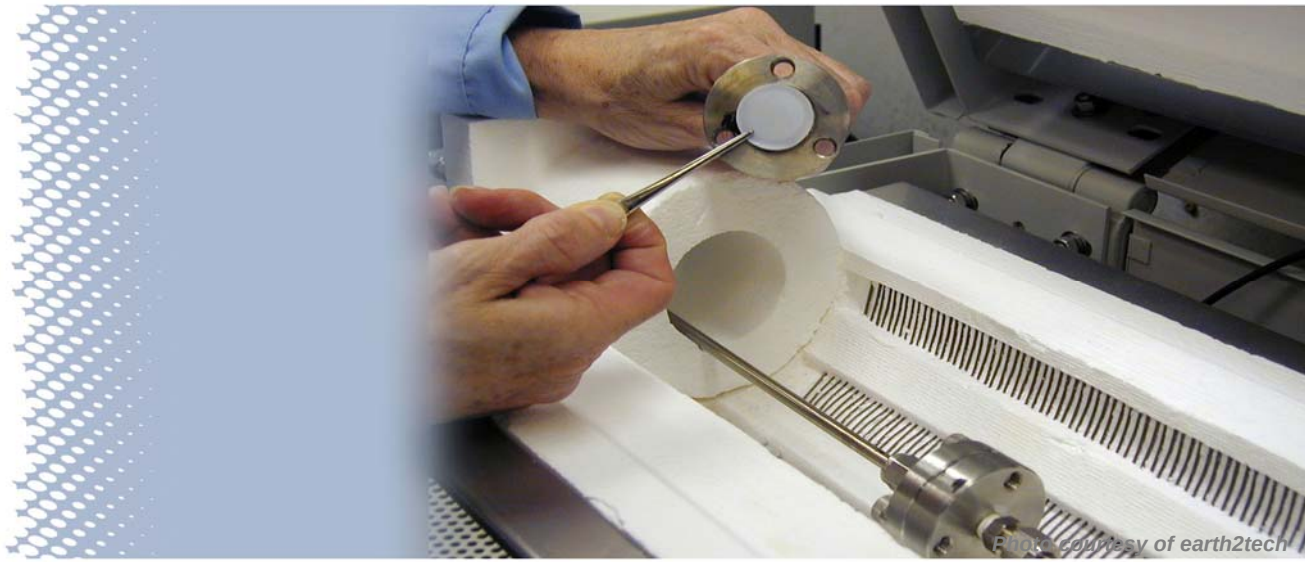
Recent scientific studies are rapidly advancing novel technological improvements and engineering developments that demonstrate the ability to minimize, eliminate, or facilitate the removal of various contaminants and green house gas emissions in power generation. The Integrated Gasification Combined Cycle (IGCC) shows promise for carbon dioxide mitigation not only because of its higher efficiency as compared to conventional coal firing plants, but also due to a higher driving force in the form of high partial pressure. One of the novel technological concepts currently being developed and investigated is membranes for carbon dioxide (CO_2) separation, due to simplicity and ease of scaling. A challenge in using membranes for CO_2 capture in IGCC is the possibility of failure at elevated temperatures or pressures. Our earlier research studies examined the use of ionic liquids on various supports for CO_2 separation over the temperature range, 37°C-300°C. The ionic liquid, 1-hexyl-3methylimidazolium Bis(trifluoromethylsulfonyl)imide, ([hmim][Tf_2N]), was chosen for our initial studies with the following supports: polysulfone (PSF), poly(ether sulfone) (PES), and cross-linked nylon. The PSF and PES supports had similar performance at room temperature, but increasing temperature caused the supported membranes to fail. The ionic liquid with the PES support greatly affected the glass transition temperature, while with the PSF, the glass transition temperature was only slightly depressed. The cross-linked nylon support maintained performance without degradation over the temperature range 37-300°C with respect to its permeability and selectivity. However, while the cross-linked nylon support was able to withstand temperatures, the permeability continued to increase and the selectivity decreased with increasing temperature. Our studies indicated that further testing should examine the use of other ionic liquids, including those that form chemical complexes with CO_2 based on amine interactions. The hypothesis is that the performance at the elevated temperatures could be improved by allowing a facilitated transport mechanism to become dominant. Several amine-based ionic liquids were tested on the cross-linked nylon support. It was found that using the amine-based ionic liquid did improve selectivity and permeability at higher temperature. The hypothesis was confirmed, and it was determined that the type of amine used also played a role in facilitated transport. Given the appropriate aminated ionic liquid with the cross-linked nylon support, it is possible to have a membrane capable of separating CO_2 at IGCC conditions. With this being the case, the research has expanded to include separation of other constituents besides CO_2 (CO, H_2S, etc.) and if they play a role in membrane poisoning or degradation. This communication will discuss the operation of the recently fabricated ionic liquid membranes and the impact of gaseous components other than CO_2 on their performance and stability.



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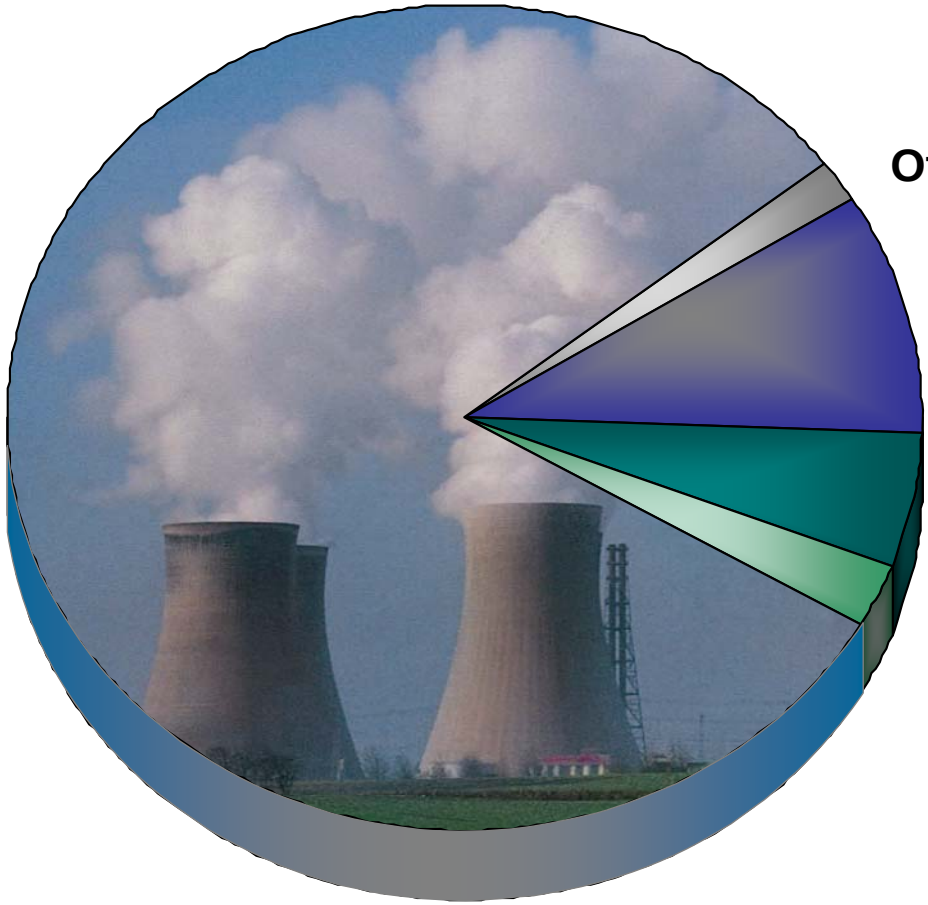
R&D Focus is on CO_2

United States Greenhouse Gas Emissions
(Equivalent Global Warming Basis)



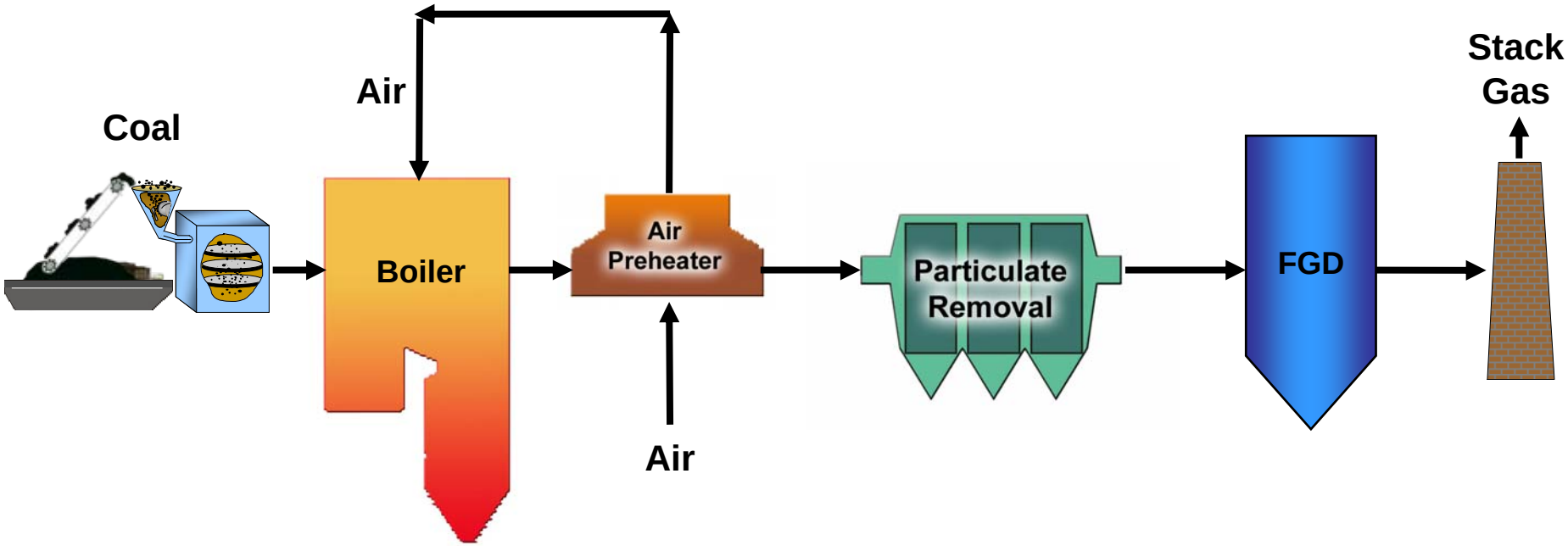
"EIA Emissions of Greenhouse Gases in the U.S.: 2000"

Greenhouse Gas Emissions

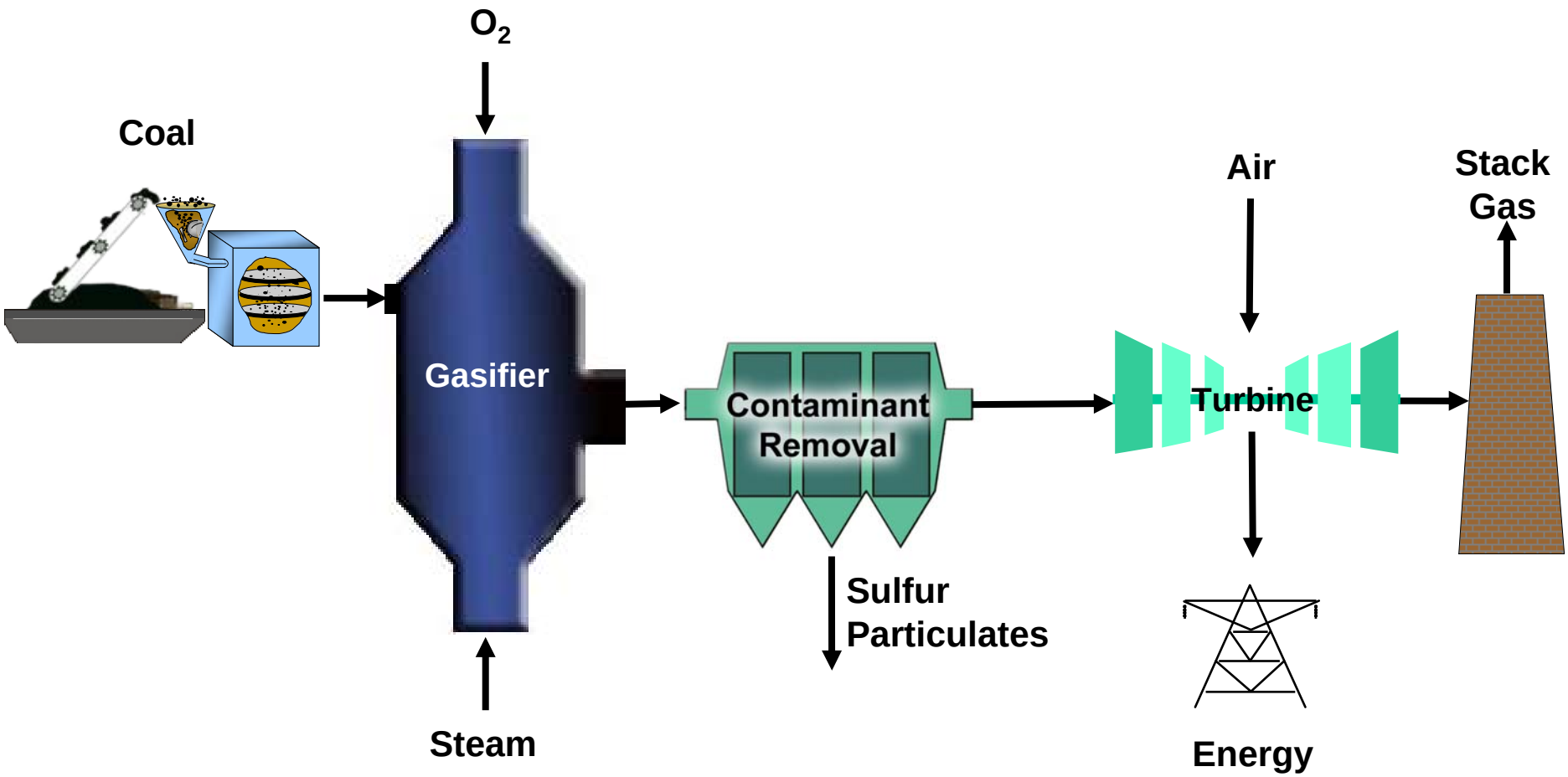
- **Anthropogenic CO_2**
  - One-third from power generation point sources
  - Majority of point sources burn coal

- **Reduction CO_2 emissions**
  - Switch to renewable energy
  - Increase process efficiency
  - Use lower-carbon content fuels or sources
  - Capture and sequester CO_2

Pulverized Coal Combustion (PCC-Flue Gas)



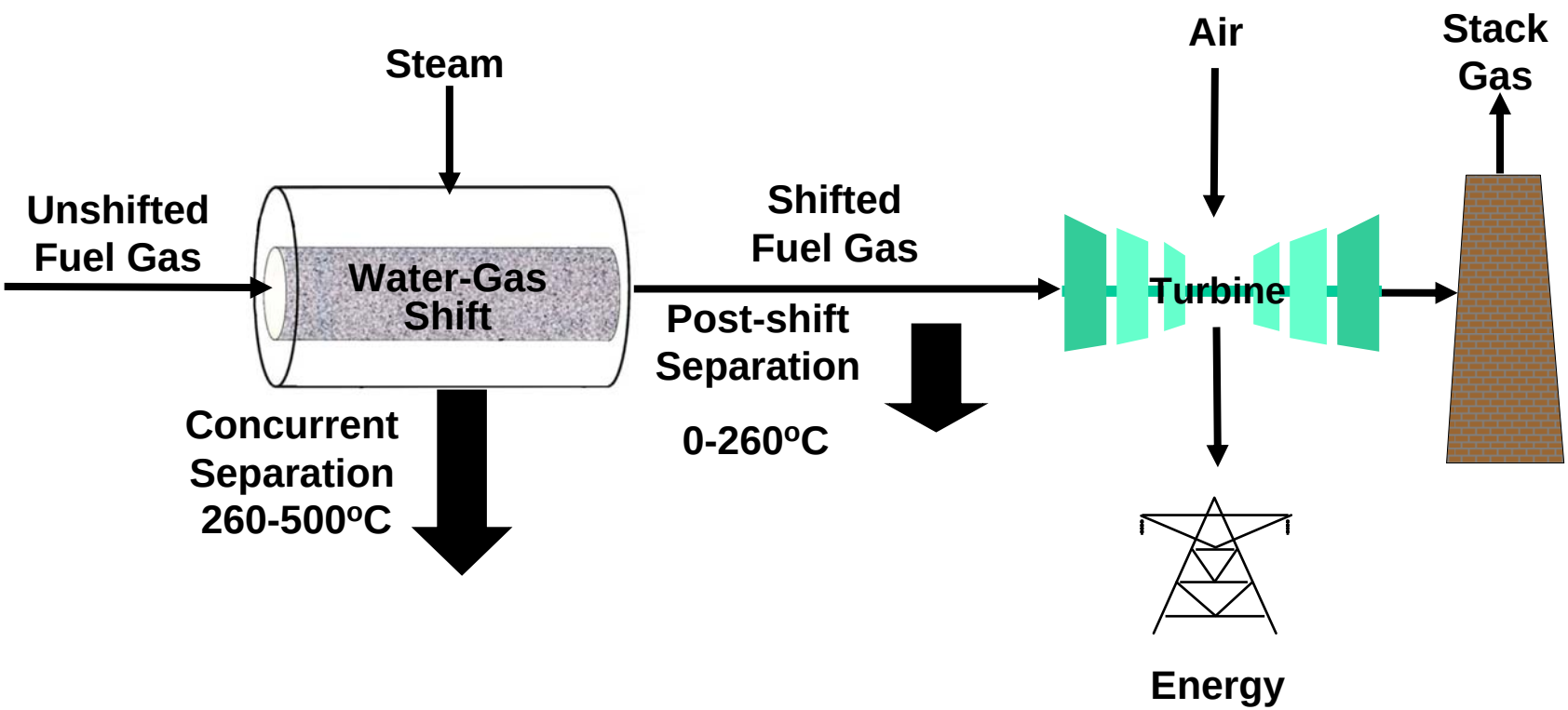
Integrated Gasification Combined Cycle (IGCC-Fuel Gas)



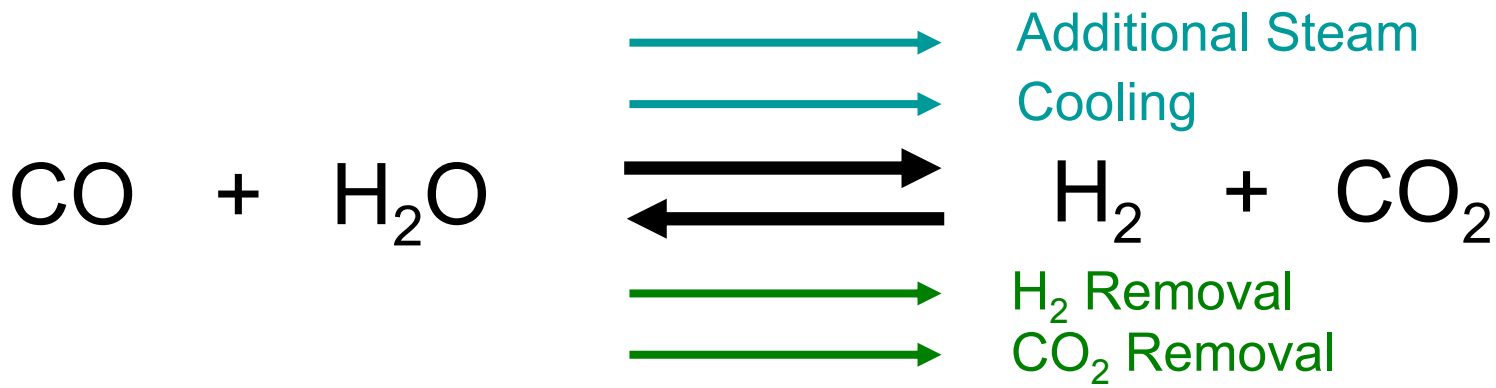
Critical Separation Challenges
Post- versus Pre-Combustion

- **Post-combustion (PCC)**
  - Low pressure + dilute volume = high volume of gas
  - Trace impurities in flue gas → reduce CO_2 adsorbing processes
  - Compressing captured CO_2 → large parasitic load
- **Pre-combustion (IGCC)**
  - CO_2 concentration (40 volume %)
  - High pressure and temperature

IGCC with CO_2 Capture

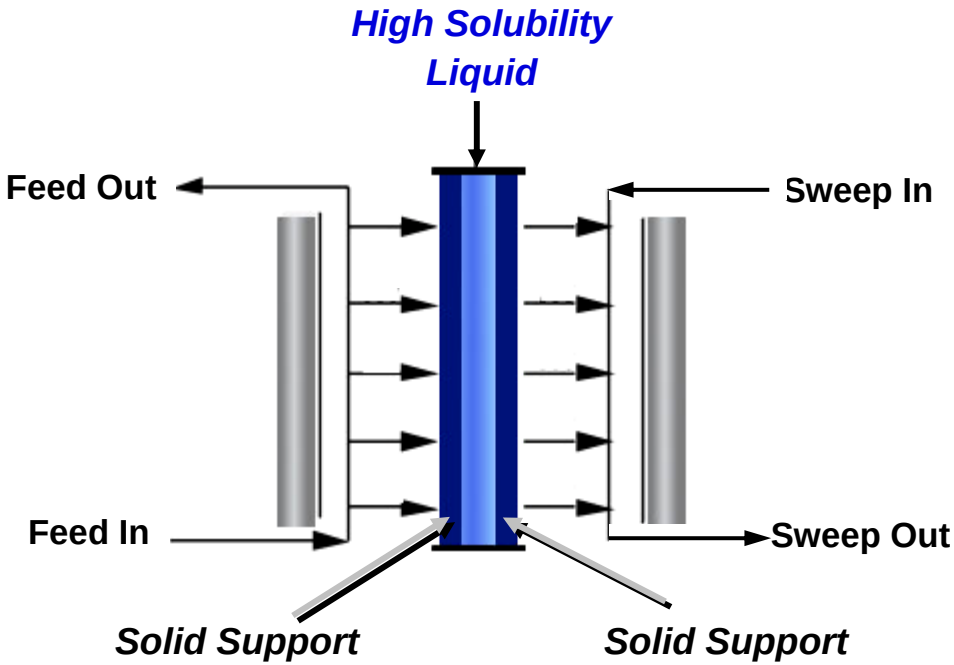


Water-Gas Shift



- **Conventional**
  - Cooling to 260°C
  - Additional Steam
- **Improvement through Separation**
  - Cooling Only to Separation Temperature
  - Only Stoichiometric Steam Required

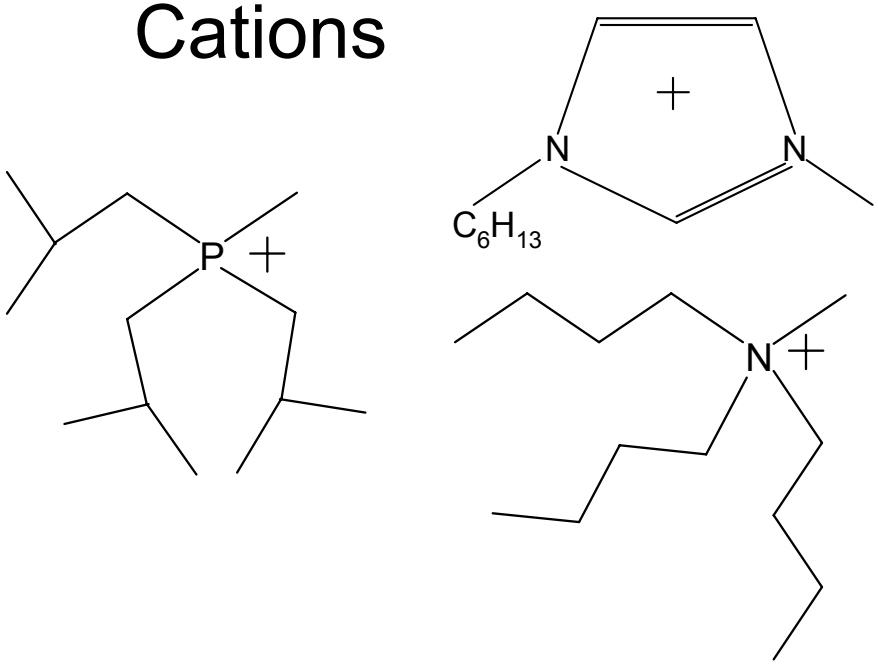
Supported Liquid Membranes



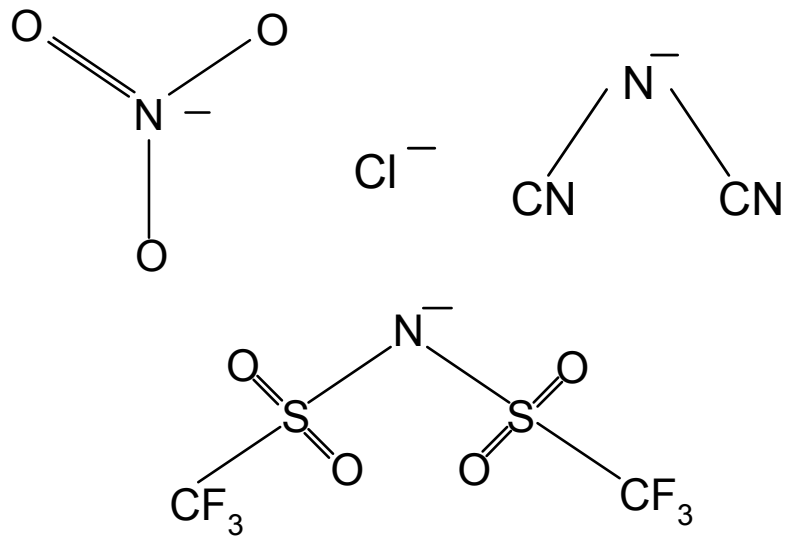
- **High liquid phase diffusivity increases permeability**
- **Potential to add complexes increasing CO_2 solubility**
- **Problems**
  - Evaporation of liquid
  - Blowout

Ionic Liquids:
A Solution to Evaporative Failure

Cations

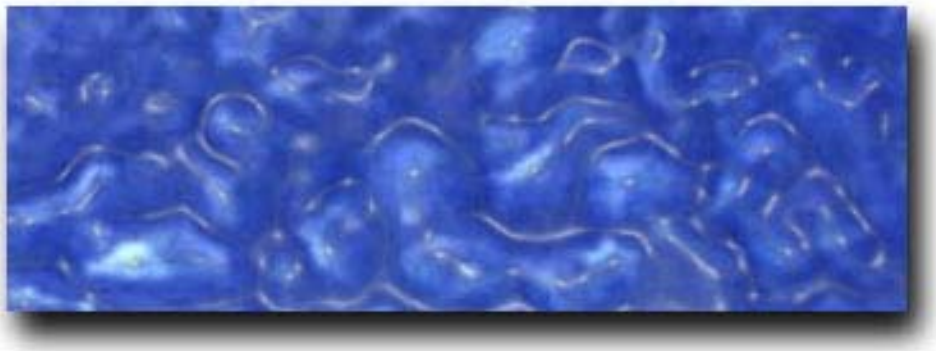


Anions

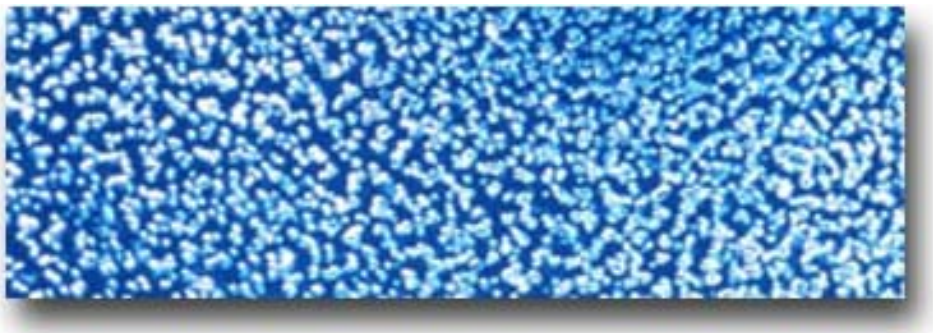


- **Negligible Vapor Pressure**
- **Thermally Stable above 200°C**
- **High CO_2 Solubility Relative to H_2, N_2, and CH_4**

Several Fabrication Options



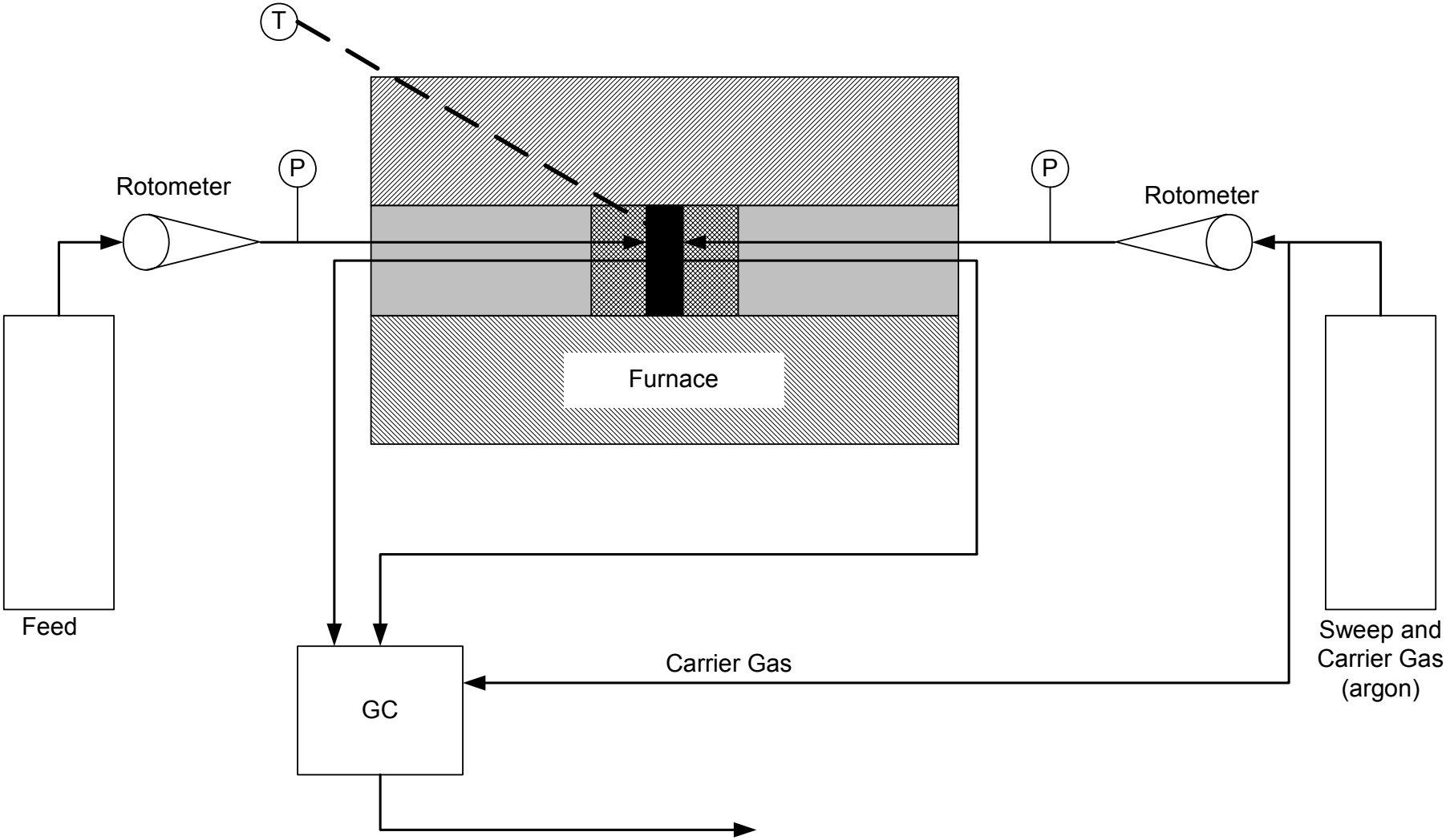
Porous Substrate



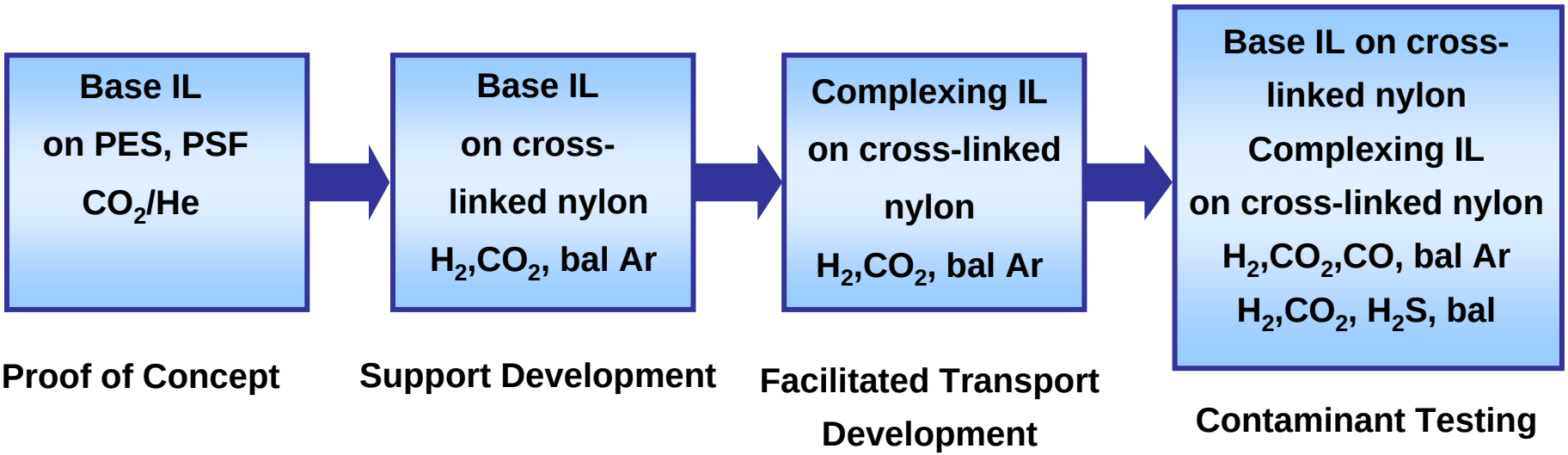
Dense Substrate

Polymerized Liquid

Constant Pressure Flux Measurements

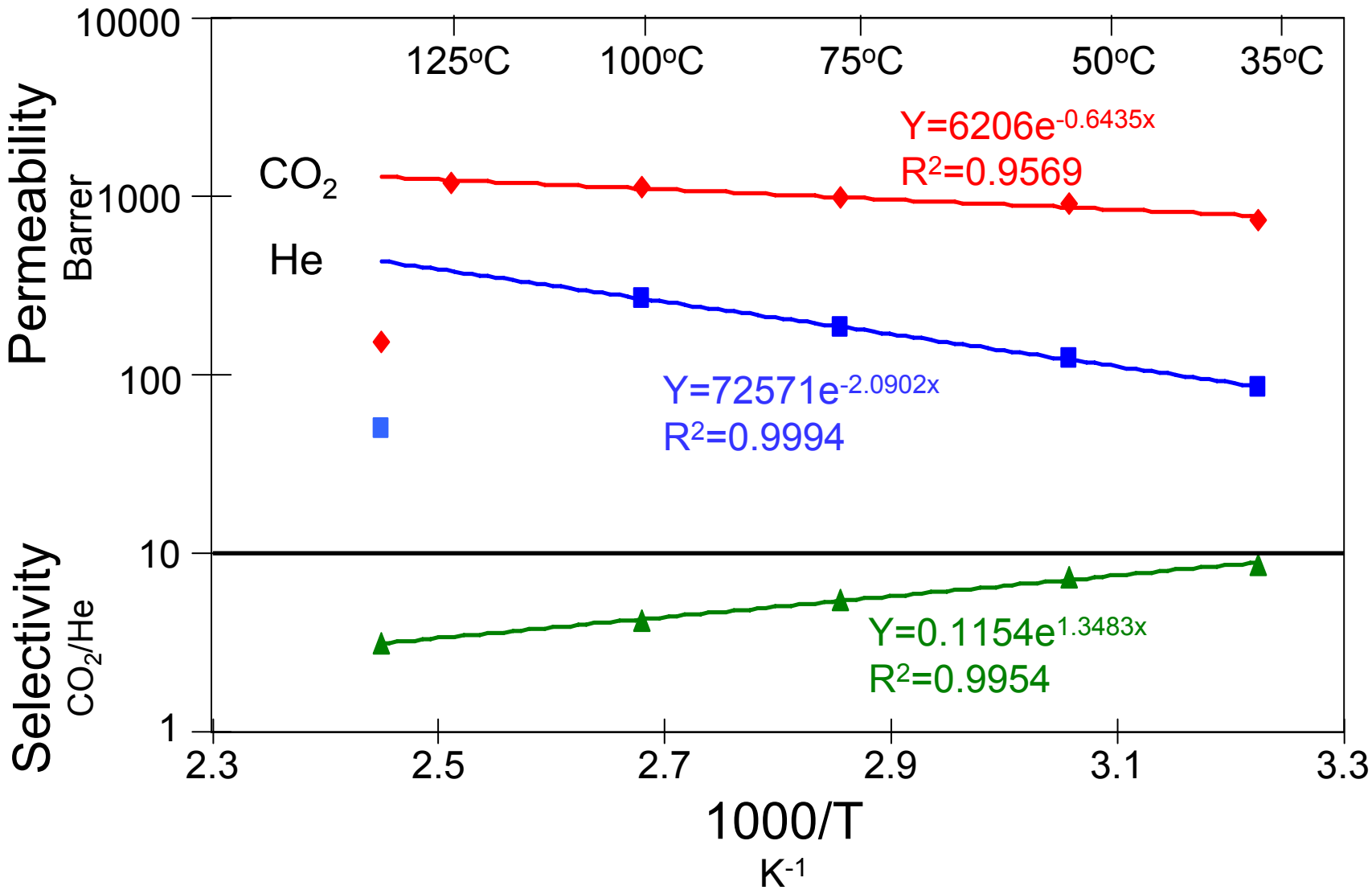


Developmental Progression



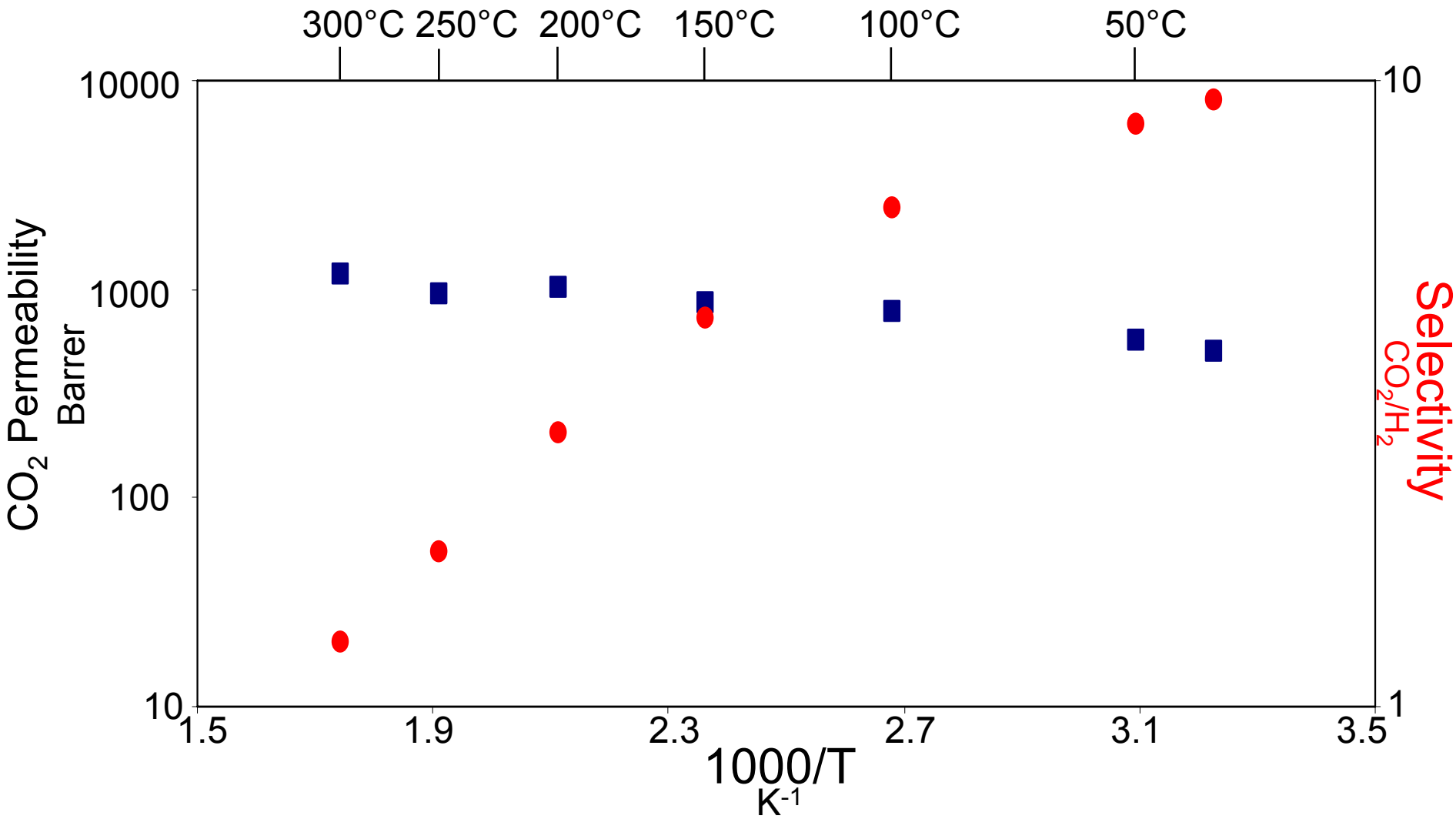
Support Failure Limits Performance

[HMIM][Tf_2N] on PSF



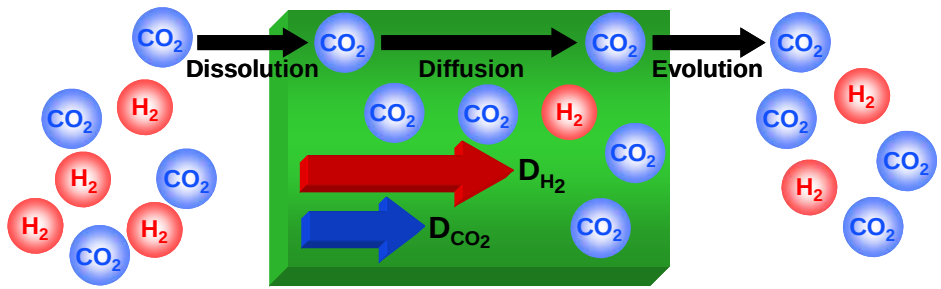
Cross-linking Stabilizes Support

[HMIM][Tf_2N] on Cross-linked Nylon



Loss of Selectivity at High Temperature: A Problem of Mechanism

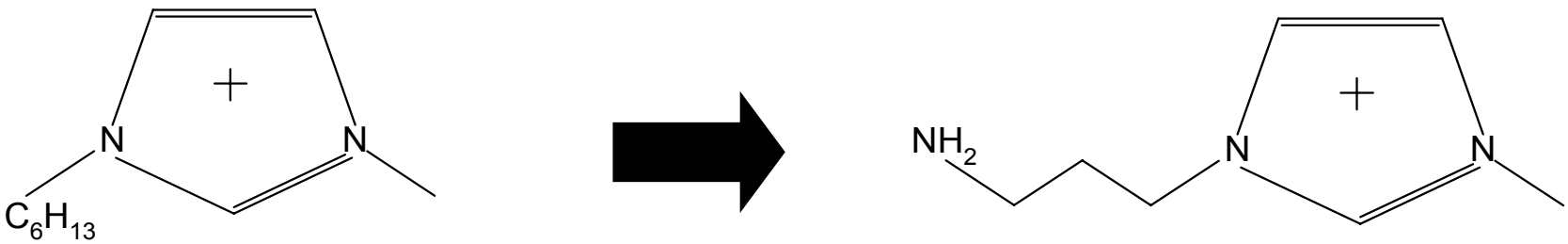
Permeability = Solubility X Diffusivity

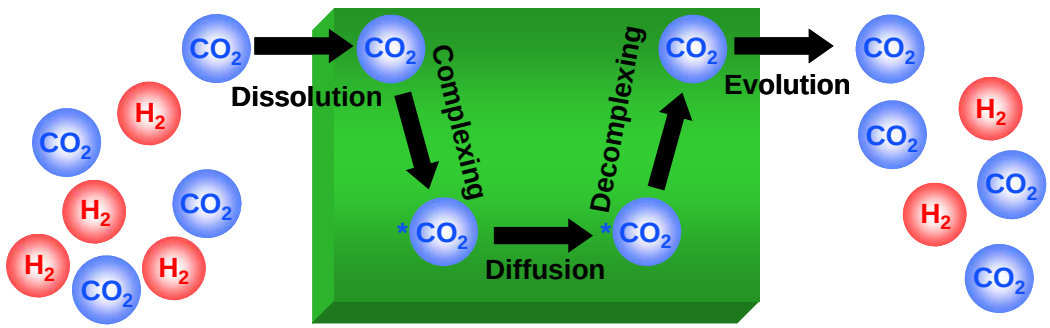


Solution Diffusion

$$\text{Selectivity} = \frac{CO_2 \text{ Permeability}}{H_2 \text{ Permeability}}$$

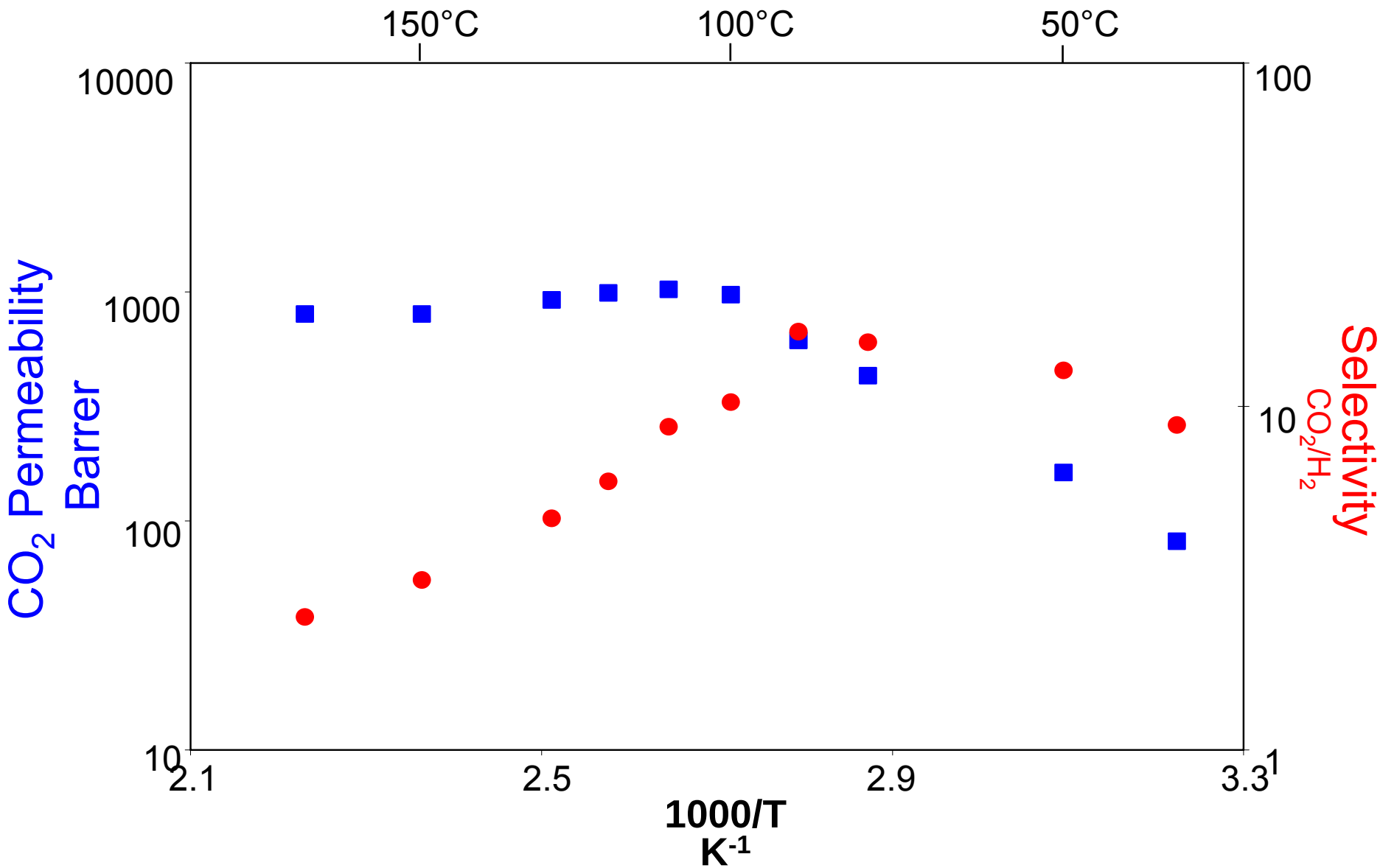
Formation of Chemical Complexes: A Potential Solution



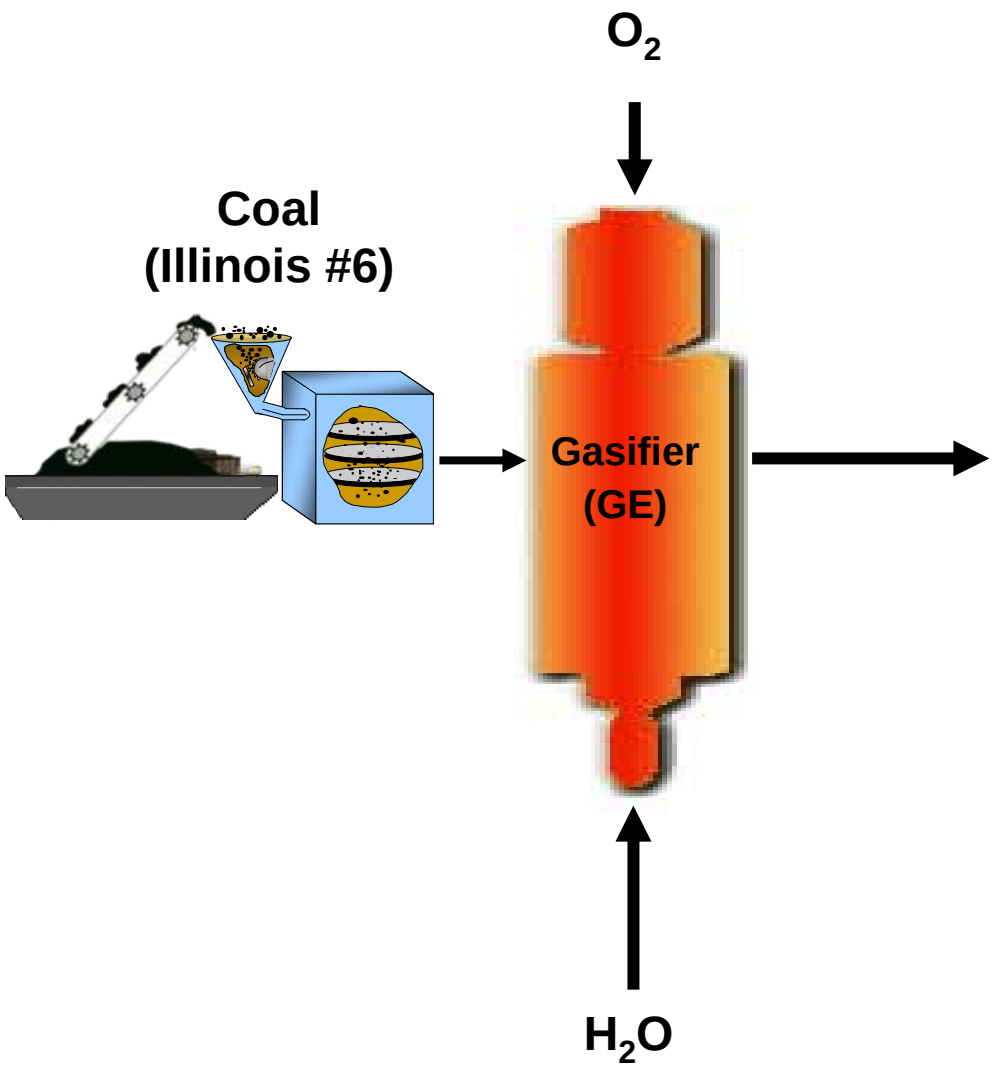


Facilitated Transport Increases Performance

$[NH_2PMIM][Tf_2N]$ on Cross-linked Nylon



Other Syngas Constituents Must be Considered



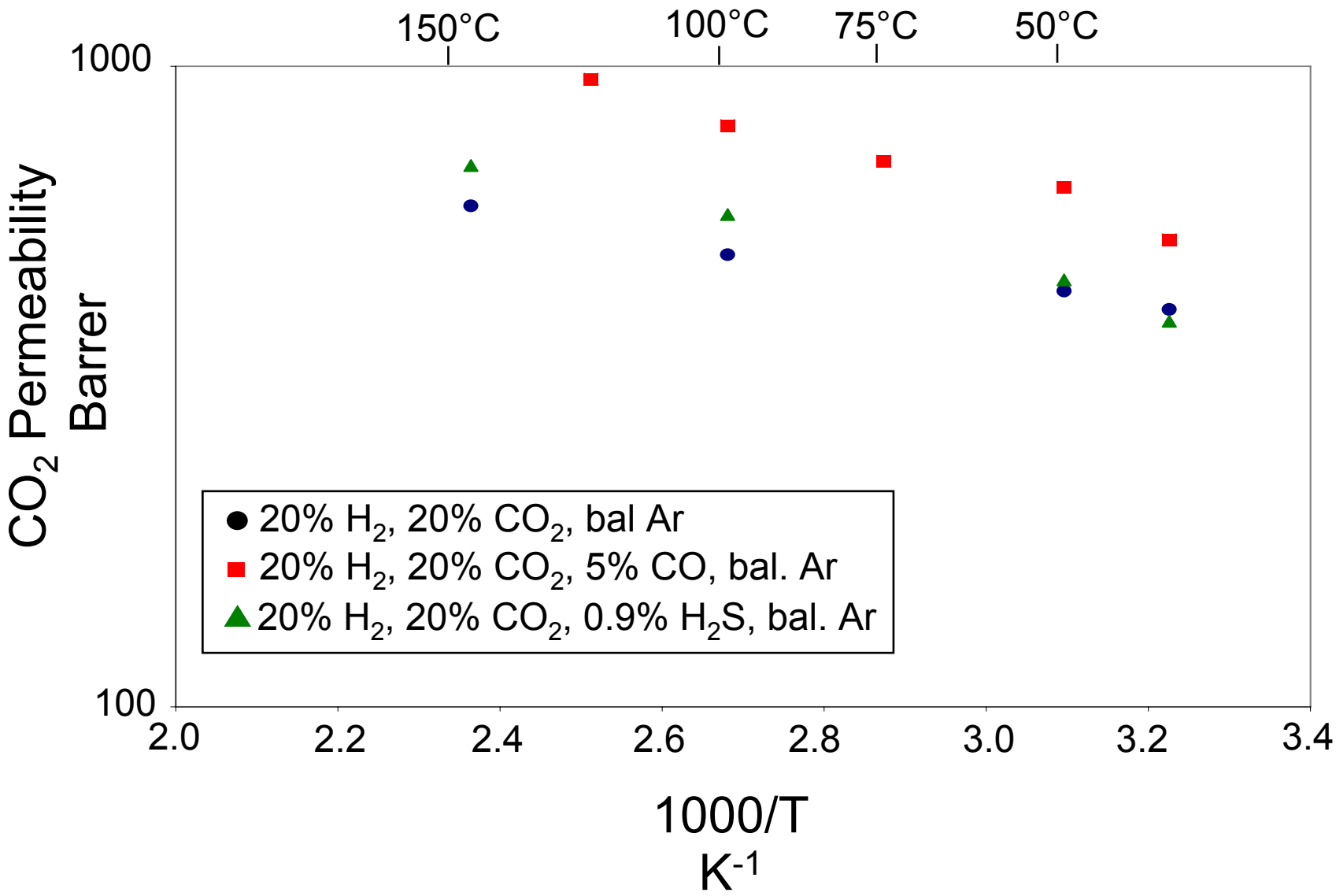
Syngas

0.79% Ar
0.10% CH_4
34.42% CO
15.11% CO_2
0.02% COS
33.49% H_2
14.29% H_2O
0.73% H_2S
0.89% N_2
0.17% NH_3

"Cost and Performance Baseline for Fossil Energy Plants" DOE/NETL-2007/1281

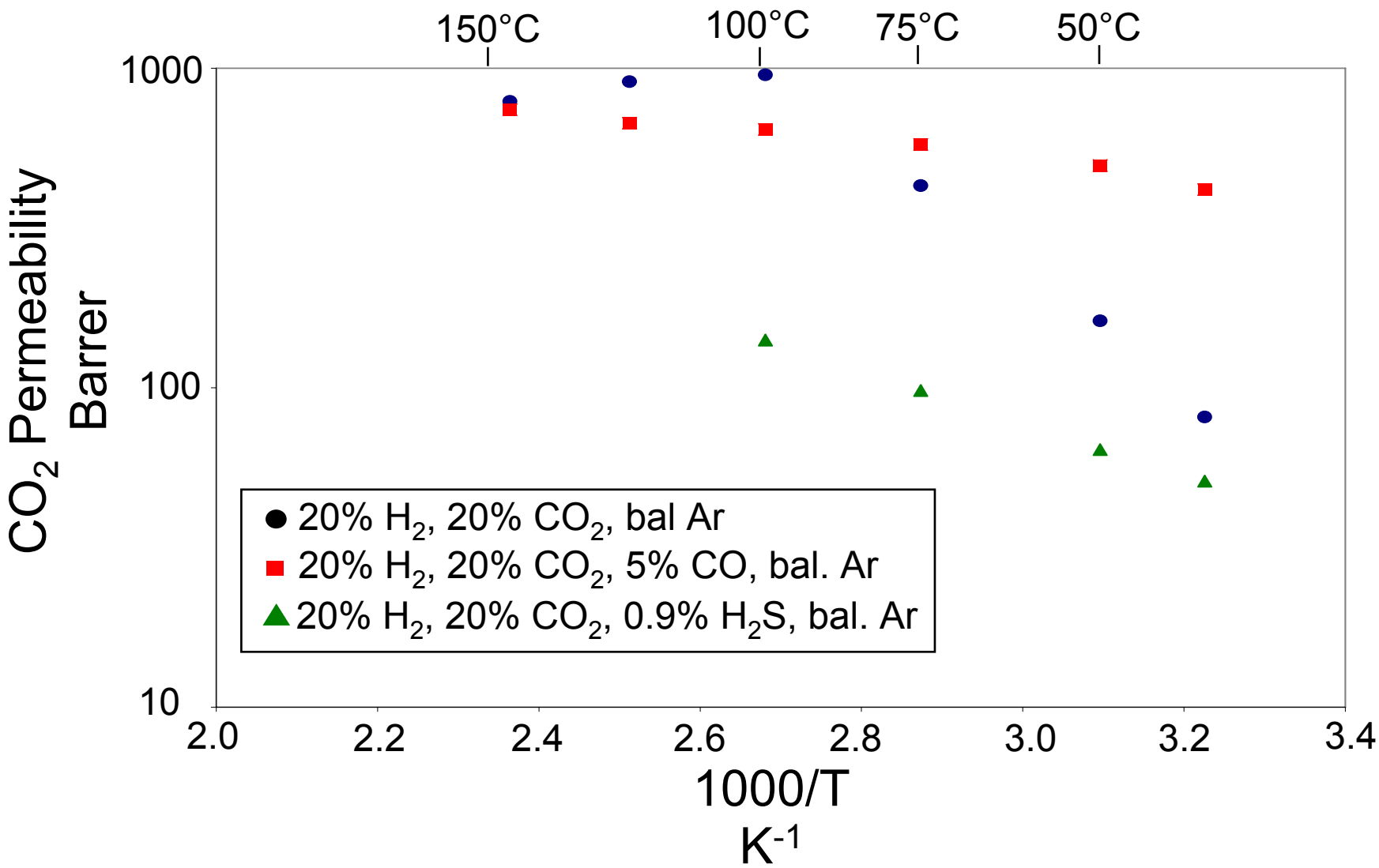
CO Increases CO_2 Permeability

[HMIM][Tf_2N] on Cross-linked Nylon



Contaminants Eliminate Facilitated Transport

[NH_2PMIM][Tf_2N] on Cross-linked Nylon



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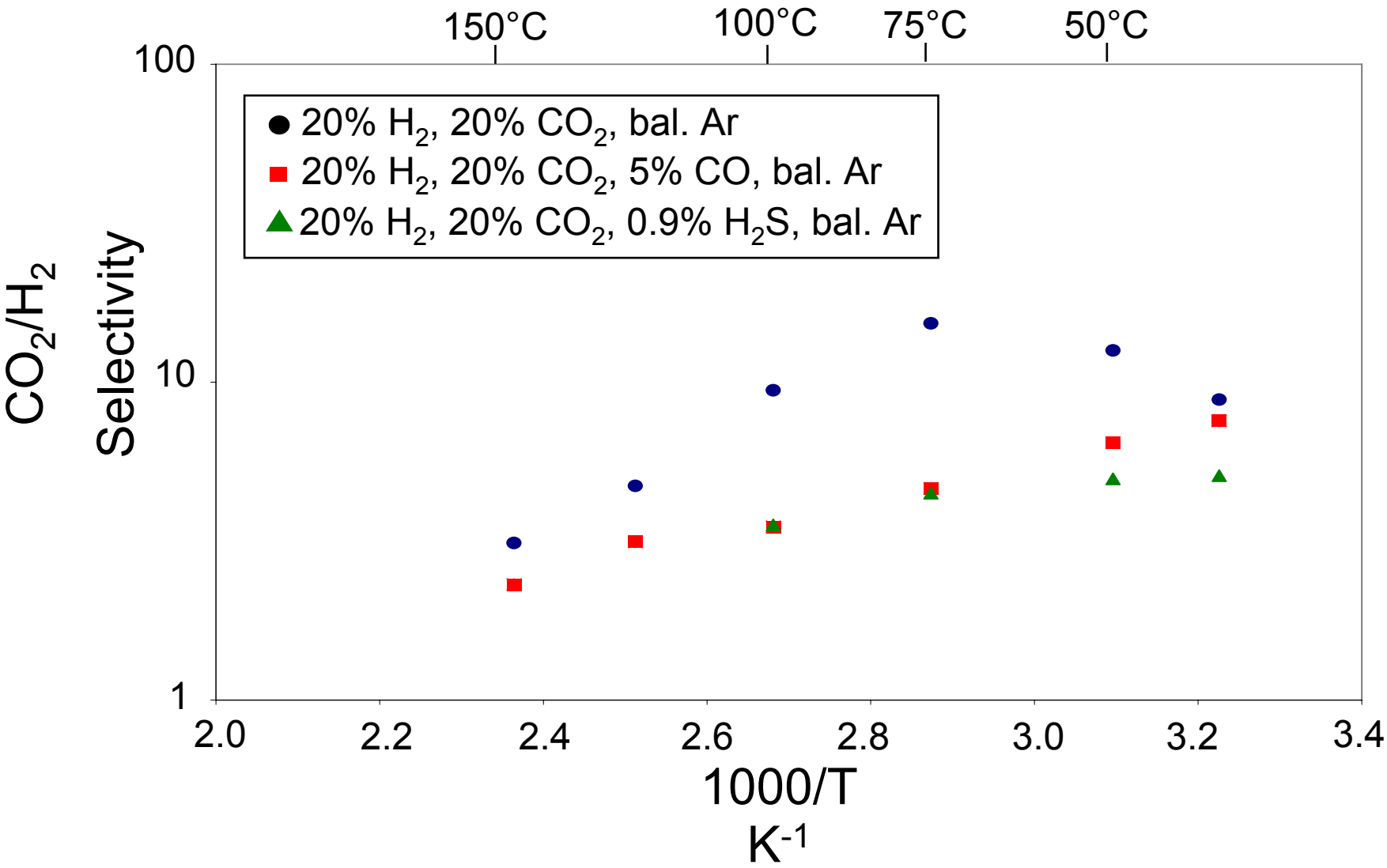
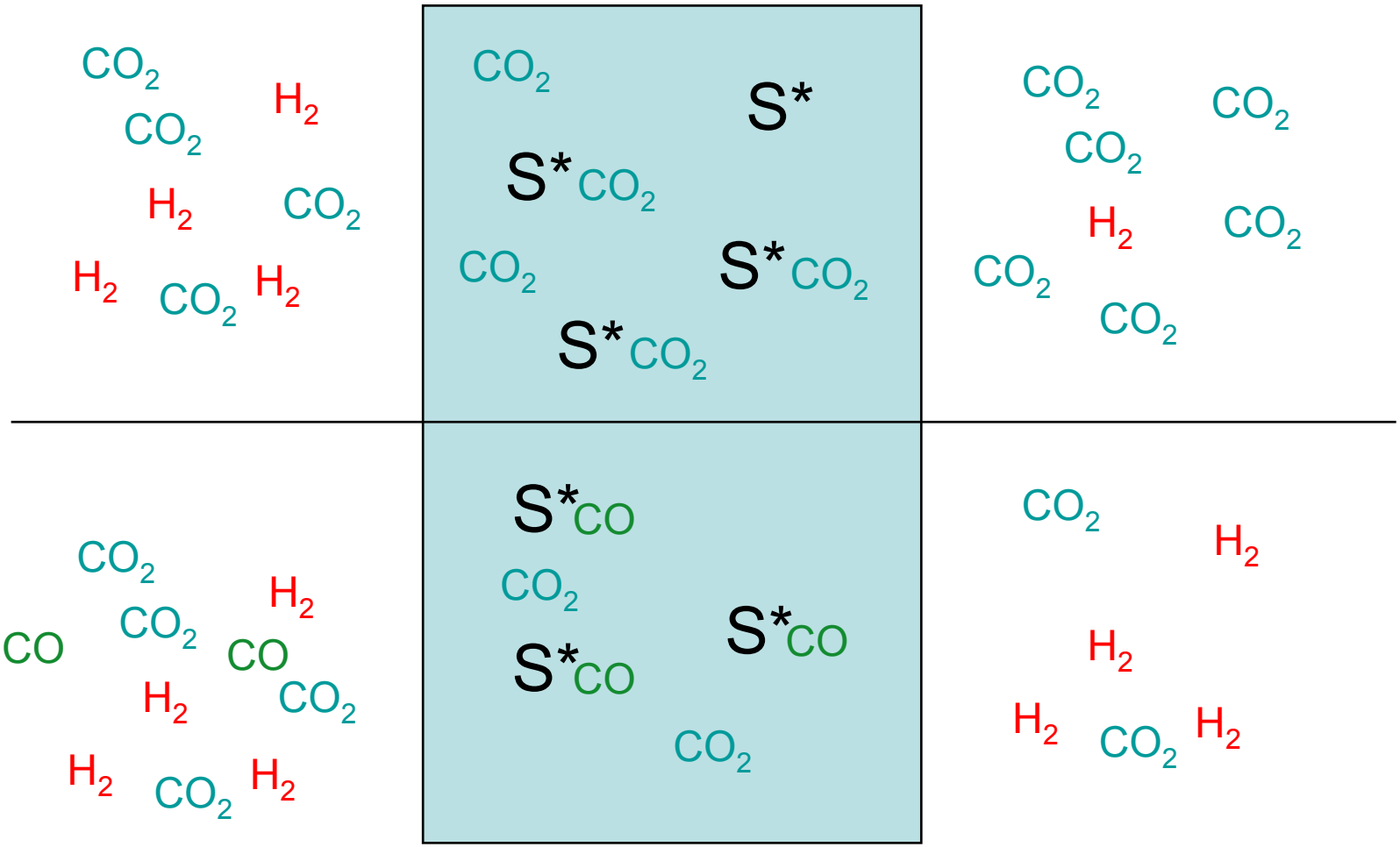


Hypothesis: Contaminants Interfere with Complex Formation



Summary

- High temperature CO_2 selective membranes may facilitate water-gas shift and enhance IGCC efficiency
- Ionic liquid membranes with cross-linked supports may be employed at water-gas shift conditions
- Fabrication of temperature-stable facilitated transport membranes is possible with ionic liquid transport media
- Facilitated transport membranes based on amine complexes show significant vulnerability to H_2S and CO
- Other complexes will be explored

Acknowledgement

The authors gratefully recognize the Brennecke and Maginn research groups at the University of Notre Dame for their efforts in the synthesis and characterization of the ionic liquids along with their invaluable expertise in these areas. They have been instrumental in the development of new ionic liquids for this study. We look forward to further rewarding collaboration.