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DOE Hydrogen Program

Cost Implications of Hydrogen Quality Requirements

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DOE Hydrogen Program Annual Merit Review

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Overview

Timeline

- Project start date: FY 2007
- Project end date: Open
- Percent complete: N/A

Barriers

- B. Stove-Piped/Siloed Analytical Capability
  - Segmented resources
- D. Suite of Models and Tools
  - Macro-system models

Budget

- Funding, FY 07: $200 K
- Funding, FY 08: $350 K
- Funding, FY 09: $200 K

Partners/Collaborators

- Energy Companies (BP, GTI)
- National Laboratories (NREL)
- International
  - Japan Gas Association
  - International Standards Org.

Objective

- Correlate impurity concentrations (in H_2) to the cost of hydrogen, as functions of
  - Process parameters (T, P, S/C, …)
  - Performance measures (H_2 recovery, efficiency)

Approach

- Define hydrogen production processes that can meet hydrogen quality requirements
  - SMR, NG-ATR, Coal Gas (CG) ATR
  - Reformate, syngas purification using PSA
- Model processes to determine sensitivity of process performance to
  - Design and operating parameters
    - *P, T, S/C, sorbent, …*
- Support data integration into H2A

Milestones

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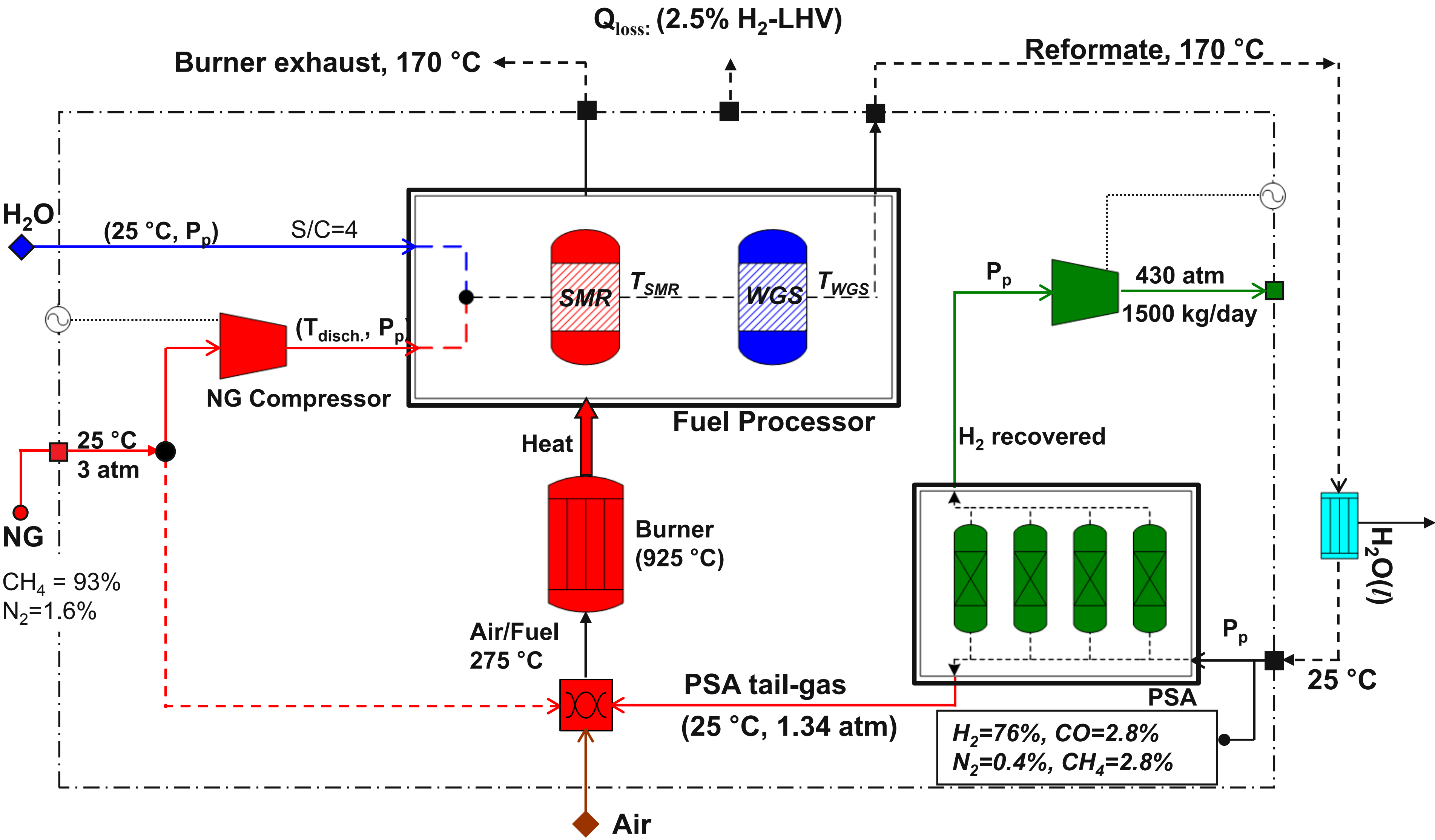
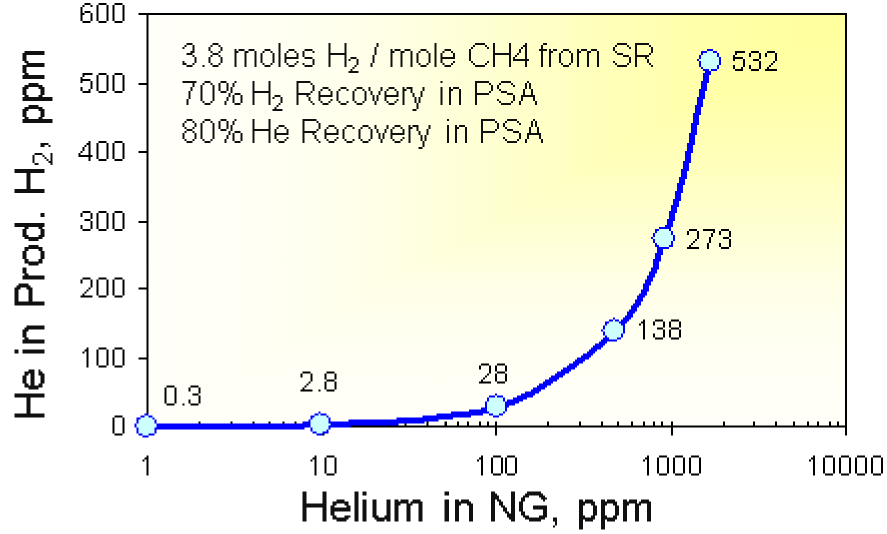
Month-Year	Milestone
Feb. 2009	With NREL, incorporate NG-SR-PSA data into H2A *In progress*
Feb. 2009	Define processes to be modeled and analyzed for hydrogen production via coal gasification and water electrolysis *Model set up for coal gas to hydrogen pathway* *(some preliminary results presented here)*
Sep. 2009	Establish impurity concentration vs. efficiency correlation for coal derived hydrogen

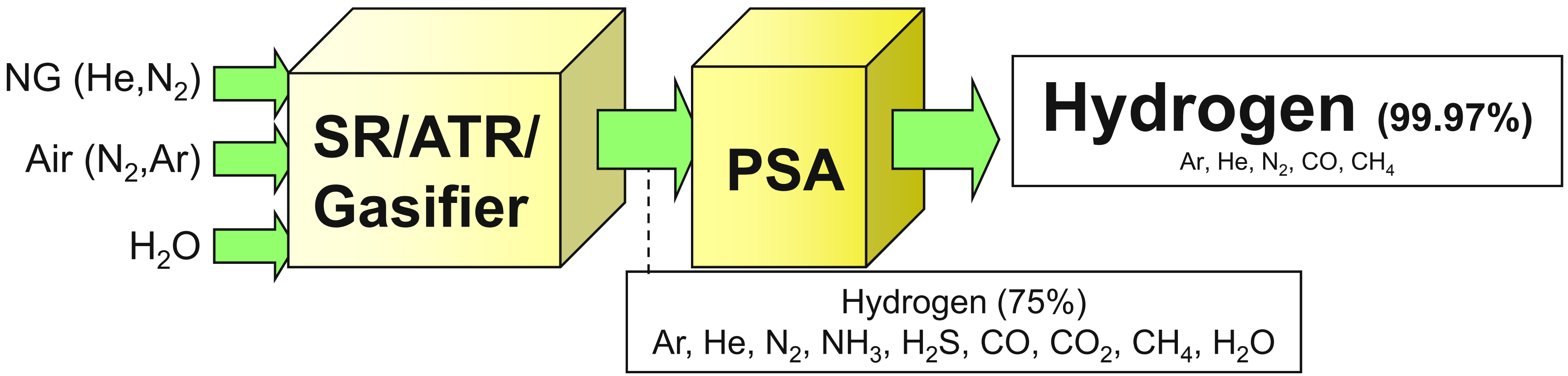
Schematic of the SMR-PSA system (Base Case)



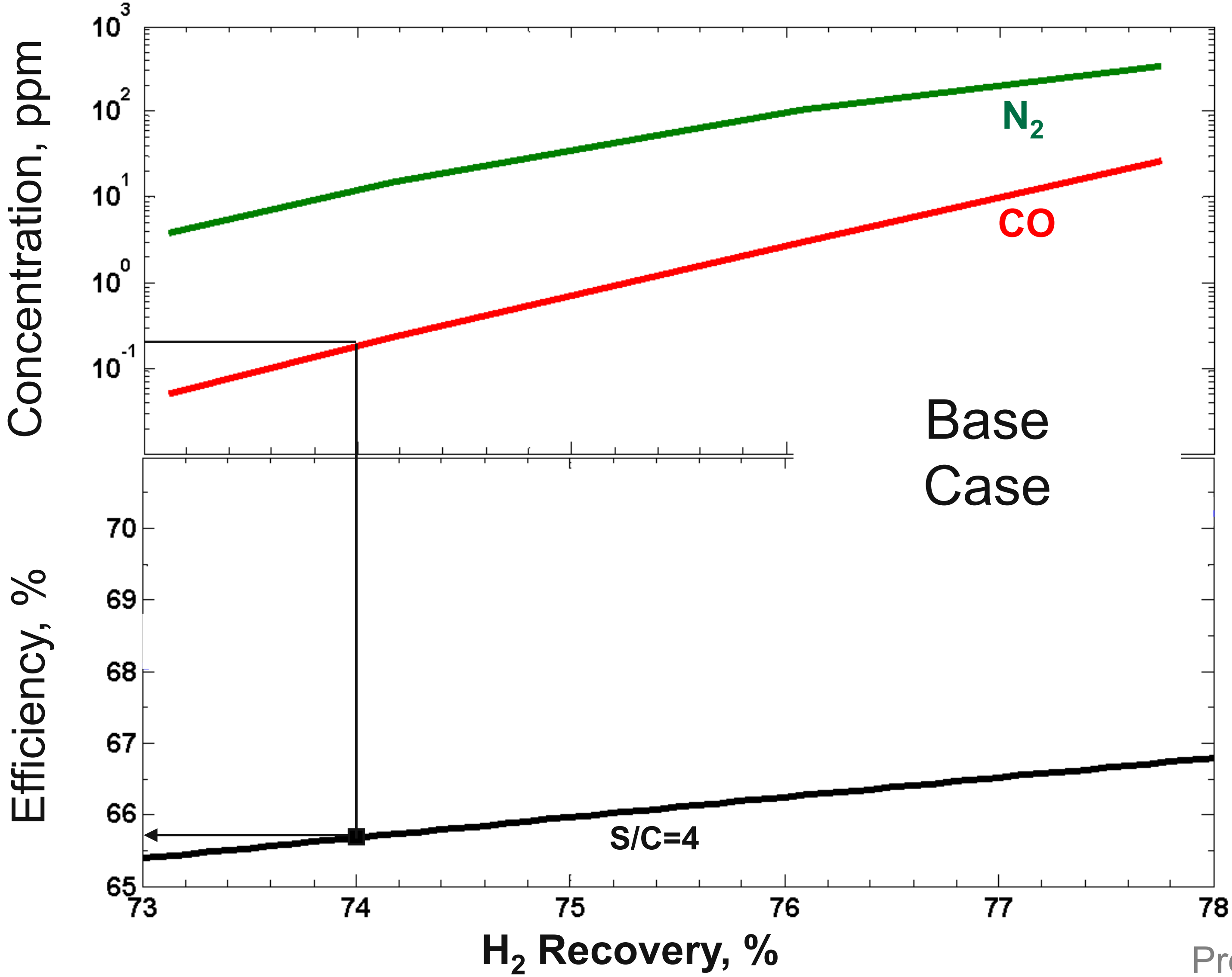
The model tracks 9 impurities through the system

- Natural gas feed contains He, N_2, S
- Air feeds (ATR, CG) contribute Ar, N_2
- Reformate to PSA contains
  - N_2, CH_4, CO_2, CO, NH_3, H_2S, He, Ar
- The PSA is very effective for removing H_2S, NH_3, H_2O, CO_2, CH_4
- Helium is not removed in the PSA
- The product hydrogen from PSA contains trace concentrations of He, CO, N_2, Ar, CO_2, CH_4



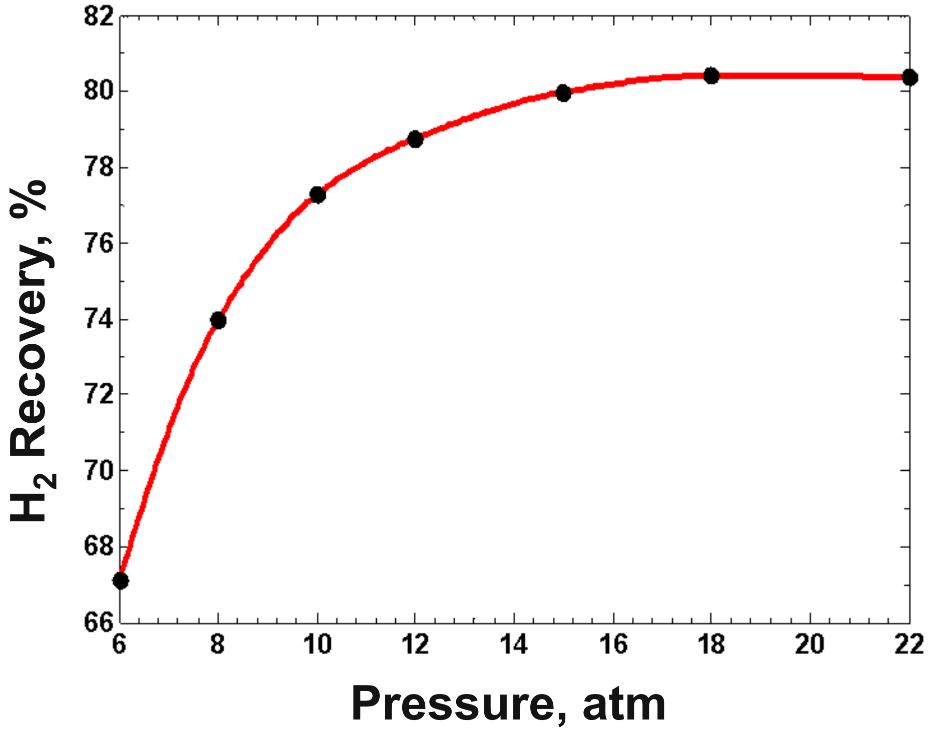


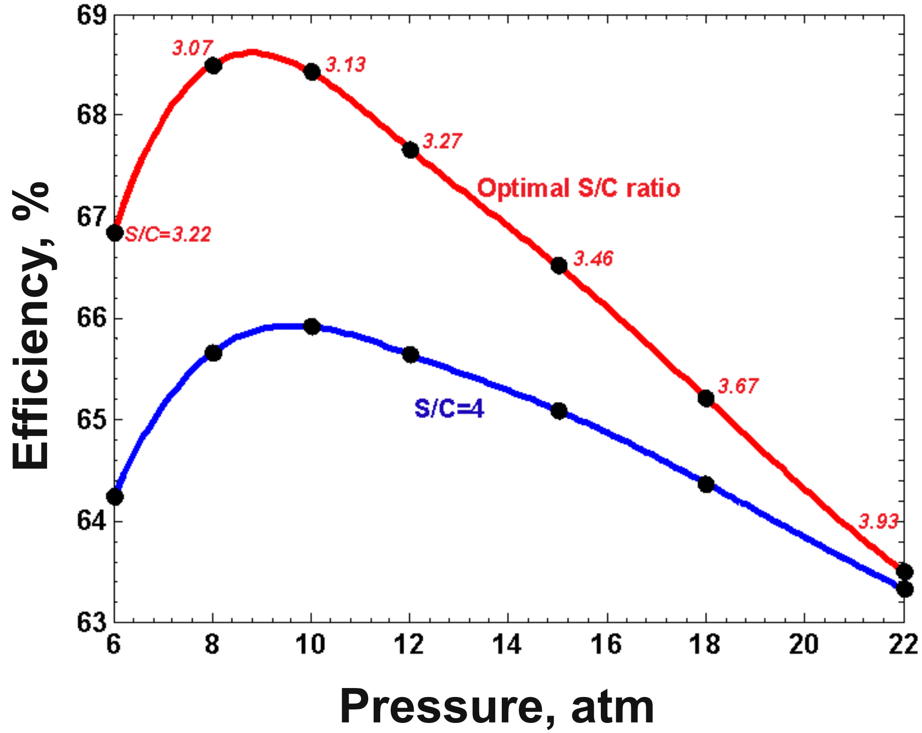
Base Case: A CO specification of 0.2 ppm limits the H_2 recovery to 74% and the efficiency to ~ 66%



Preliminary Data

Effect of Pressure
The process efficiency peaks at 10-12 atm





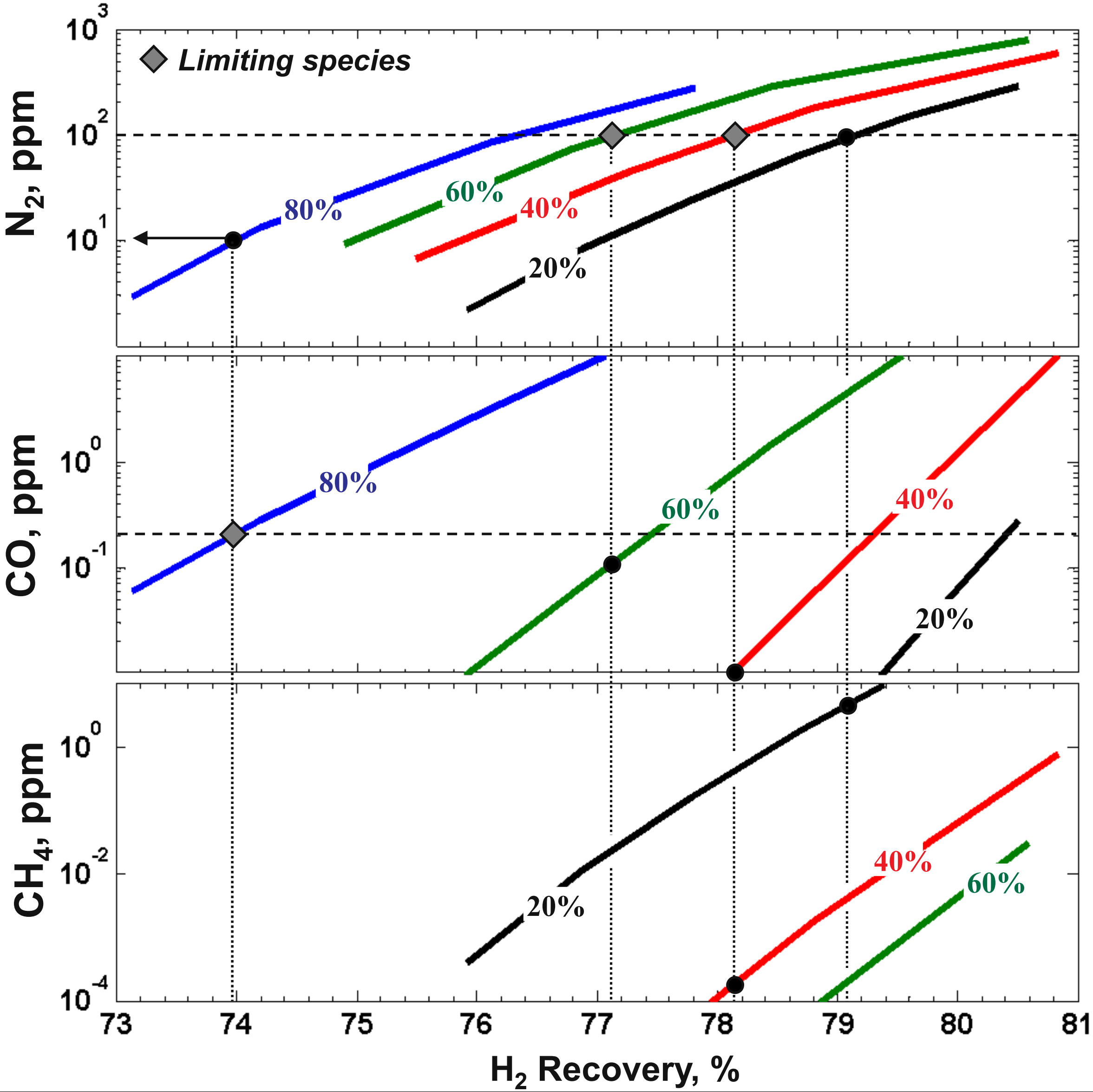
Higher pressures

- Improve impurity adsorption in PSA
- Increase hydrogen loss during PSA bed regeneration
- Reduce hydrogen concentrations in reformer product gas (i.e., PSA feed)

Preliminary Data

Effect of Carbon / Zeolite Proportion:

With increasing zeolite fraction, the limiting species changes from CO to N_2



Preliminary Data

Variations in Natural Gas Composition: Some NG contains much higher concentrations of N_2

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Variation of natural gas composition (%)		
Species	Mean	10 percentile[1]
CH_4	93.1	83.9
C_2H_6	3.2	5.7
C_3H_8	0.7	1.1
C_4H_{10}	0.4	0.3
CO_2	1.0	1.4
N_2	1.6	6.1
O_2	0.0	1.5
LHV (kJ/mol)	817	785

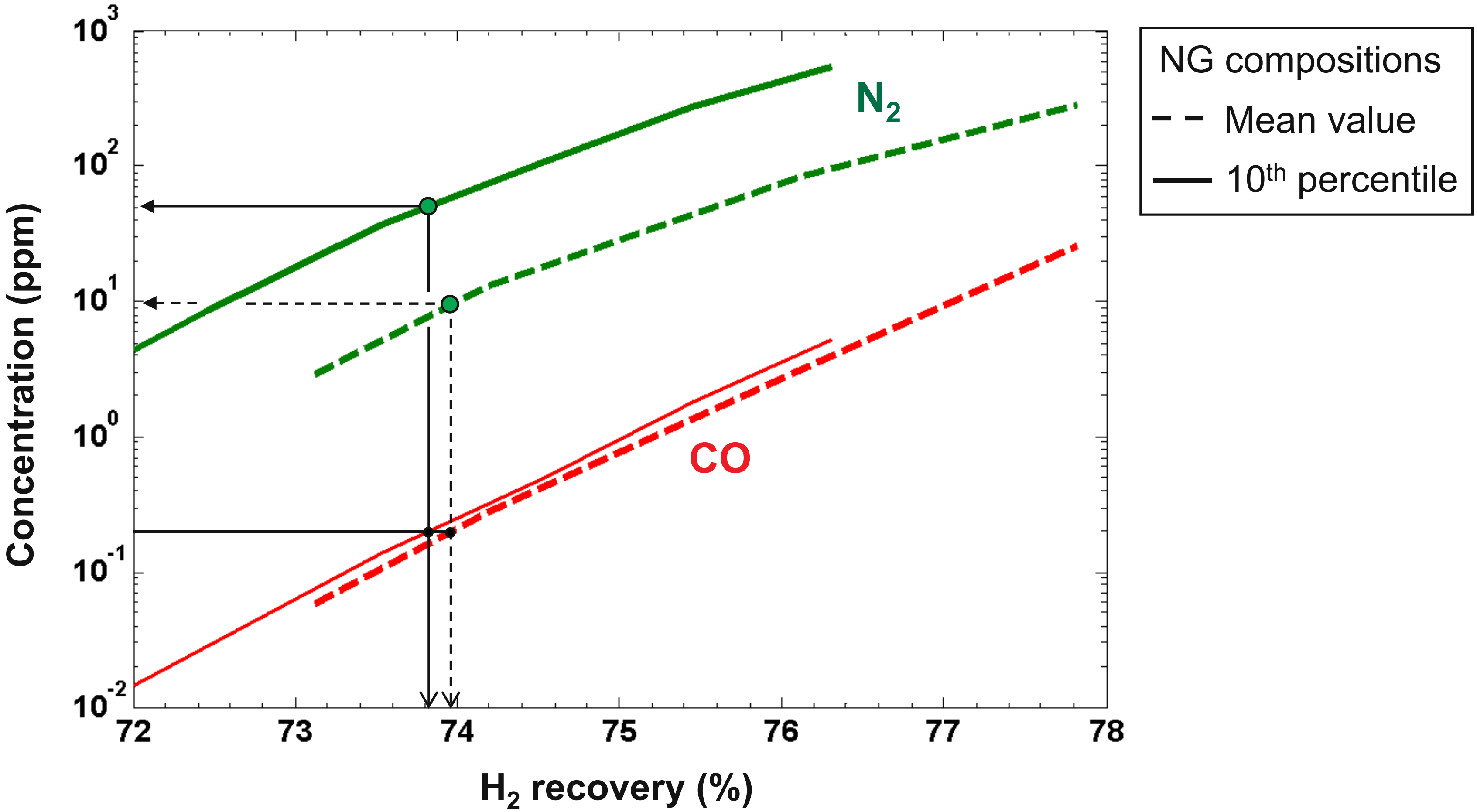
P:	***8 atm***
S/C:	***4 (-)***
T_{SMR}:	***750 ℃***
T_{WGS}:	***435 ℃***

Reformate composition to PSA (%-dry)*		
Species	Mean	10^{th} percentile
H_2	76.4	75.4
CH_4	2.8	2.7
CO_2	17.5	17.7
CO	2.8	2.8
N_2	0.4	1.4

****Feed to PSA also includes 100 ppmv H_2S***

[1]Blazek, C.F., Kinast, J.A. and Freeman, P.M. (1993). Compressed natural gas measurement, A.G.A. Distribution/Transmission Conference, Orlando, Florida, May 16-19

Variations in Natural Gas Composition: N_2 concentration in product H_2 increases by a factor of ~6



- CO still limits the hydrogen recovery from the PSA

Preliminary Data

Hydrogen cost is a weak function of CO concentration

(based on NG price of \$7.6 / 1000 ft^3 or \$7.8 / MMBTU)

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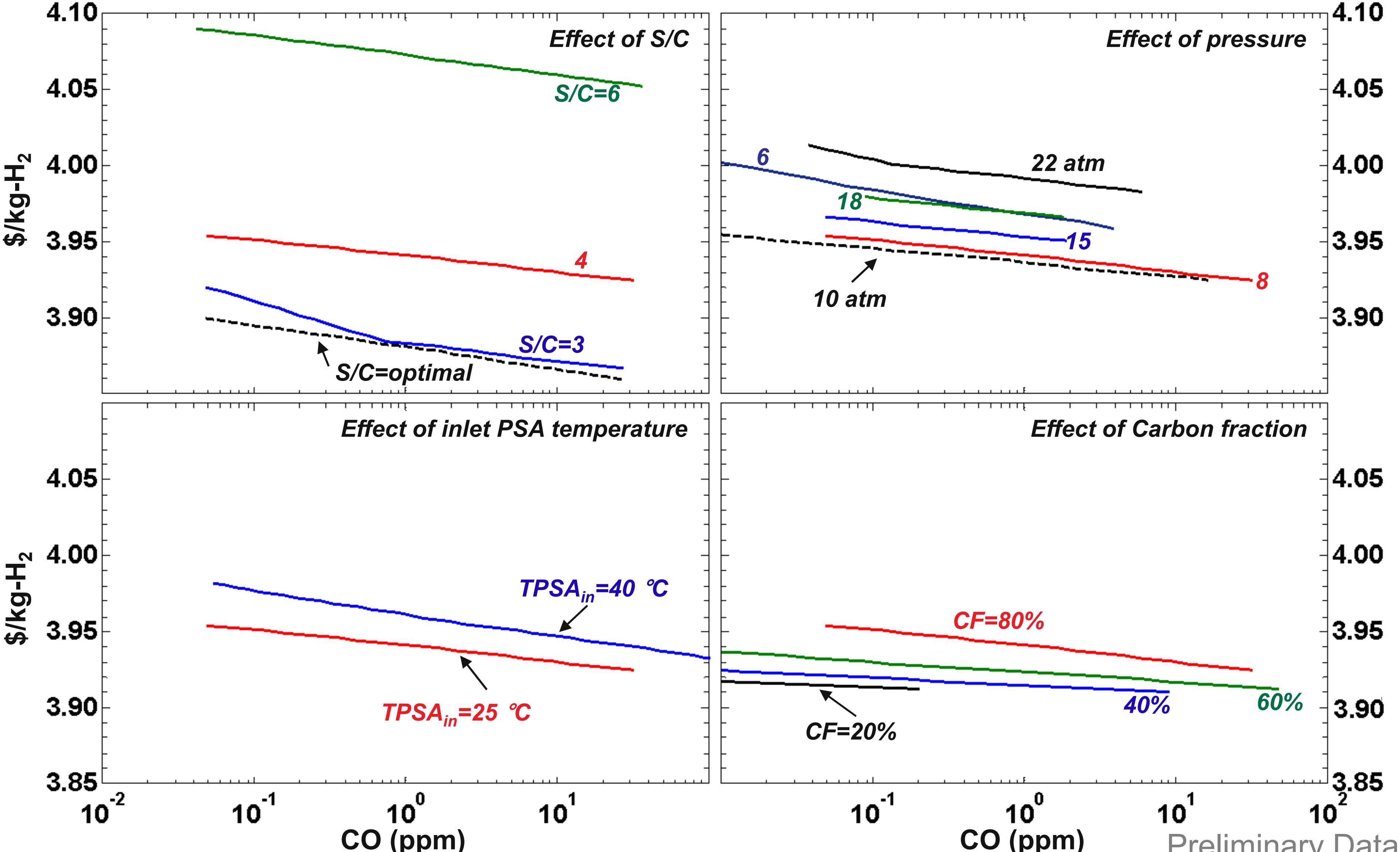

Preliminary Data

Schematic for a H_2 production system using natural gas ATR and PSA

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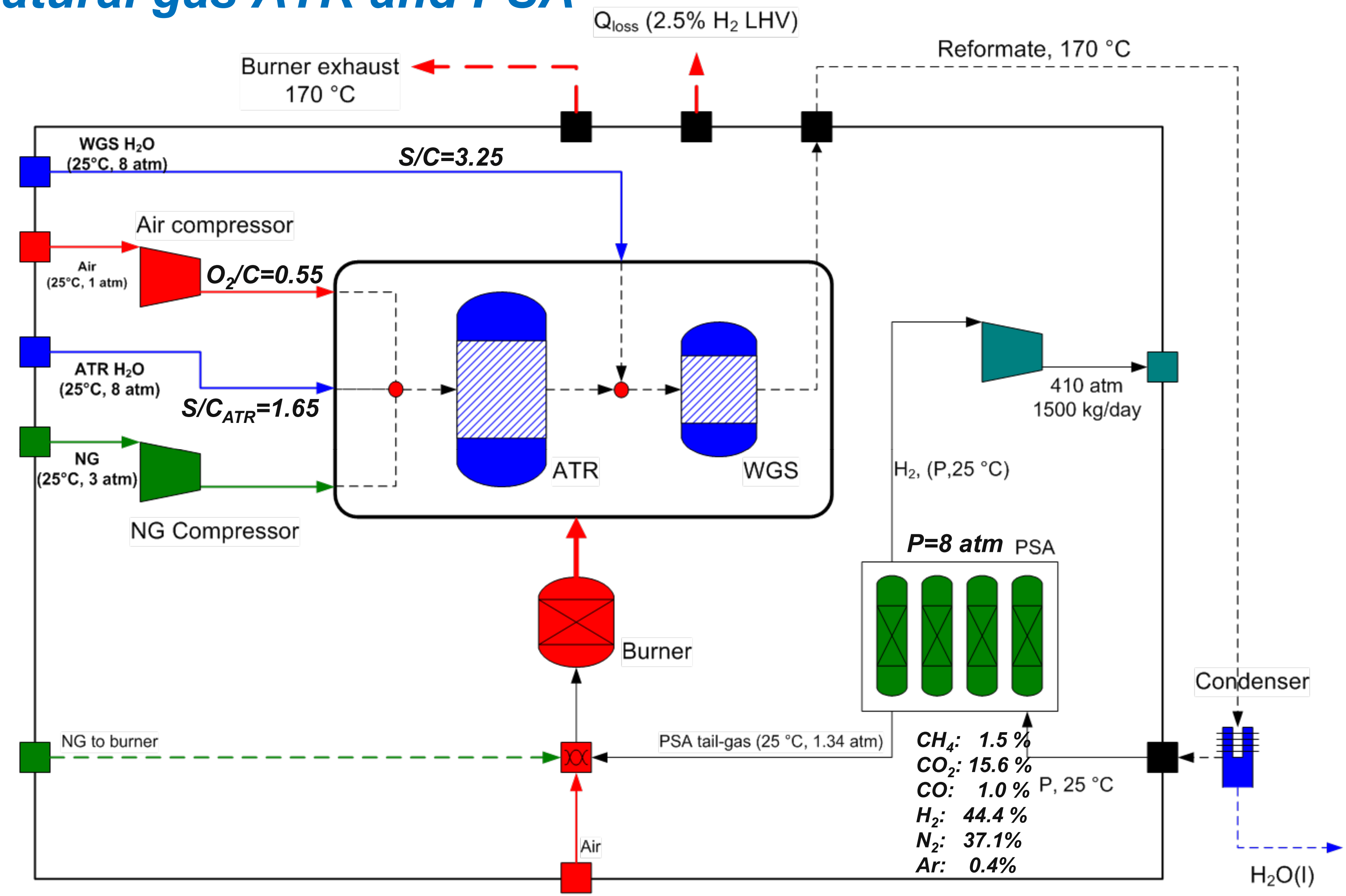
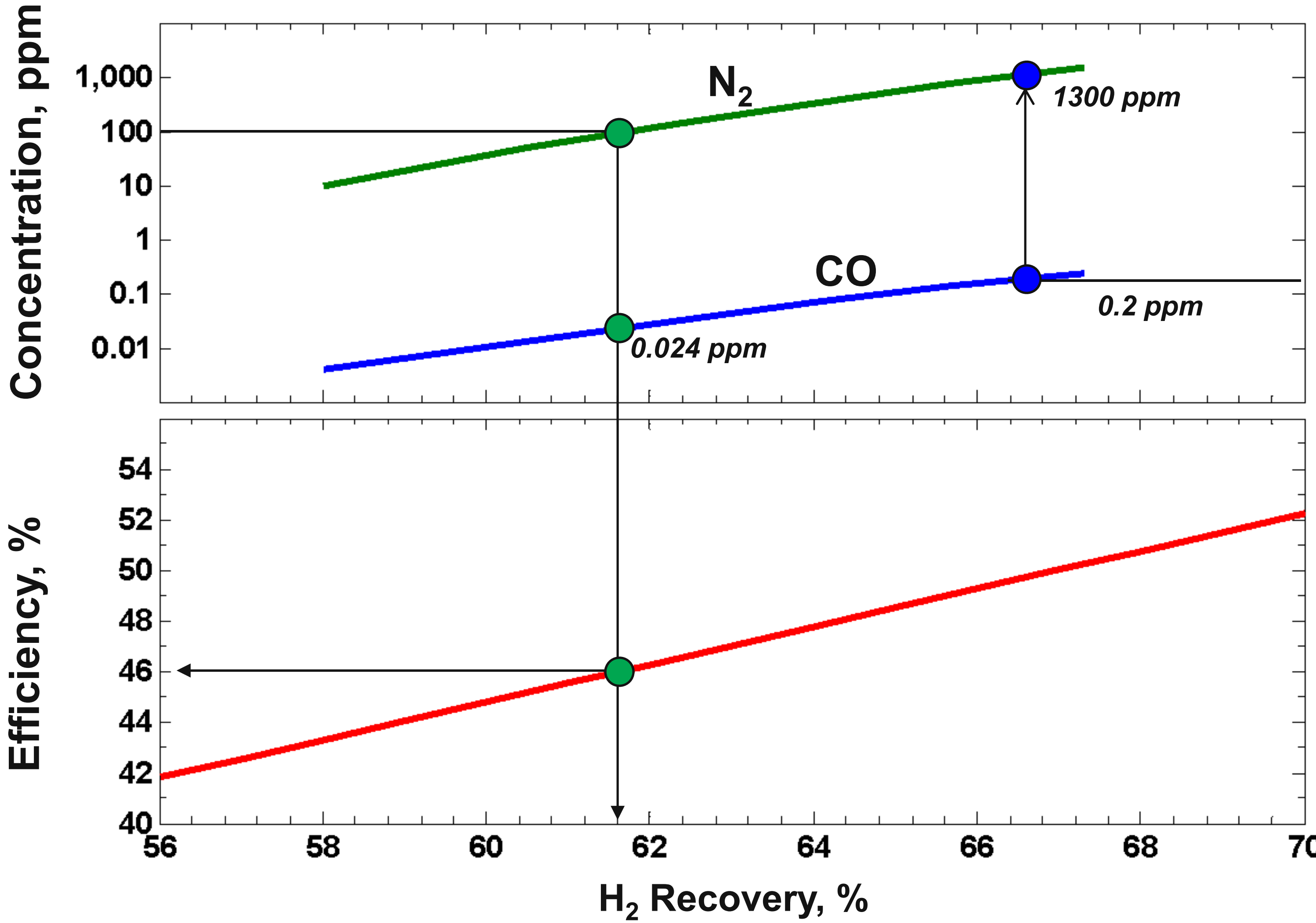


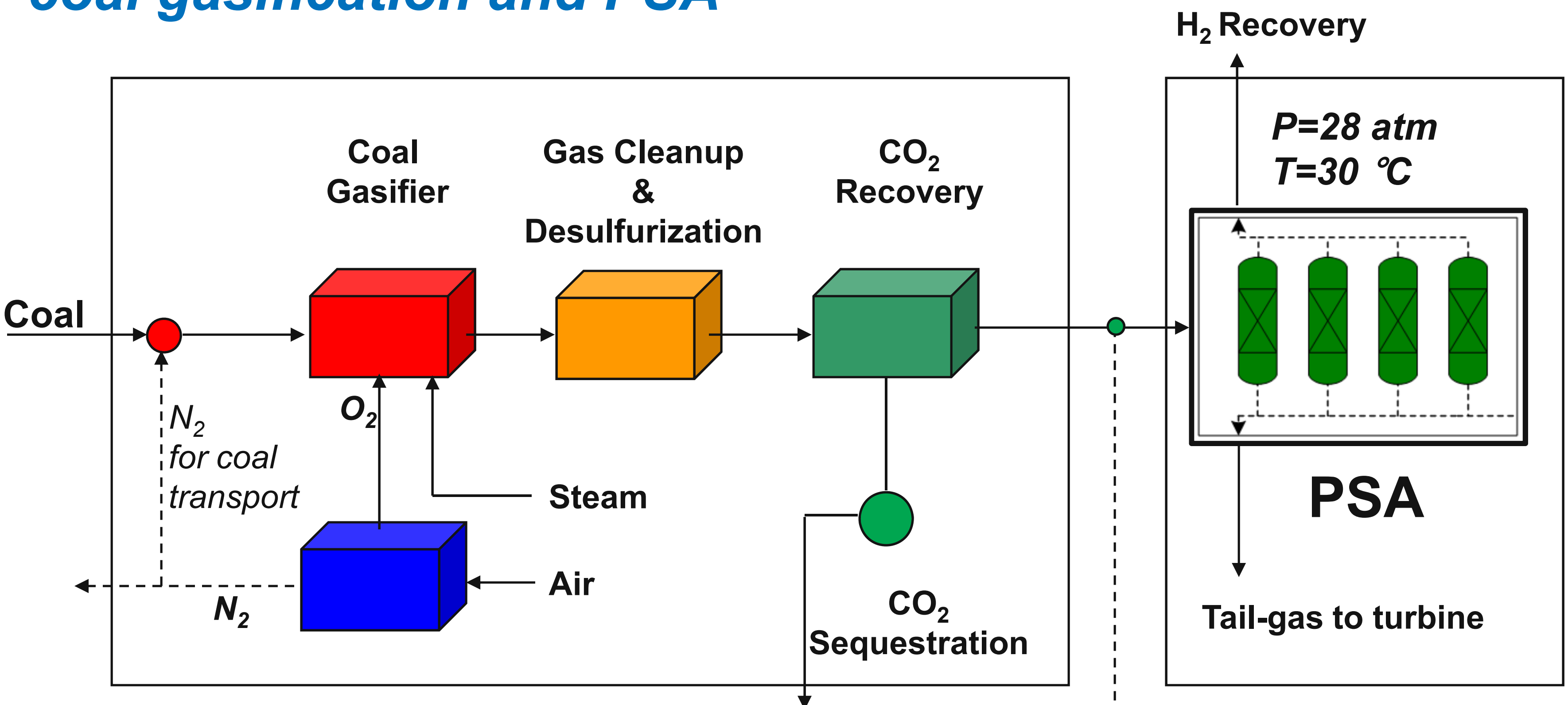
Preliminary Data

Natural Gas ATR-PSA: Nitrogen limits the hydrogen recovery



Argon is slightly less than 10 ppm when recovery exceeds 66%

Schematic for a H_2 production system using coal gasification and PSA

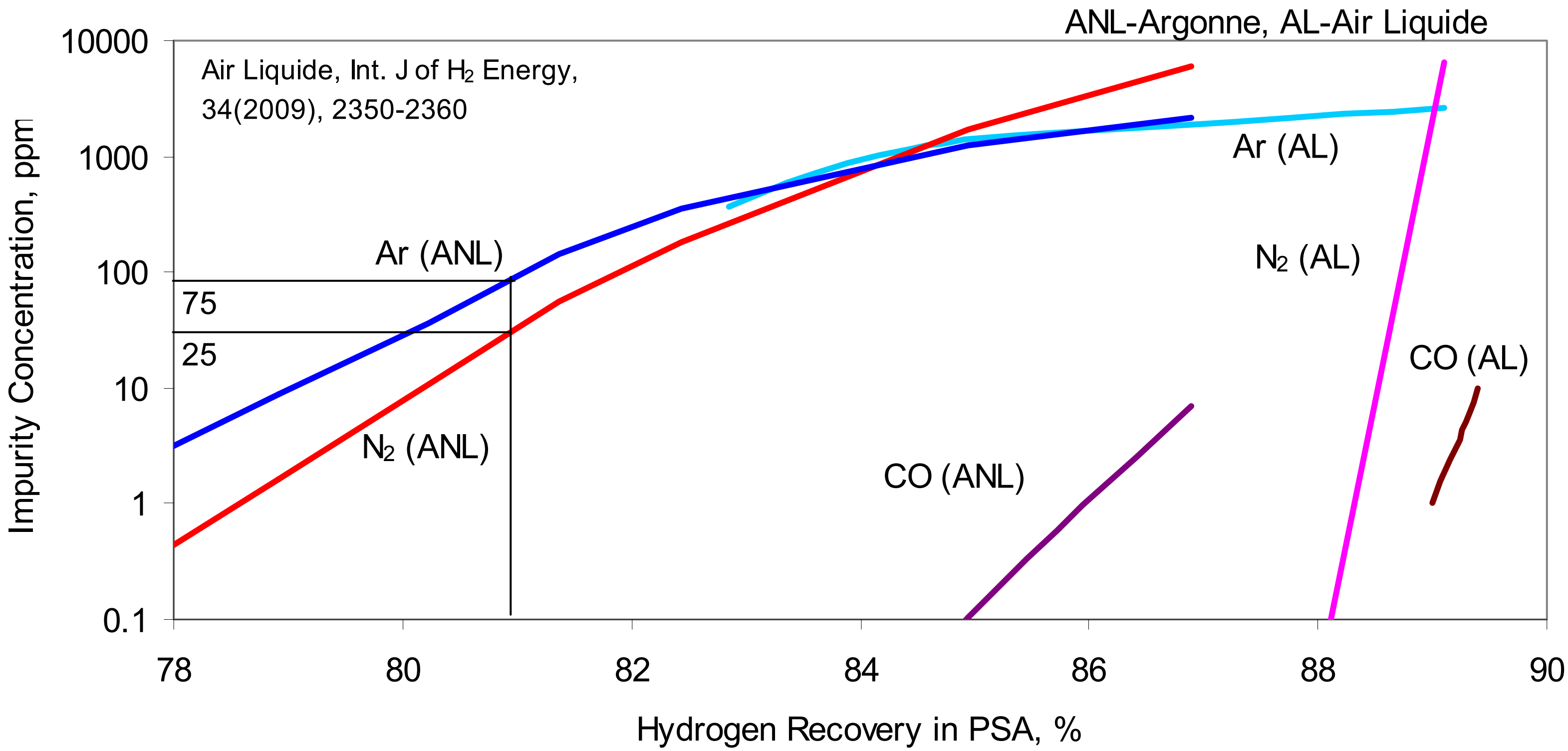


*	
H_2:	87.8 %
N_2:	5.0 %
CO_2:	3.9 %
CO:	2.6 %
Ar:	0.9 %
CH_4:	100 ppm

Besancon et al. – Air Liquide (2009) Journal of power sources

Preliminary Data

H$_2$ from Coal Gasification and PSA: Inerts (nitrogen and argon) limit the hydrogen recovery



Argonne Model

- 4 adiabatic beds, 2 pressure equalizations
- Adsorbent mix: 60% activated carbon (BPL), 40% Zeolite 5A
- Tail-gas pressure: 1.3 bar-a

Air Liquide Model (Besancon, J Power Sources, 34(2009))

- 6 Beds
- Adsorbent mix: unknown
- Tail-gas pressure: 1.3 bar-a

Summary of Technical Accomplishments

- A rigorous model of the PSA system has been set up as part of a flexible systems model (using Comsol Multiphysics and MATLAB)
  - 9 species can be tracked through the system
- The pathway for NG-SR-PSA has been studied over a broad range of design and operating parameters
  - The effect of several design and operating parameters on hydrogen quality and system efficiency has been established
  - Constraint: to meet SAE/ISO guideline values
- The system model results have been correlated with the cost of hydrogen (using H2A)
- Preliminary studies have been conducted for two additional pathways
  - NG-ATR-PSA
  - Coal Gas - PSA

Collaborations

- Presented results to stakeholders at numerous meetings
  - ISO, Conferences, Tech Team
- Participated in modeling workshop with Japan Gas Association, GTI, and BP to validate model with field data
- Working with NREL to collect field data from gas supplier
- Exploring the (confidential) sharing of model results and field data with an energy company and a hydrogen producer (electrolysis)

Conclusions

- The cost of hydrogen is only slightly affected by the impurity specification (guideline) in the NG-SR-PSA system studied
- CO specification limits the hydrogen recovery for NG-SR for most process conditions
  - N_2 may become limiting species in a few cases
    - *When the beds are loaded with high zeolite content*
    - *When the natural gas contains high concentrations of nitrogen*
  - He passes through the NG-SR process
    - *Emerges at a lower concentration*
- For ATR of NG with PSA purification, Ar or N_2 specification may limit H_2 recovery
- Similarly, for coal gas reforming followed by PSA, the H_2 recovery may be limited by Ar or N_2

Future work

- Evaluate the impurity concentrations likely from other hydrogen production pathways
  - ATR, coal gasification, electrolysis
  - Coal gasification processes may be larger, central production plants
- Validate the NG-SR model results with field data
  - Incorporate more complex PSA systems if needed
- Incorporate our model results into H2A

Acknowledgements

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