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DOE Hydrogen Program

Hydrogen Quality Issues for Fuel Cell Vehicles

DOE Hydrogen Quality Working Group: Activities and Progress

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Project ID # AN6

Overview

Timeline

- Project start date: FY 2006
- Project end date: Open
- Percent complete: N/A

Barriers

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

Budget

- Funding, FY 06: $425 K
- Funding, FY 07: $435 K

Partners/Collaborators

- OEMs, energy companies, National Laboratories
- Project management: Argonne

Objectives

- Develop a process to determine hydrogen quality requirements for fuel cell vehicles, based on life-cycle costs
  - identify how fuel quality influences the life-cycle costs of the various components of the overall "hydrogen system"
  - develop models to evaluate the effects of fuel quality on the costs of the hydrogen system components
- Identify information gaps and the R&D needed to fill those gaps (along with who/how best to conduct that R&D)

These objectives are being addressed by the DOE Hydrogen Quality Working Group (H2QWG)

Makeup of the H2QWG

- DOE Hydrogen Program's Technology Development Managers from the various teams:
  Fuel Cell, Hydrogen Storage, Production & Delivery, Systems Analysis, Codes & Standards, Cross-Cutting

- U. S. automobile companies and fuel cell developers:
  DaimlerChrysler, Ford, General Motors, UTC Power

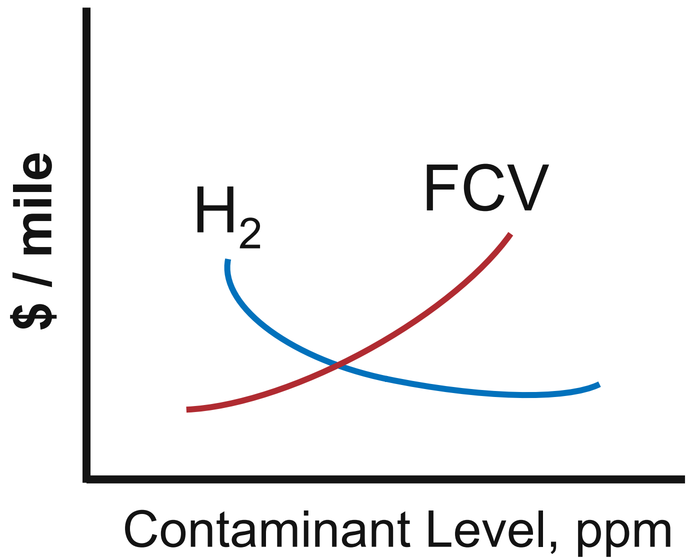
- Energy companies:
  BP, Chevron, ConocoPhillips, ExxonMobil, Shell

- National Laboratories
  Argonne, Los Alamos, National Renewable Energy Laboratory

  Argonne is helping to coordinate the activities of the H2QWG

Approach

- Develop a process based on the cost and energy usage over the life-cycle of the FCV
  - assess influence of fuel quality on various components of the "hydrogen system"
    - *production*
    - *purification*
    - *use in fuel cells*
    - *analysis and quality verification.*
  - develop models to quantify life-cycle costs of hydrogen system components.
  - estimate the relationships between the impurity level and the $/mile or some similar cost measure

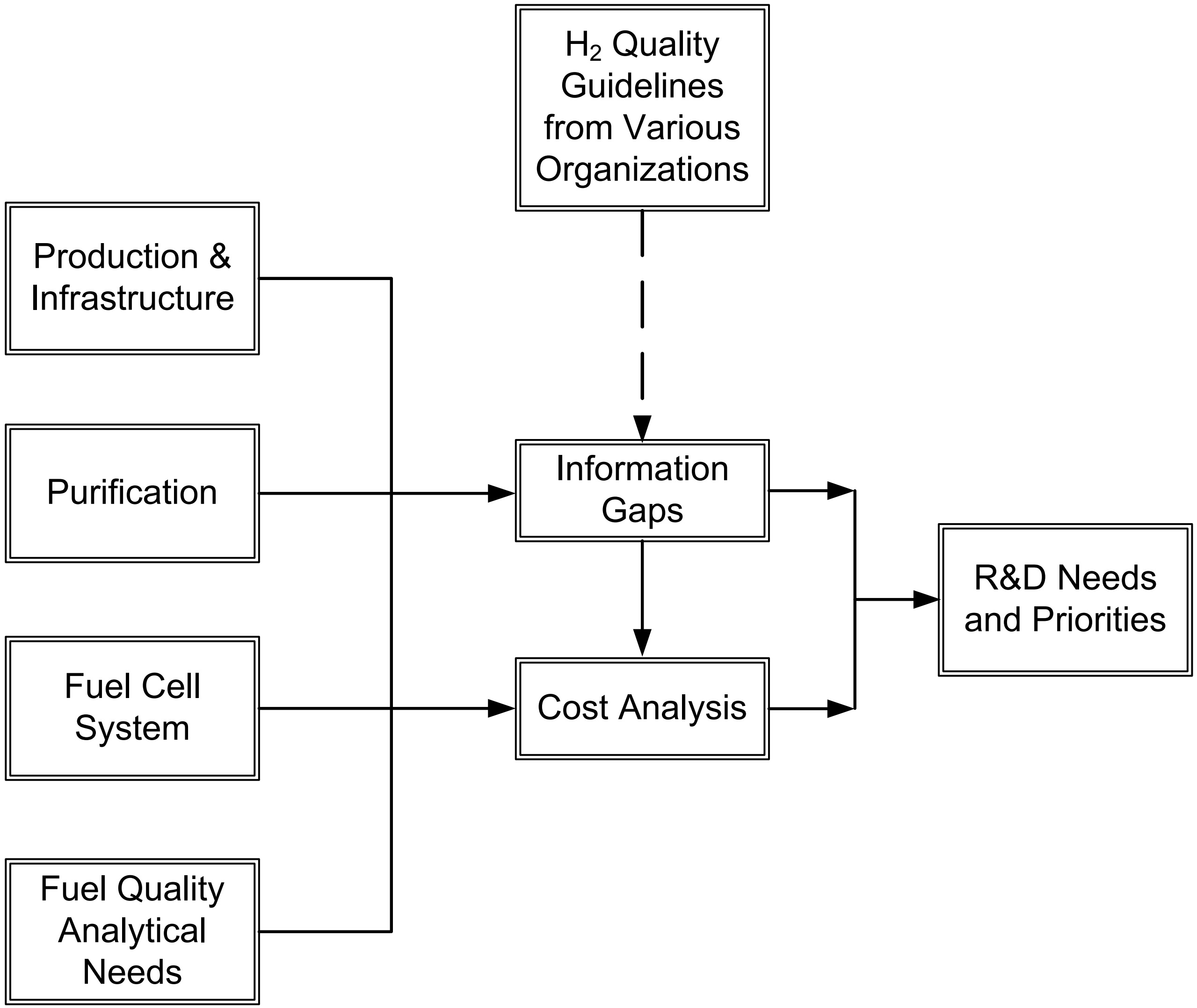


- Develop a roadmap for the process

H2QWG activities include roadmap development, information gathering, and modeling

- Developed an initial “Framework” document to help define the work of the Group
- Held in-person meetings, 3 to 4 times a year, along with interim discussions by e-mail, telephone, etc.
- Focused on different issues at the different meetings, with input on specific issues by experts in the field
  - defined the scope of the problem and the scope of H2QWG activities
  - obtained input from fuel cell developers, gas suppliers, etc.
  - obtained input on gas analysis technologies, corresponding ASTM activities, costing methodologies
- Initiated a database on critically assessed relevant published literature
- Worked with model developers at Argonne and other organizations to help develop and validate performance and life-cycle cost models
- Provided frequent briefings and updates to various Tech Teams, others

Aim of the activities is to identify information gaps and develop cost analyses for the four components



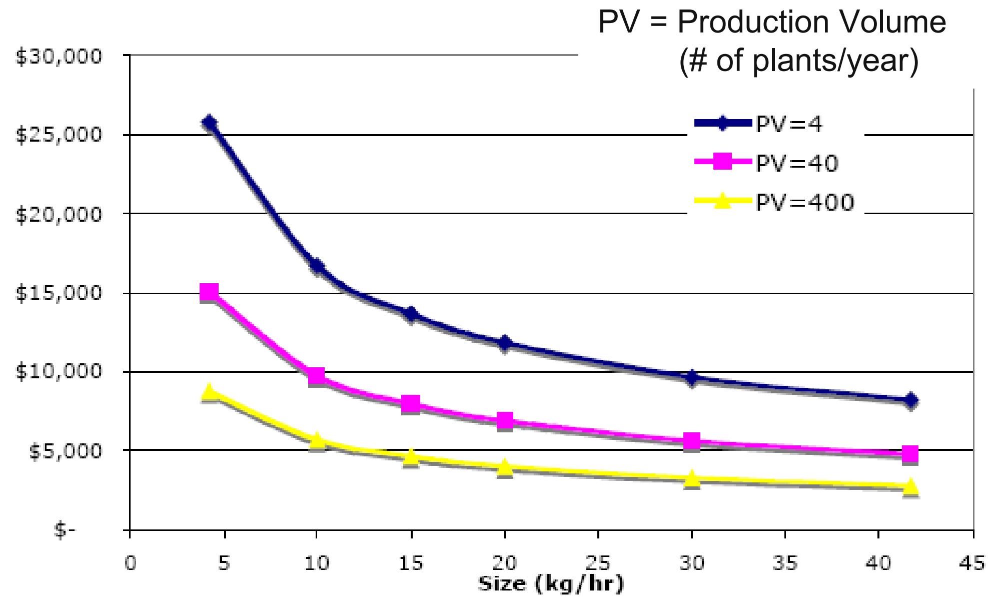
The focus is on the near- to mid-term (to 2015)

- 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

Example:
Costs for SMR production and PSA purification

- Production by SMR
  - at 600,000 kg/day, H_2 cost is $1/kg
  - at 1,500 kg/day, H_2 cost is $2/kg
  - at 100 kg/day, H_2 cost range is $3.50 to $9.40/kg

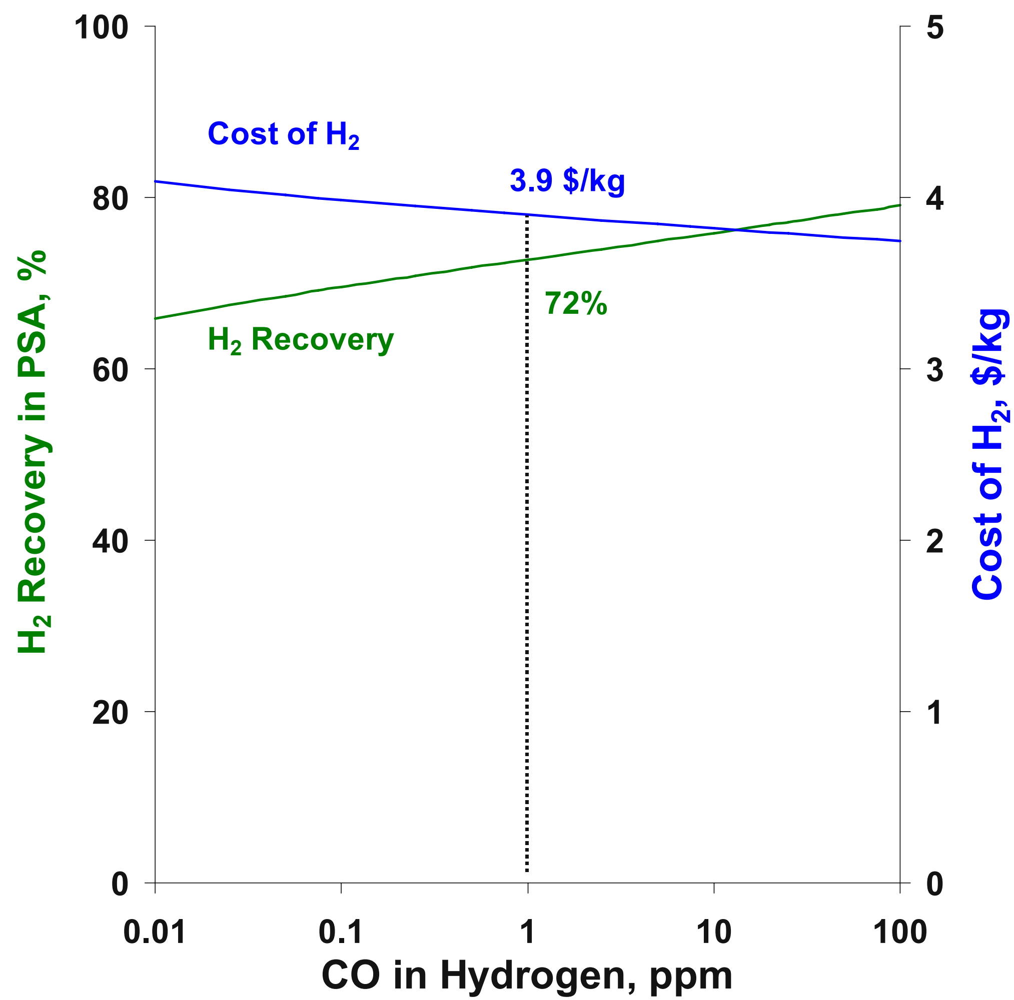
- Purification by PSA
  - may add ~ 5-20% to cost of H_2
  - PSA cost = f(H_2 recovery, scale, process parameters, reformate composition,...)
  - H_2 recovery is sensitive to $O_2 > N_2 >> CH_4 > CO$
  - At smaller capacities, recovery fraction has a proportionately larger impact on operating and life-cycle costs



Courtesy : D. Papadias

Progress & Accomplishments
Modeling the SMR/PSA production/purification path

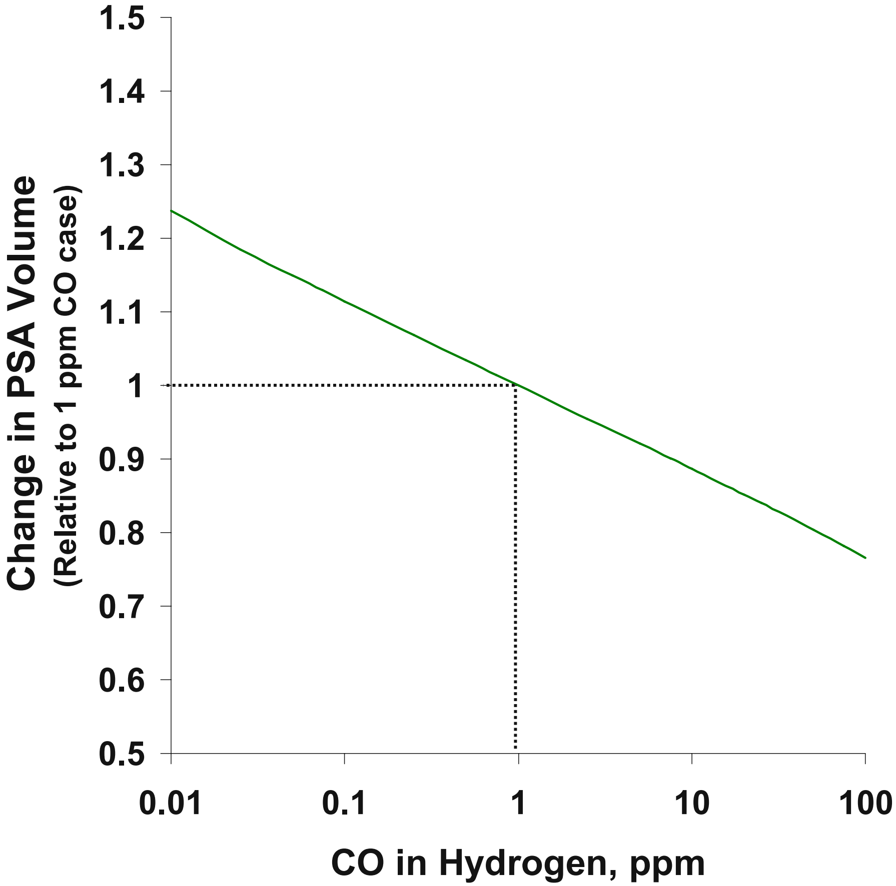
- The modeled system includes
  - S/C in reformer = 3.0
  - Reformate enters PSA with concentrations corresponding to equilibrium at 435°C
  - PSA removes CO, CO_2, CH_4, H_2S with activated carbon bed
  - Four bed system
  - Assumed parameters
    - *1000 kg/day*
    - *NG Cost – 7 \$/GJ*
    - *S/C = 3 (in reformer)*
    - *Pressures: Inlet = 150 psig*
  - Cost data from literature [1] assuming PSA outlet contained 10 ppm CO

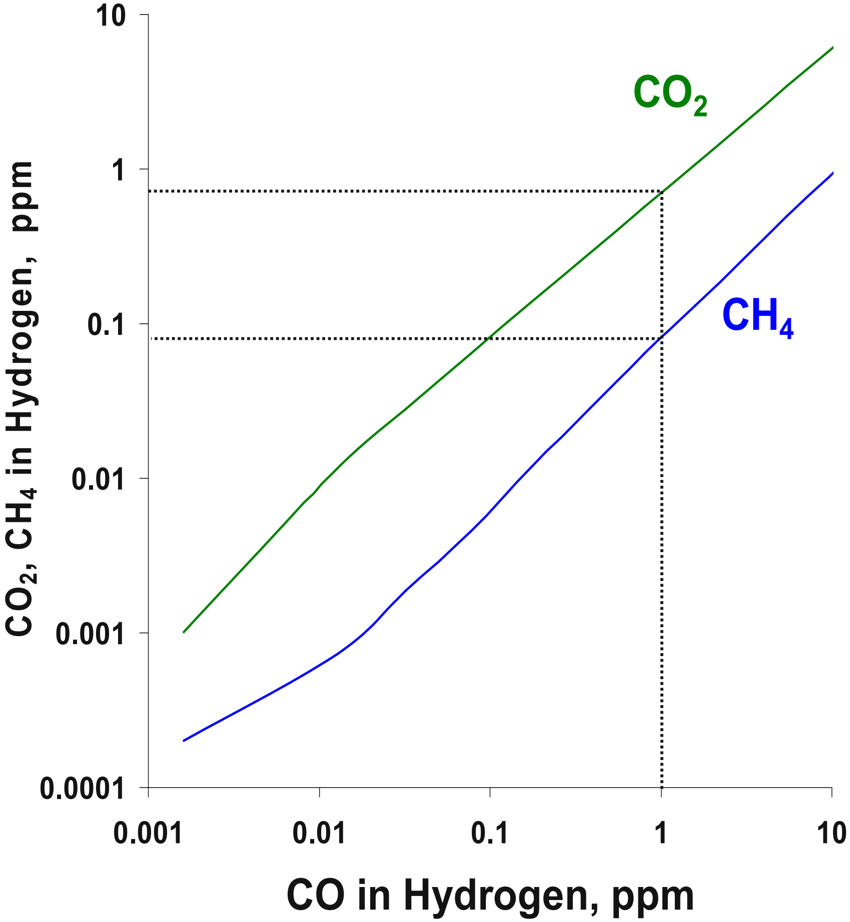


Courtesy : D. Papadias

[1] Weinert, J., "A Near-term Economic Analysis of Hydrogen Fueling Stations," MS Thesis, U. of California, Davis, 2005.

Progress & Accomplishments
The PSA model shows that bed volume increases with tighter CO specifications





Courtesy : D. Papadias

Progress & Accomplishments
The PSA model has been expanded to include

- Nitrogen in the list of impurities (CH_4, CO, CO_2, N_2)
  The inclusion of N_2 will impact the cost (PSA unit, … , cost of H_2)
- Multi-bed capability (carbon + zeolite beds)
- Effect of H_2 adsorption on adsorbents
- Enthalpy balance (adsorbent + PSA wall + heat losses)

Summary of H2QWG activities and accomplishments

- Pulled together key stakeholder groups: government, OEMs, fuel cell developers, energy companies, national laboratories
- Met with industrial gas suppliers, gas purification vendors, and others, to begin gathering information on hydrogen purification costs
- Reviewed literature and helped develop models for fuel cell performance degradation due to type and concentration of hydrogen contaminants
- Prepared a comprehensive draft Roadmap; the appendices contain species-specific discussions on test data, effects on fuel cell performance and durability, effectiveness of H_2 purification methods, modeling, and R&D needs

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)

Future work

- Discuss and recommend R&D needs, priorities, processes, and time-frame
- Enable exchange and dissemination of technical information to DOE and stakeholders (e.g., species summaries, database, etc.)
- Compare model results (performance, cost) with industrial data / experience to assess information gaps
- Identify the key impact factors (cost, energy) in the “hydrogen system” from model results and industry experience
- Review developments and their impact on hydrogen quality decisions
  - fuel cell performance, engineering mitigation options
  - process and purification options
  - analytical methods
- Finalize Roadmap and support DOE projects towards improved models and experimental methods

Additional Slides

Roster of the H2QWG

DOE Hydrogen Program

Active Members		
Ahmed	Shabbir	ANL
Anderson	Arlene	DOE/EE
Arbuckle	Sheral	Ford
Balasubramanian	Bhaskar	CTX
Casey	Edward	ConocoPhillips
Collins	William	UTCPower
Davis	Pat	DOE/EE
Devlin	Pete	DOE/EE
Duffy	Michael	NREL
Garland	Nancy	DOE/EE
Garland	Roxanne	DOE/EE
Garzon	Fernando	LANL
Gupta	Nikunj	Shell
Joseck	Fred	DOE/EE
Kumar	Romesh	ANL
Manheim	Amy	DOE/EE
Milliken	JoAnn	DOE/EE
Mitchell	George	DCX
Ohi	Jim	NREL
Gregoire Padro	Catherine	LANL
Paster	Mark	DOE/EE
Rockward	Tommy	LANL
Satyapal	Sunita	DOE/EE
Simnick	Jim	BP
Steele	Mike	GM
Stetson	Ned	DOE/EE
Stroh	Ken	LANL
Thomas	George	EE
Gromis	Adam	CaFCP

For Information (Tech Team Co-Leads, BPG,		
Austgen	Dave	Shell
Curry-Nikansah	Maria	BP
Freeman	Scott	DCX
Jorgensen	Scott	GM
Kaufman	Joe	ConocoPhillips
Parks	George	ConocoPhillips
Roessler	David	GM
Rogers	Jerry	GM
Schneider	Jesse	DCX
Smith	Brad	Shell
Tran	Doanh	DCX
Tunison	Gene	ExxonMobil
Watkins	Matt	ExxonMobil
Yoshida	Phyllis	DOE/EE
Zalesky	Rick	ChevronTexaco

Hydrogen purification drivers (PSA)

Courtesy: Balasubramanian, B., April 5, 2006, Washington DC

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 (H_2)	Weak	99.99%	40-45%		75-80%		Impacts PSA recovery & Capital Cost
Oxygen (O_2)		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 (N_2)		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 (CH_4)		2 ppm (incl THC)	0.5 – 2%	10000	0.5 – 3%	15000	Impacts PSA recovery & Capital Cost
Carbon Dioxide (CO_2)		2 ppm	15-17%	85000	15 -18%	90000	Relatively easy to remove
Total HC's		2 ppm (incl CH4)	0.1 %	500	0.5%	2500	Relatively easy to remove
Ammonia	Strong	0.1 ppm	Low ppm		Low ppm		Relatively easy to remove
Total Sulfur	Strong	0.004 ppm					Relatively easy to remove
Halogenates	Strong	0.05 ppm					Relatively easy to remove
Water (H_2O)	Strong	5 ppm	Dew Point		Dew Point		Relatively easy to remove

Progress & Accomplishments
Data are being sought from commercial sources for model validation

- For pressure swing adsorbers
  - H_2 recovery and H_2 cost = function (contaminant, level, plant capacity, P, …)

- For fuel cells
  - performance loss = function (contaminant, level, Pt loading, current density, T, P, duration of exposure, …)
  - cost both as fuel cell cost (including durability) and as additional hydrogen consumption cost

- For hydrogen quality verification
  - analysis cost = function (contaminant, detection limit, type and frequency of analysis,...)