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PURIWG Meeting: DOE Hydrogen Quality Working Group Update and Recent Progress

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DOE Hydrogen Quality Working Group (H2QWG) Objectives

- Develop a process to determine hydrogen quality requirements for fuel cell vehicles based on life-cycle costs
  - evaluate impact of fuel quality requirements on hydrogen production and purification costs
  - evaluate impact of contaminants on fuel cell performance, durability, and related life-cycle costs

- Identify information gaps and the R&D needed to fill those gaps
  - recommend approaches to funding and conducting the needed R&D

H2QWG has prepared a draft Roadmap and submitted it to DOE for review and comment

The focus is on the near- to mid-term (to 2015)

- Production: only distributed (forecourt) production by
  - reforming of natural gas (ATR & SMR)
  - reforming of renewable fuels, e.g., ethanol (i.e., E-95 & E-85)
  - electrolysis (alkaline and PEM electrolyzers)
- Purification by:
  - pressure-swing adsorption (may be aided by TSA)
  - hydrogen-permeable membrane separators
- Use in fuel cell systems (considering only compressed gas on-board hydrogen storage):
  - performance/cost/durability impact of
    - active contaminants
    - inert (non-electrochemically active) contaminants
- Analysis and quality verification
  - available analytical technologies (mostly research laboratory)
  - standardized (commercially accepted) technologies

Draft Roadmap
Summary findings (preliminary)

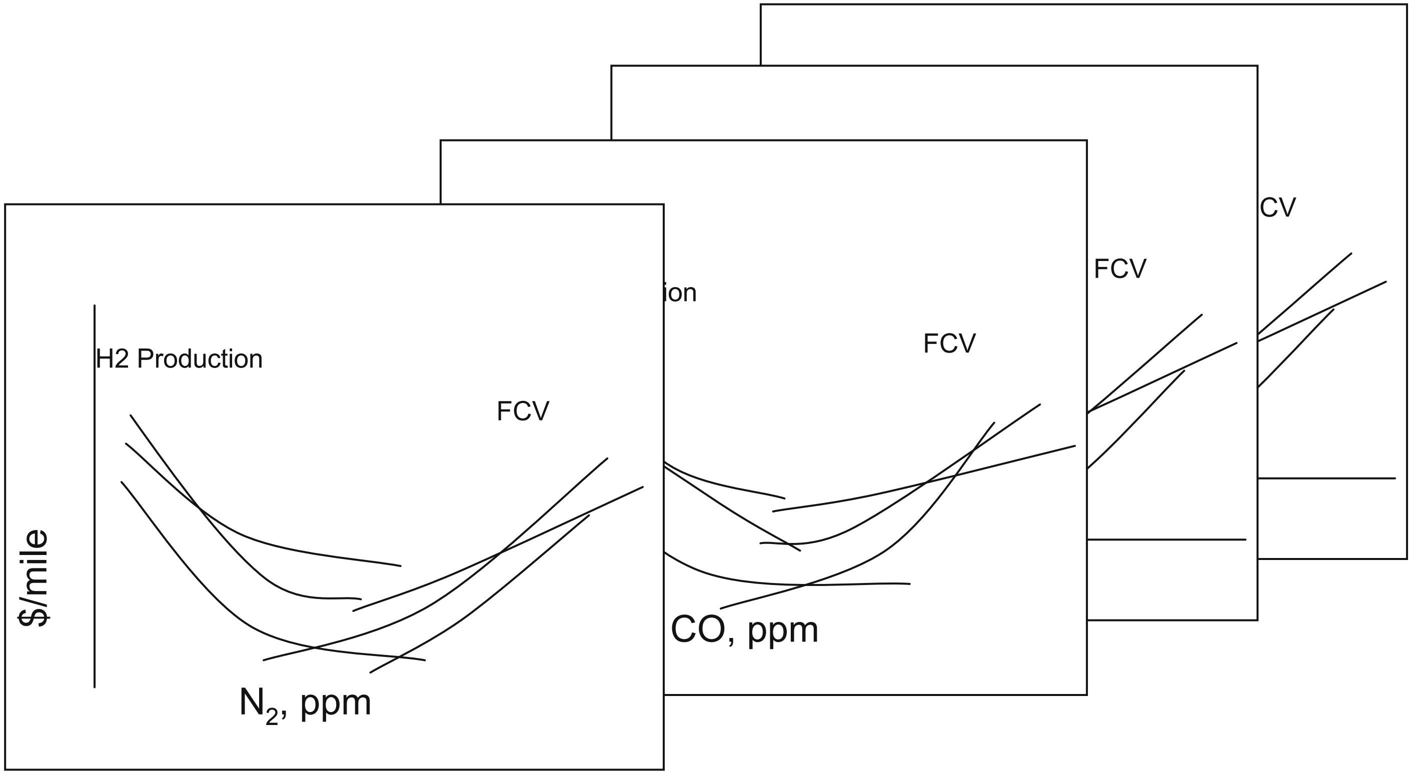
- PSA technology can achieve most of the H_2 impurity guidelines proposed by SAE / ISO, but it may add 5-20% to the cost of H_2
- PSA is ineffective for removing helium
- There are some contaminants for which PSA's effectiveness has not been reported (e.g., formic acid)
- The proposed levels for CO_2, O_2, and inert gases may be overly restrictive
- Testing and analysis may be a very significant cost factor, both for certification and for control of hydrogen quality

Draft Roadmap Recommendations (preliminary)

- If stringent quality specifications are necessary, need better quantification of the cost and performance of PSA vs. H_2 quality to determine life-cycle costs
- Need better quantification of the cost and performance of fuel cells, and the costs of overcoming the deleterious effects of specific contaminants
- Need low-cost methods for gas sampling and analysis for certification and on-line quality control (and fuel quality regulation enforcement)

Modeling and experimental data will be used to assess the impact of specific fuel impurities on life-cycle costs

- Study individual contaminants
- Evaluate potentially different effects for different production / purification and fuel cell operating conditions



The H2A spreadsheet generates the cost of hydrogen

- Based on options / assumptions available in H2A

- The current H2A model does not reflect sensitivity to hydrogen quality
  - Add effects of hydrogen recovery and process efficiencies

- Component models are being developed to support the H2A
  - Argonne is modeling a steam reformer + PSA process
  - Results will be incorporated into H2A
    - *Look-up tables*
    - *Interface with component module*

- End Result
  - Cost of hydrogen (trend) = f (Process pathway, conditions, efficiency, contaminant level, etc.)

Held a hydrogen quality modeling workshop at Argonne on August 30-31, 2007

- Purpose: to describe models being developed for hydrogen purification by pressure-swing adsorption, PSA (and to assess impurity effects on fuel cell performance and durability)
  - Describe the significant components and processes in the models
  - Provide details of input parameters
    - *Sensitivity of output results to input parameters*
  - Define data needed to validate / refine models
    - *Unfortunately, only limited experimental activity in the literature*
  - Work with other modelers, experimentalists, and the fuels industry (including efforts sponsored by NEDO in Japan)

Hydrogen purification drivers (PSA)

Species	Adsorption Force	ISO TC 197 WG 12 (14687) Draft Spec	ATR Mol %	Purification Ratio for ATR	SMR Mol %	Purification Ratio for SMR	OVERALL EFFECT
Helium (He)	Zero	100 ppm (total inert)	500 ppm	5	500 ppm	5	NOT POSSIBLE
Hydrogen (H2)	Weak	99.99%	40-45%		75-80%		Impacts PSA recovery & Capital Cost
Oxygen (O2)		5 ppm	50 ppm	10	-	-	Impacts PSA recovery & Capital Cost
Argon (Ar)		100 ppm (total inert)	500 ppm	5	500 ppm	5	Impacts PSA recovery & Capital Cost
Nitrogen (N2)		100 ppm (total inert)	34-38%	3800	1000 ppm	10	Impacts PSA recovery & Capital Cost
Carbon Monoxide (CO)		0.2 ppm	0.1 -1%	50000	0.1-4%	200000	Impacts PSA recovery & Capital Cost
Methane (CH4)		2 ppm (incl THC)	0.5 – 2%	10000	0.5 – 3%	15000	Impacts PSA recovery & Capital Cost
Carbon Dioxide (CO2)		2 ppm	15-17%	85000	15-18%	90000	Relatively easier to remove
Total HC's		2 ppm (incl CH4)	0.1 %	500	0.5%	2500	Relatively easier to remove
Ammonia	Strong	0.1 ppm	Low ppm		Low ppm		Relatively easier to remove
Total Sulfur	Strong	0.004 ppm					Relatively easier to remove
Halogenates	Strong	0.05 ppm					Relatively easier to remove
Water (H2O)	Strong	5 ppm	Dew Point		Dew Point		Relatively easier to remove

DOE H2QWG Draft Roadmap. Courtesy, Bhaskar Balasubramanian (Chevron)

Typical conditions and results for the SMR→WGS→PSA

- Plant size : 1,500 kg/day of H_2 leaving the WGS
- Steam-Methane-Reforming (SMR) + Water-Gas-Shift (WGS)
  - Steam / carbon molar ratio: 3 – 6
  - Pressure: 8-20 atm
  - SMR exit gas composition at equilibrium at 750°C
  - WGS exit gas composition at equilibrium at 435°C
  - Heat loss: 7% of fuel LHV
  - Water, helium not currently included in the PSA model
  - PSA beds operate isothermally

Natural Gas Composition	
CH_4	93.1 %
C_2H_6	3.2 %
C_3H_8	0.7 %
C_4H_{10}	0.4 %
CO_2	1.0 %
N_2	1.6 %

→ **Steam Reformer** →

Reformate Composition	
	S/C = 4
H_2	76.4 %-dry
CH_4	2.8 %-dry
CO_2	17.5 %-dry
CO	2.8 %-dry
N_2	0.4 %-dry
H_2S	100 ppmv

Typical 9-step cycle in PSA (in each sorbent bed)

Example, for a PSA feed at 8 atm

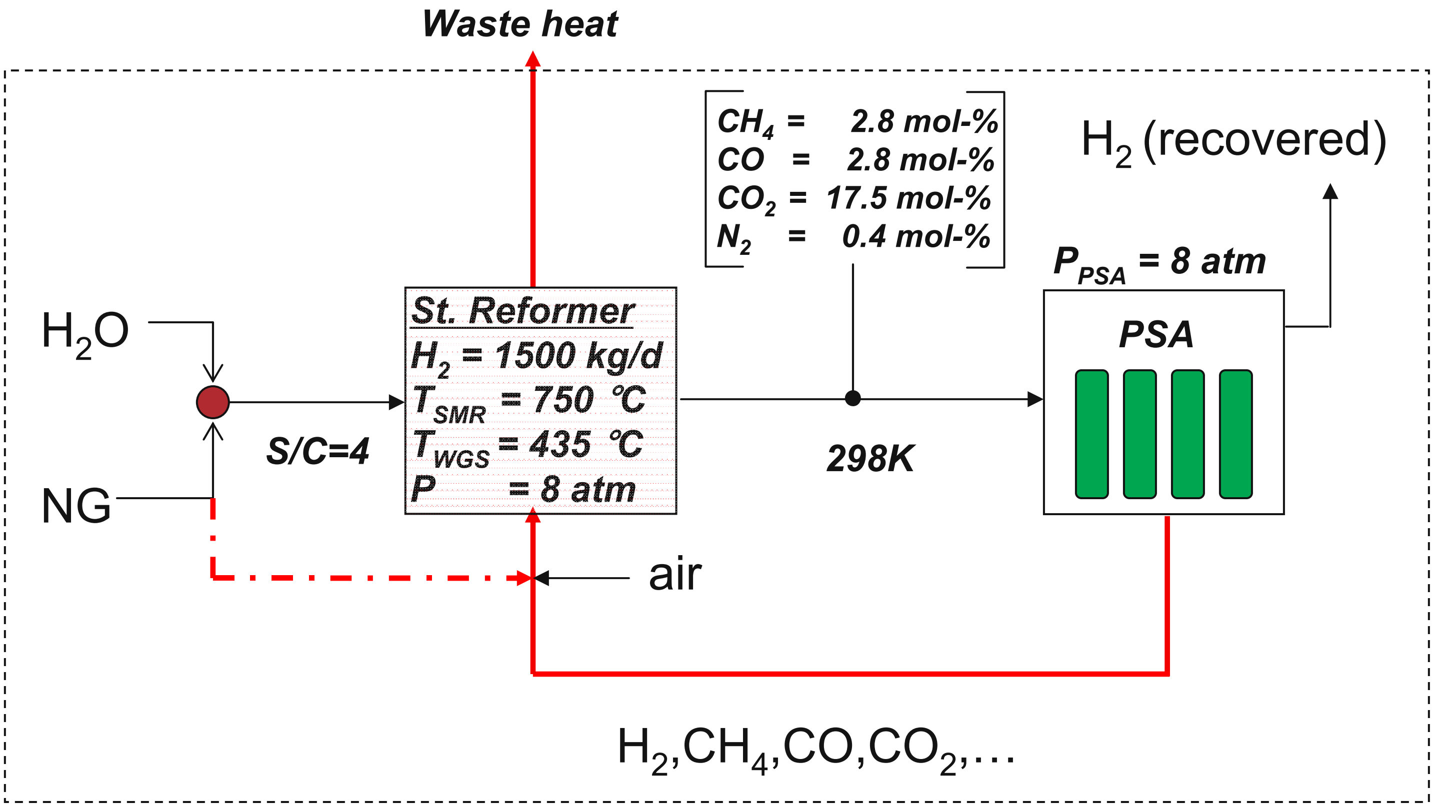
1. Adsorption, 240 s (Reformate in, unadsorbed H_2 product out, 8 atm)
2. Pressure equalization, 30 s (to 5.1 atm)
3. Co-current depressurization, 130 s (to 3.1 atm)
4. Pressure equalization, 30 s (to 2.2 atm)
5. Counter-current depressurization, 80 s (to 1.3 atm)
6. Purge, 130 s (at 1.3 atm)
7. Re-pressurization, 30 s (to 2.2 atm)
8. Re-pressurization, 30 s (to 5.1 atm)
9. Pressurize with product, 210 s (to 8 atm)

Unadsorbed gas, from step 1, is the product hydrogen stream

Tail Gas, from steps 5 and 6, goes to the SR burner

***Ind. Eng. Chem. Res.* 1994, 33,** 1600-1605.

The model calculates the PSA output and the efficiency of the SMR-based process

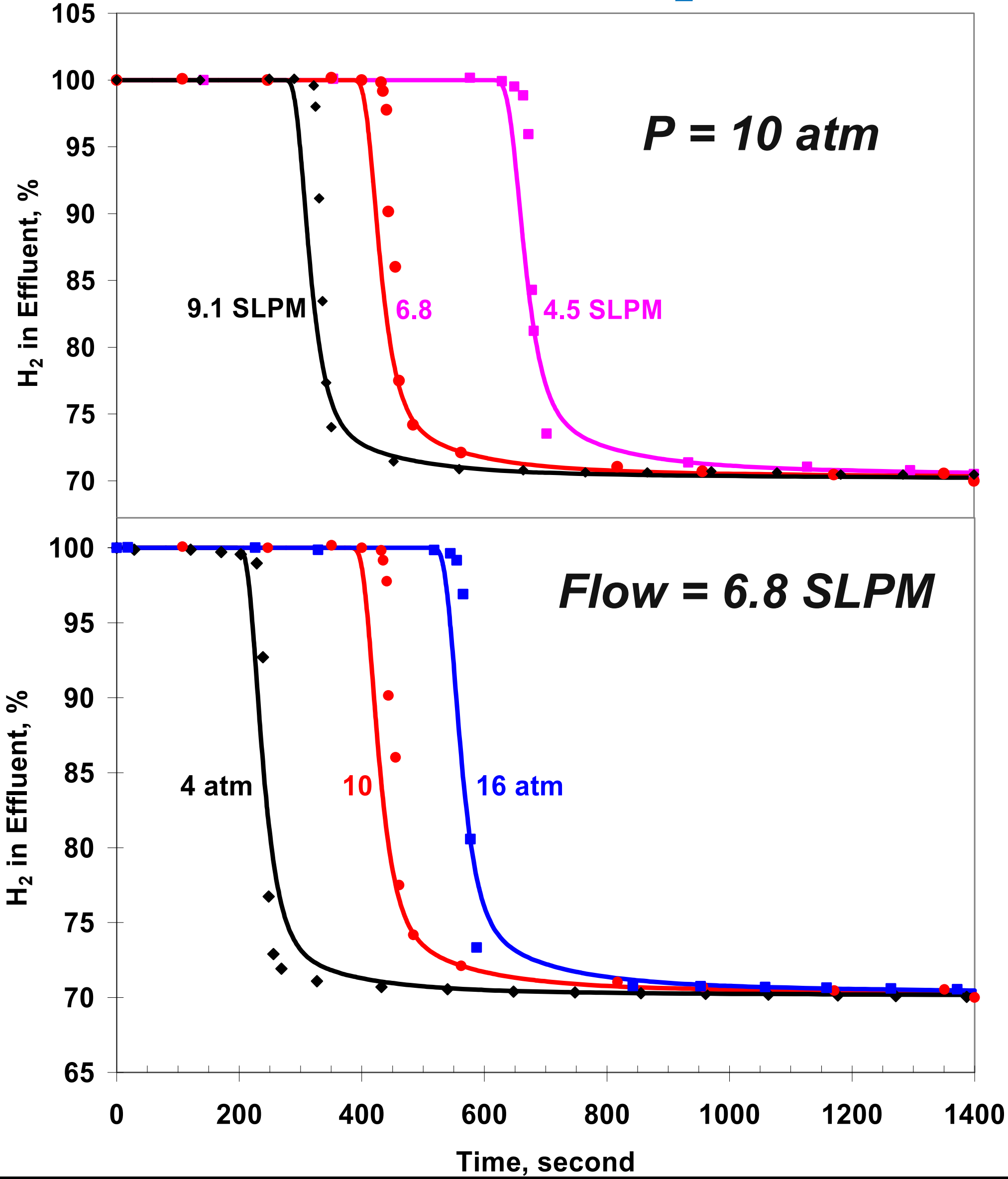


$$\text{Efficiency} = \frac{(\text{LHV of Recovered } H_2)}{(\text{LHV of NG})}$$

The base case conditions

Steam/Carbon	S/C	4	mol/mol
Steam Reformer Exit Temperature	T_{SR}	750°	C
WGS Exit Temperature	T_{WGS}	435°	C
Steam Reformer Pressure	P_{SR}	8.2	atm
PSA Pressure	P_{PSA}	8.2	atm
PSA Inlet Temperature	T_{PSA}	25	°C
Carbon / Zeolite Proportion		80 / 20	%

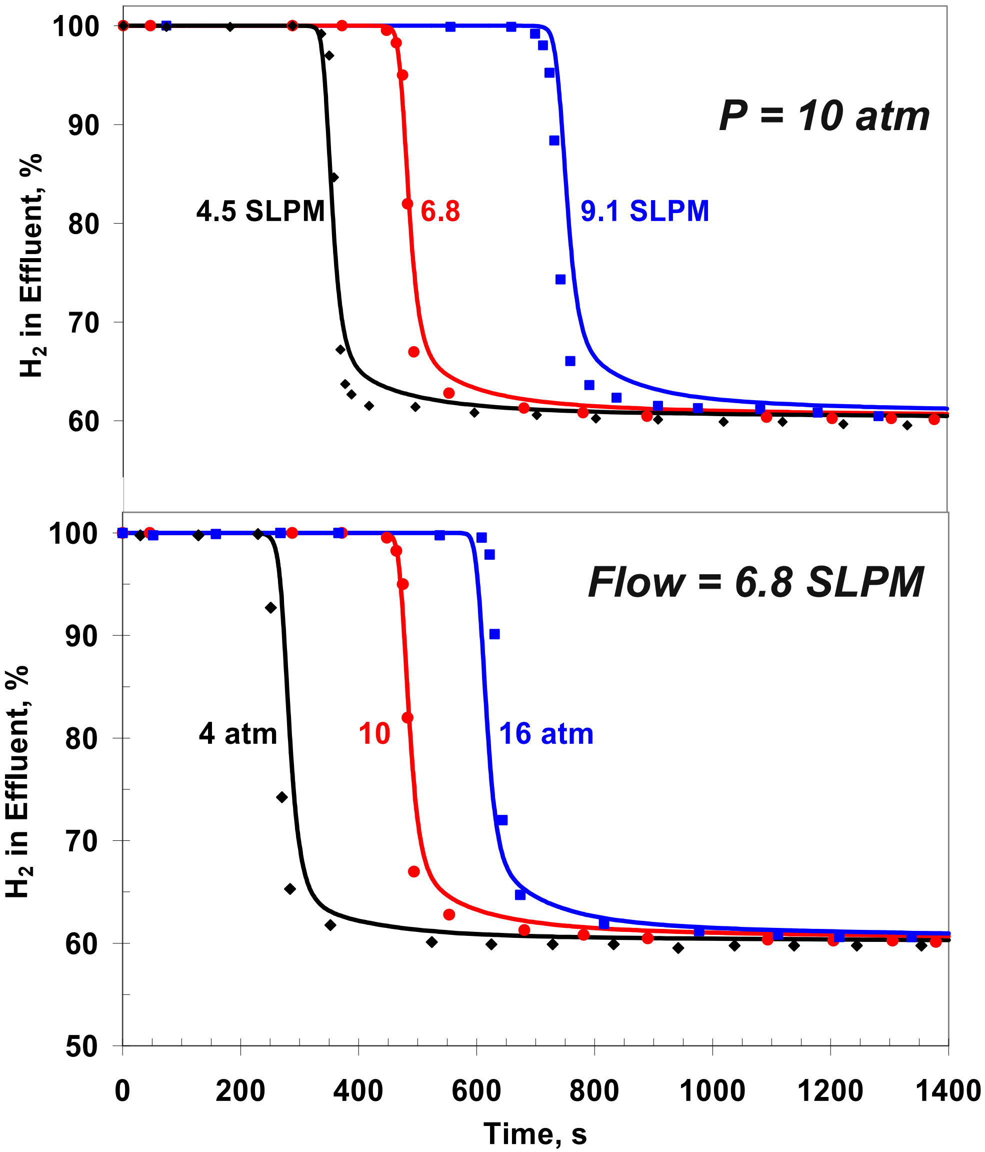
Model comparison: H_2/CO breakthrough (binary)



Parameter	Value
H_2	70 %
CO	30 %
$T_{ambient}$	26°C
Inlet T	26°C
Bed Length	100 cm
Bed Diameter	3.71 cm
Bed Volume	1.08 L
Carbon (PCB, Calgon)	50 cm
Size	0.23 cm
Zeolite (5A, Grace)	50 cm
Size	0.31 cm

Experimental data:
Jee et al. (2001), Ind. Eng. Chem. Res. 40, 868-878

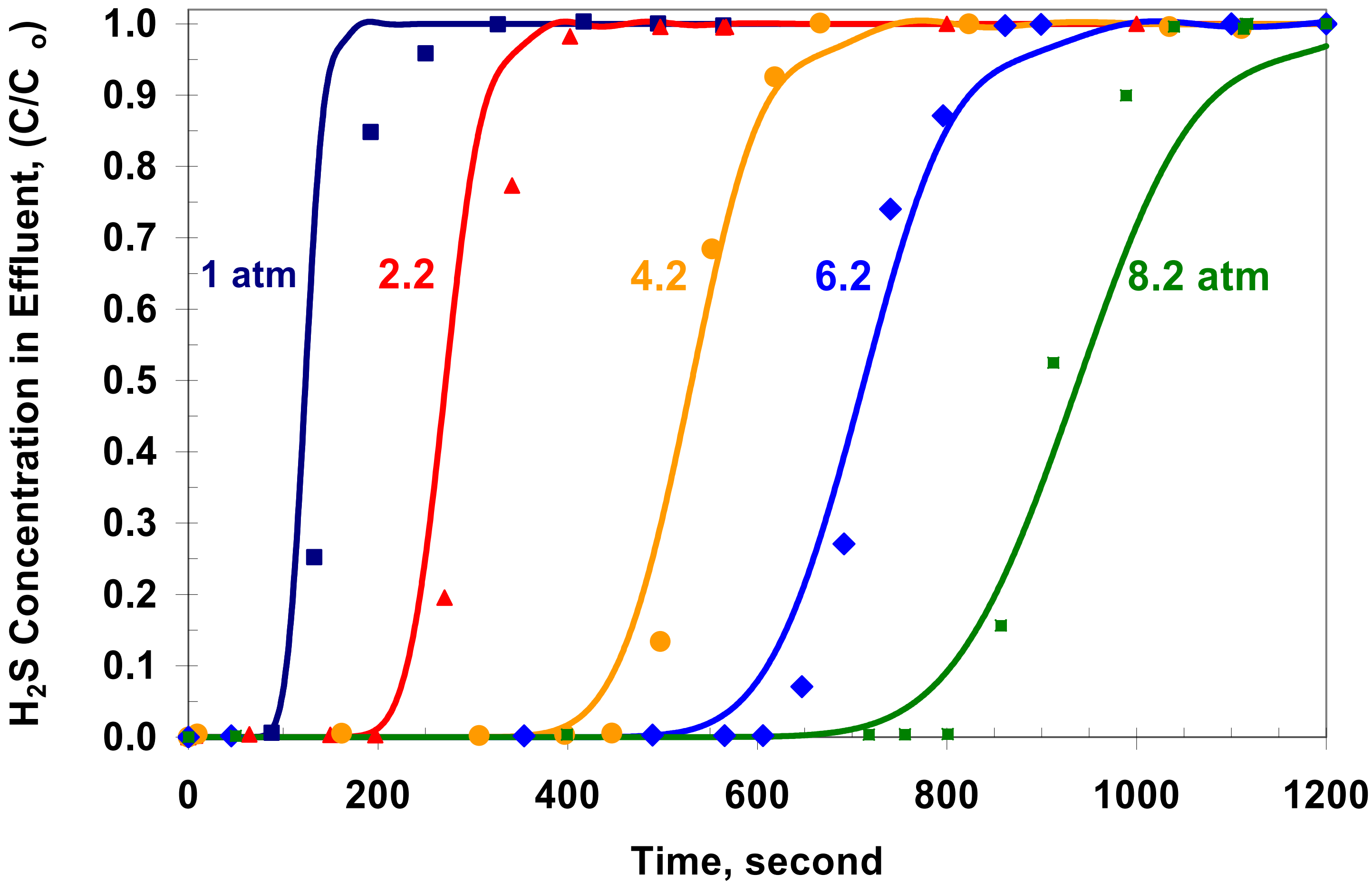
Model comparison: $H_2/CH_4/CO$ breakthrough (ternary)



Parameter	Value
H_2	60 %
CH_4	30
CO	10 %
$T_{ambient}$	26°C
Inlet T	26°C
Bed Length	100 cm
Bed Diameter	3.71 cm
Bed Volume	1.08 L
Carbon (PCB, Calgon)	50 cm
Size	0.23 cm
Zeolite (5A, Grace)	50 cm
Size	0.31 cm

Experimental data:
Jee et al. (2001), Ind. Eng. Chem. Res. 40, 868-878

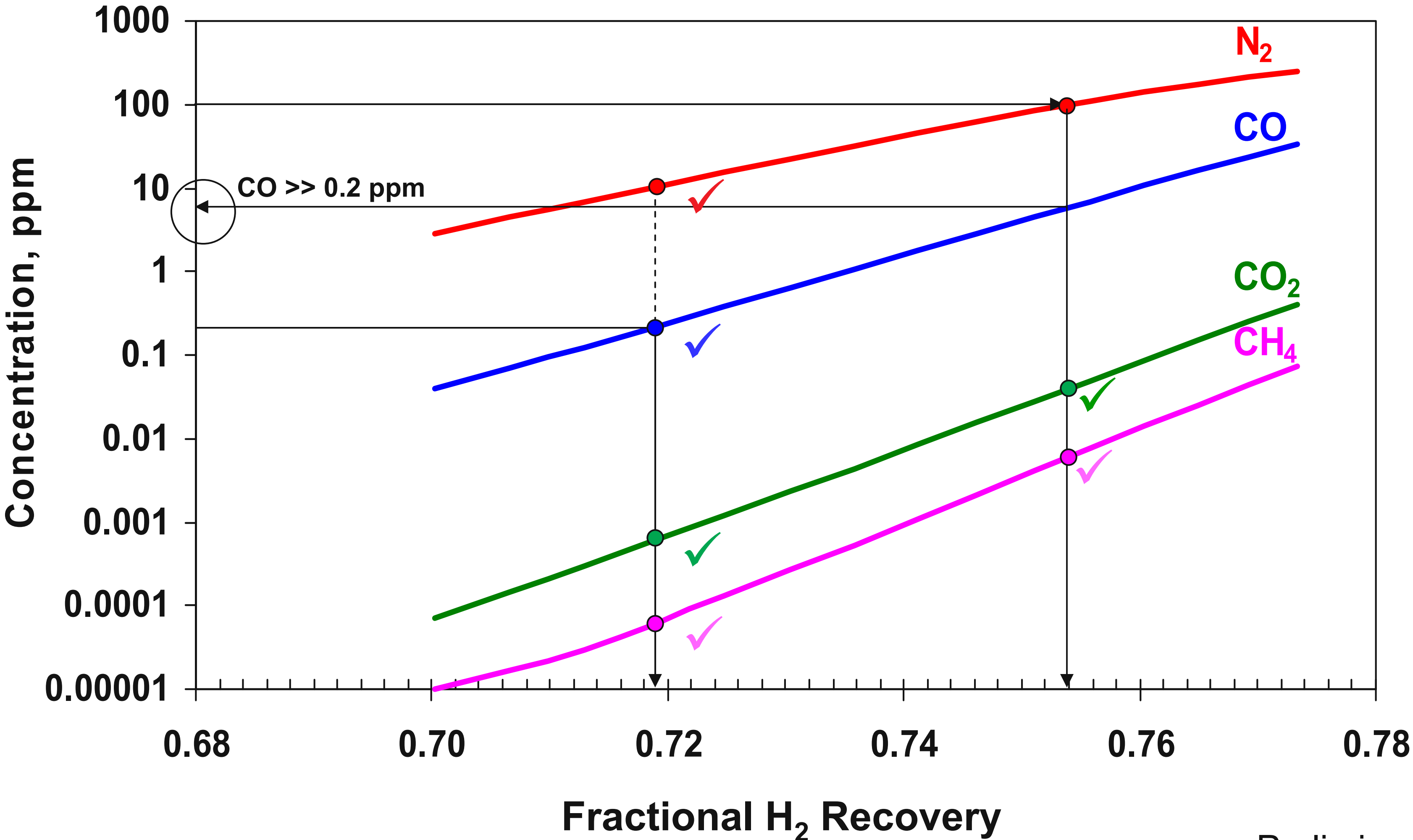
Model comparison: H_2S/CH_4 breakthrough curves (binary)



F = 0.4 SLPM
H_2S = 170 ppm
T = 290 K

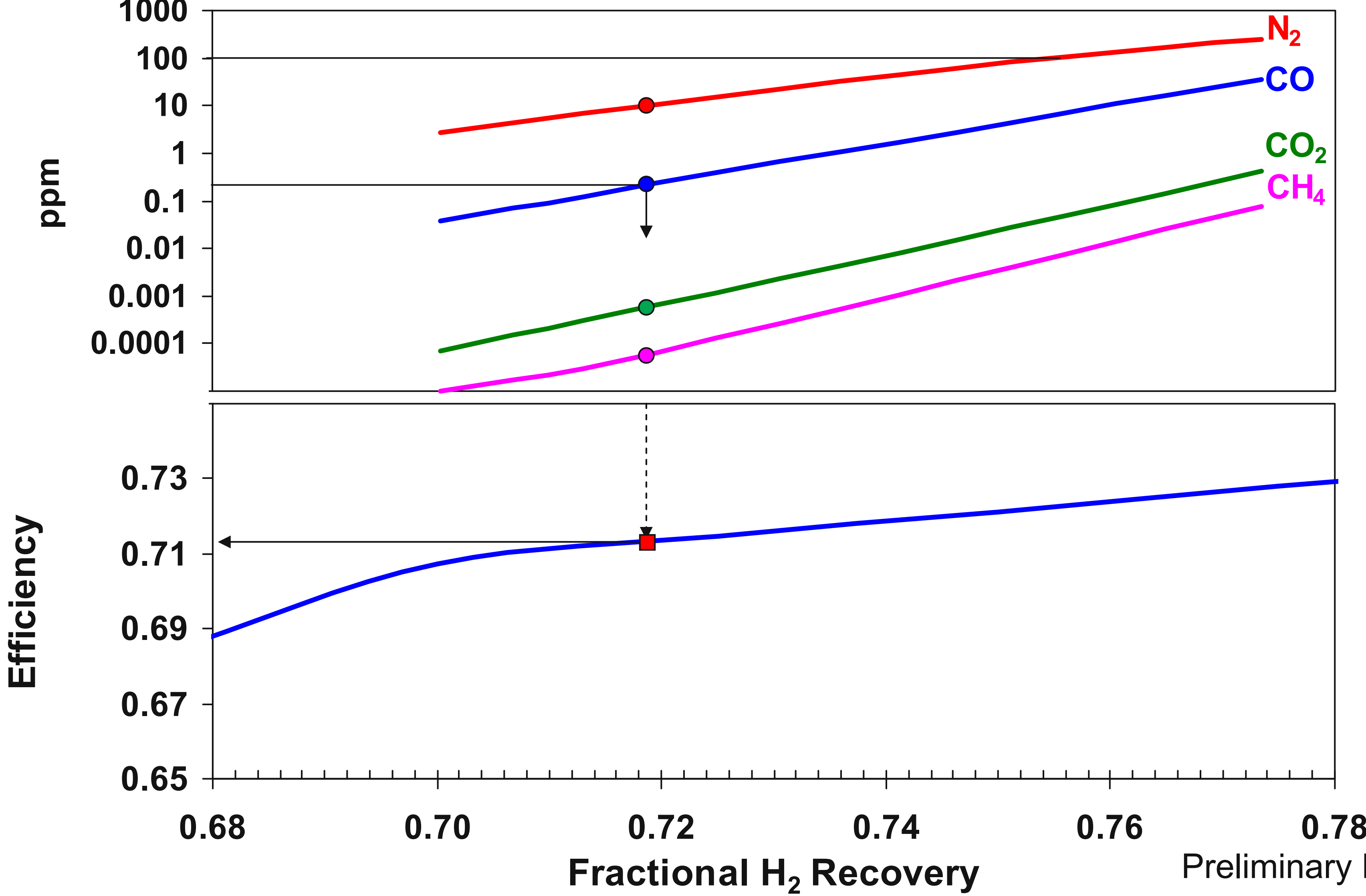
Experimental data:
Zhou et al. (2006), AIChE J. 52, 2066-2071

For the base case, a requirement of 0.2 ppm CO, rather than 100 ppm N_2, limits the hydrogen recovery fraction



Preliminary Data

For the base case assumptions and conditions, the model calculates a process efficiency of 72%



Preliminary Data

Status of PSA modeling and future work

- A model has been set up to correlate impurity concentration with hydrogen recovery and the production / purification efficiency

- Summary preliminary results
  - Guideline value for CO, rather than N_2 or other species, limits H_2 recovery fraction
  - Steam-to-carbon ratio in the SMR has a strong effect on efficiency, but not on H_2 recovery
  - SMR and PSA operating pressures significantly affect process efficiency

- Continued model development will include
  - Effect of moisture in reformate feed to PSA
  - Adiabatic beds
  - Sorbent types and proportions

- Additional worksheets have been developed in the DOE H2A model to include the effect of process efficiency on hydrogen production costs

Summary

- The H2QWG has prepared and submitted to DOE a draft roadmap for continuing activities to address issues of hydrogen quality for automotive fuel cell systems

- A PSA model is being developed to correlate specific contaminant levels in product H_2 to hydrogen recovery and process efficiency (for SMR/PSA pathway)
  - Preliminary cases examined for several species and design/ operating parameters and adding others
  - Mechanism developed to incorporate results into the H2A costing methodology (via process efficiency)
  - Currently seeking industrial input to help validate model and modeling approach