Fuel Quality Impacts on Hydrogen Production, Purification and Use in Fuel Cell Automobiles

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Fred Joseck
U.S. DOE Hydrogen Program

D. Papadias, S. Ahmed, R. Kumar
Argonne National Laboratory

Outline

- Rationale
- Objectives and Approach
- Distributed SMR/PSA Hydrogen Production Pathway
- Preliminary results of modeling and analysis
  - Sensitivity to various design and operating parameters and to variations in natural gas compositions
  - Effects of impurity specifications on per kg and life-cycle costs of hydrogen for fuel cell vehicles
  - Additional costs of hydrogen analysis and quality verification
- Summary

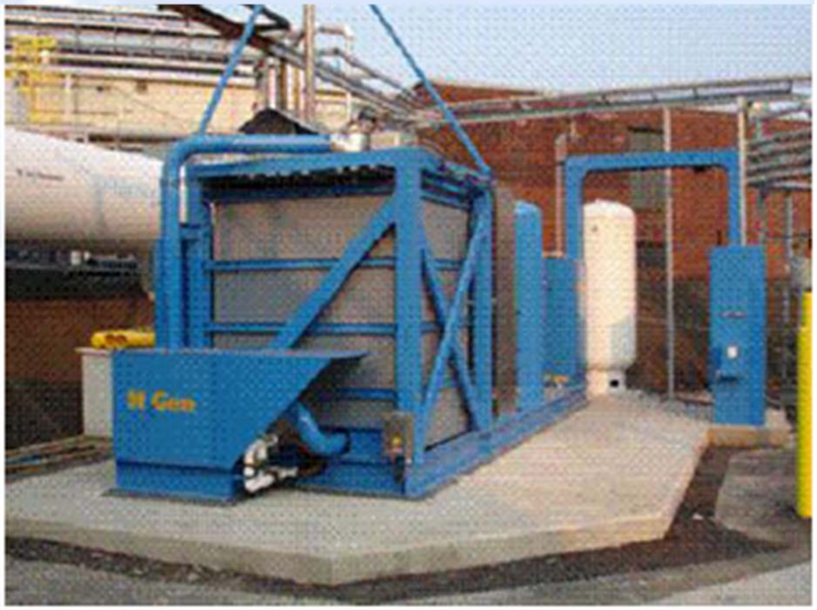
Rationale – Fuel Quality can Affect the Cost and Durability of the Fuel Cell Vehicle

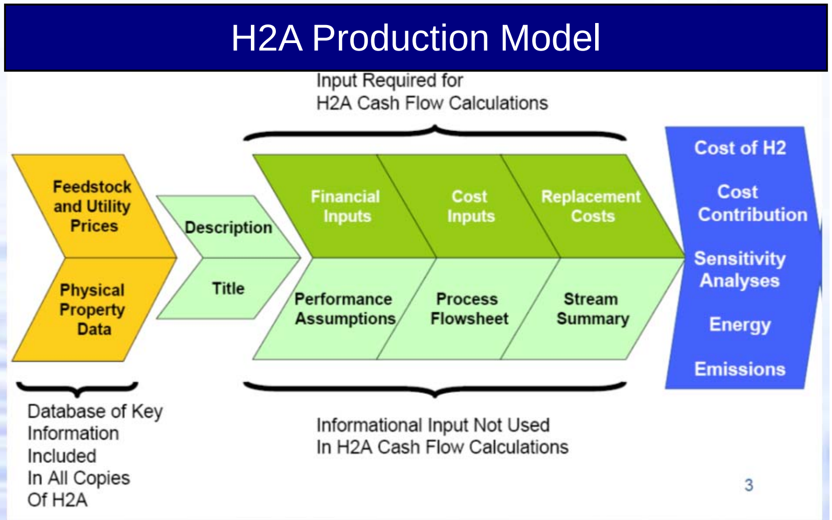
- Impurities in the fuel hydrogen will diminish fuel cell performance
  - Some cause irreversible damage
- The types and levels of impurity in hydrogen depend on the hydrogen production pathway
- Natural gas (NG) is the most likely source of hydrogen for fuel cell vehicles (FCV) in the *near-term*
- Developing fuel quality standards can benefit from establishing quantitative relationships between the levels of impurity species and
  - life-cycle cost of fuel hydrogen
  - life-cycle cost of the vehicle fuel cell

Objectives and Approach

- Predict impurity levels in hydrogen
  - produced from the steam reforming of natural gas (SMR)
  - purified by pressure swing adsorption (PSA)
  - as a function of fuel quality and process parameters

- Assess the sensitivity of the cost of hydrogen to impurity levels
  - process model for technical evaluation
  - H2A model for effects on costs




H2A Production Model

Input Required for
H2A Cash Flow Calculations

Feedstock and Utility Prices

Physical Property Data

Description

Title

Financial Inputs

Cost Inputs

Replacement Costs

Performance Assumptions

Process Flowsheet

Stream Summary

Cost of H2

Cost Contribution

Sensitivity Analyses

Energy

Emissions

Database of Key
Information
Included
In All Copies
Of H2A

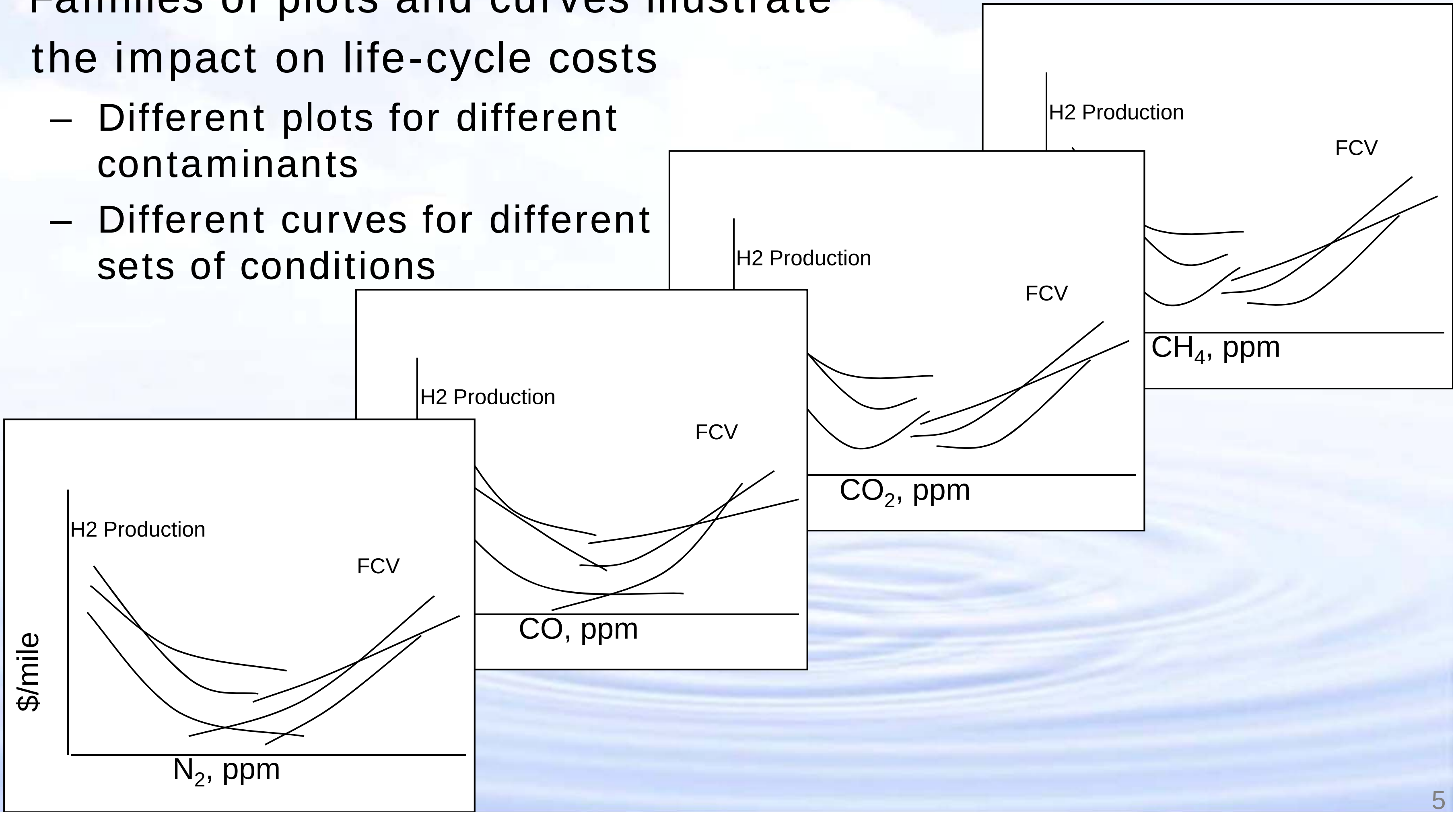
Informational Input Not Used
In H2A Cash Flow Calculations

3

Hydrogen Quality Impacts on Pathway Life-Cycle Costs

Different contaminants in the product hydrogen have different impacts on separation, fuel cell performance, and pathway life-cycle cost

- Families of plots and curves illustrate the impact on life-cycle costs
  - Different plots for different contaminants
  - Different curves for different sets of conditions



SAE Suggested Impurity Limits for FCV Hydrogen

Sulfur content in hydrogen for FCVs is the lowest of all contaminants

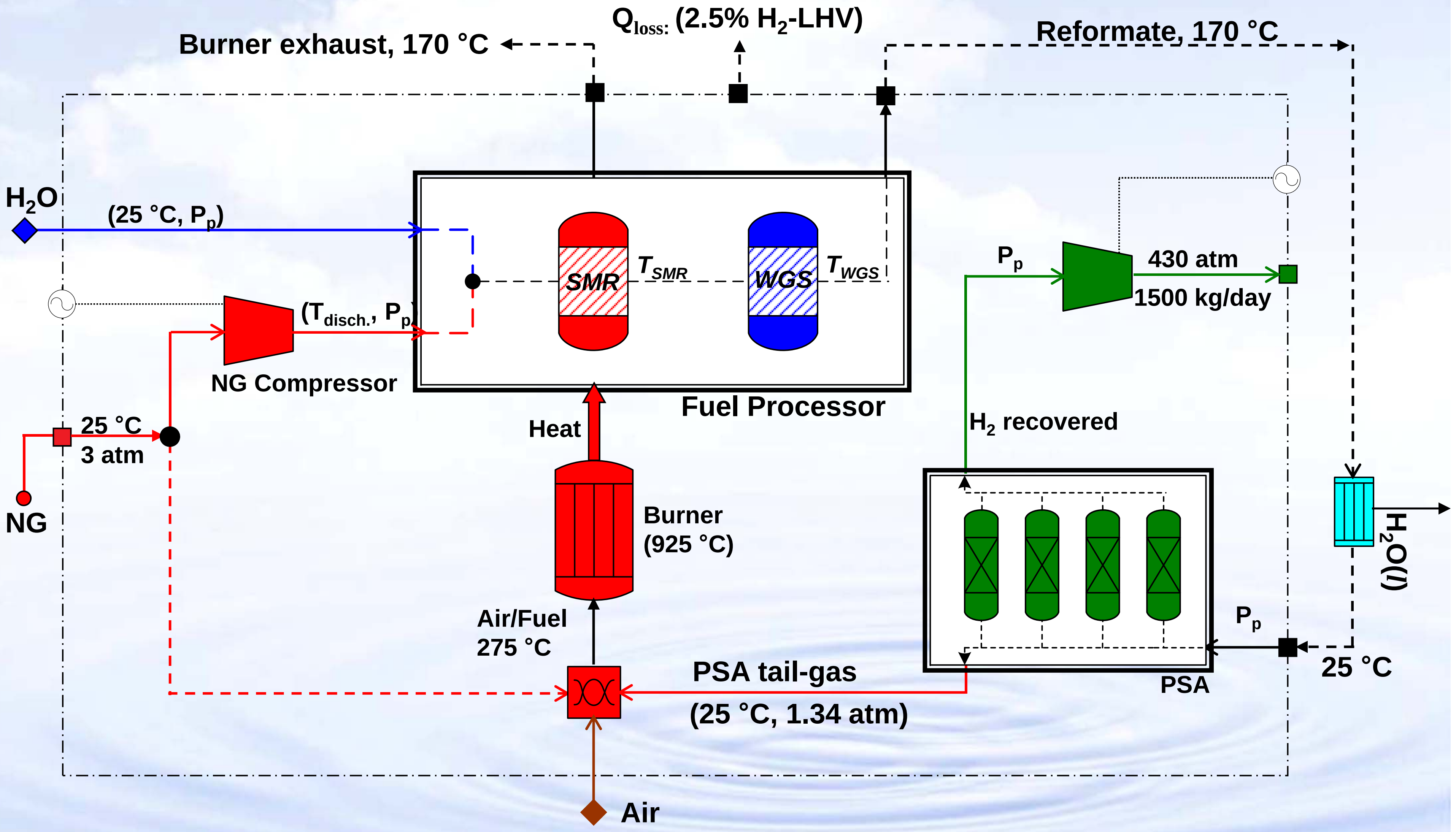
For the SMR-PSA hydrogen production pathway

- He in NG feedstock remains in product hydrogen
  - He is not removed by PSA
- N_2 (& Ar) present in NG
  - PSA can remove N_2 and Ar from reformate
- PSA can remove CO, CO_2, and CH_4, from reformate
- PSA is highly effective for removing S and NH_3

Suggested SAE Fuel Cell Hydrogen Quality	
Hydrogen, minimum	99.97 %
Impurities & Limits*	Maximum
Helium (He)	300 ppm
Nitrogen (N_2) + Argon (Ar)	100 ppm
Total Hydrocarbons (HC) (C_1 basis)	2 ppm
Carbon Dioxide (CO_2)	2 ppm
Carbon Monoxide (CO)	0.2 ppm
Ammonia (NH_3)	0.1 ppm
Sulfur (S, as H_2S, COS, etc.)	0.004 ppm

*Total impurities, excluding helium, must be less than 100 ppm.

Distributed SMR-PSA Hydrogen Pathway Process



Distributed SMR-PSA Process Model

Reference Case Assumptions

- Plant Size: **1,500 kg/day** of H_2 leaving the PSA unit
- Steam-Methane-Reforming (SMR) + Water-Gas-Shift (WGS)
  - Steam / Carbon Molar Ratio (S/C): **4**, range 3 – 6
  - Pressure : **8 atm (118 psia)**, range 8 - 22 atm (118 - 325 psia)
  - Gases exit SMR at equilibrium at **750°C**
  - Gases exit WGS at equilibrium at **435°C**
- PSA: Fixed cycle timing and number of beds

Average 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%

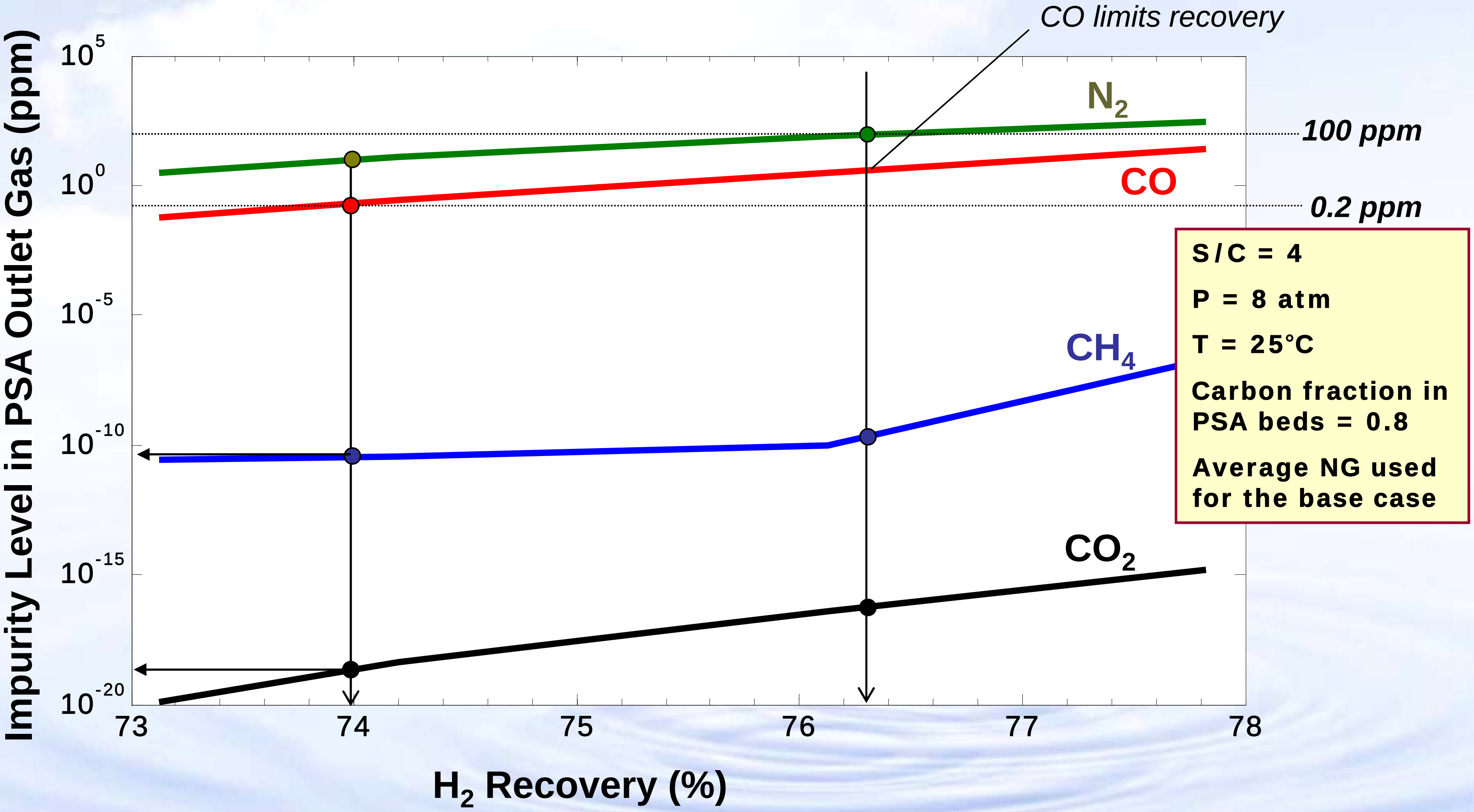
Steam Reformer/ Water-Gas Shift

Reformate Composition	
H_2	76.4%
CH_4	2.8%
CO_2	17.5%
CO	2.8%
N_2	0.4%
H_2S	100 ppm

Preliminary Data

Base Case: Meeting the Hydrogen Quality Specification

CO is the controlling contaminant in meeting the hydrogen specifications



S/C = 4

P = 8 atm

T = 25°C

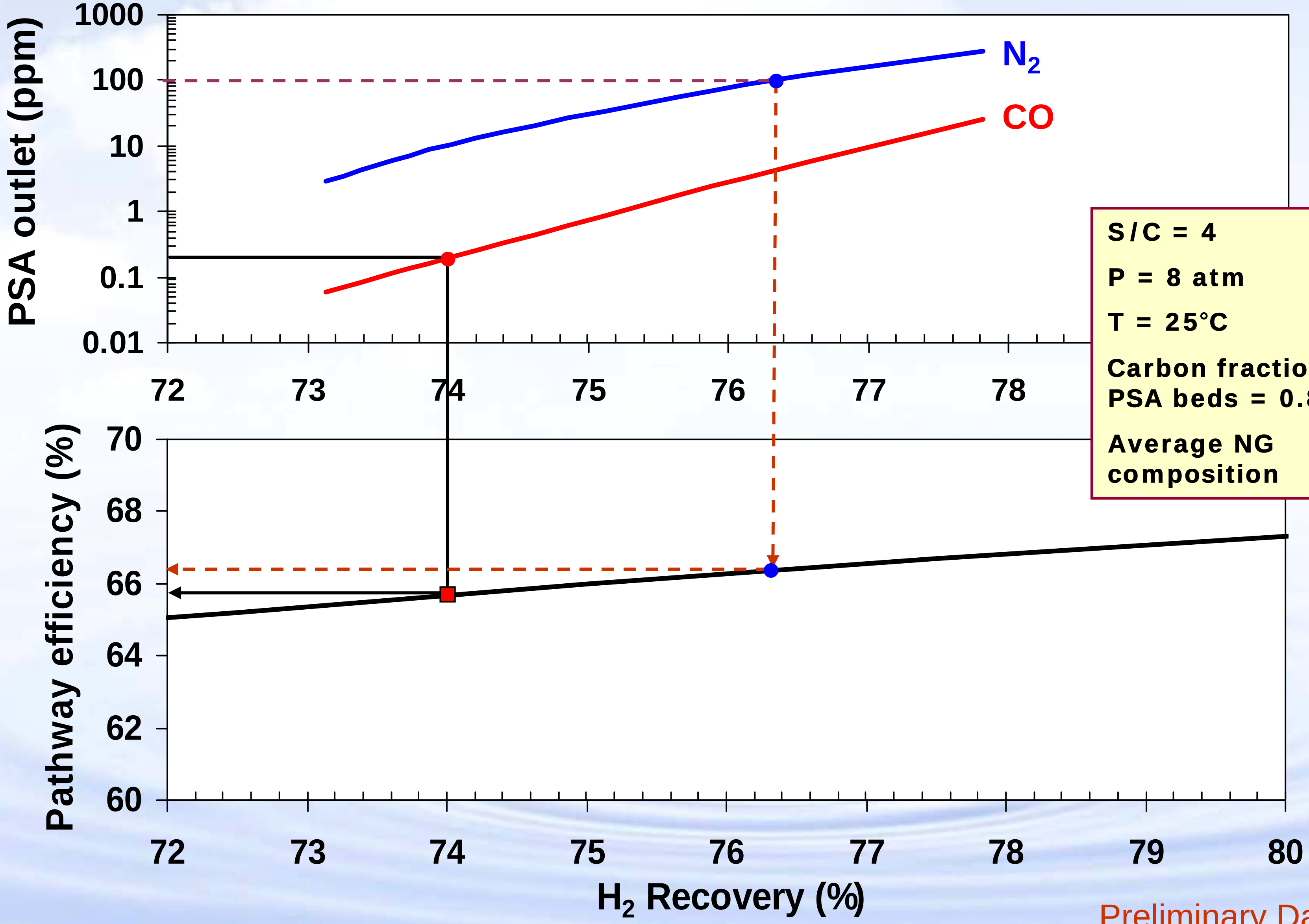
Carbon fraction in PSA beds = 0.8

Average NG used for the base case

Preliminary Data

Base Case: Meeting the CO Specification

CO specification of 0.2 ppm limits hydrogen recovery to 74%, pathway efficiency to 66%



S/C = 4

P = 8 atm

T = 25°C

Carbon fraction in PSA beds = 0.8

Average NG composition

Preliminary Data

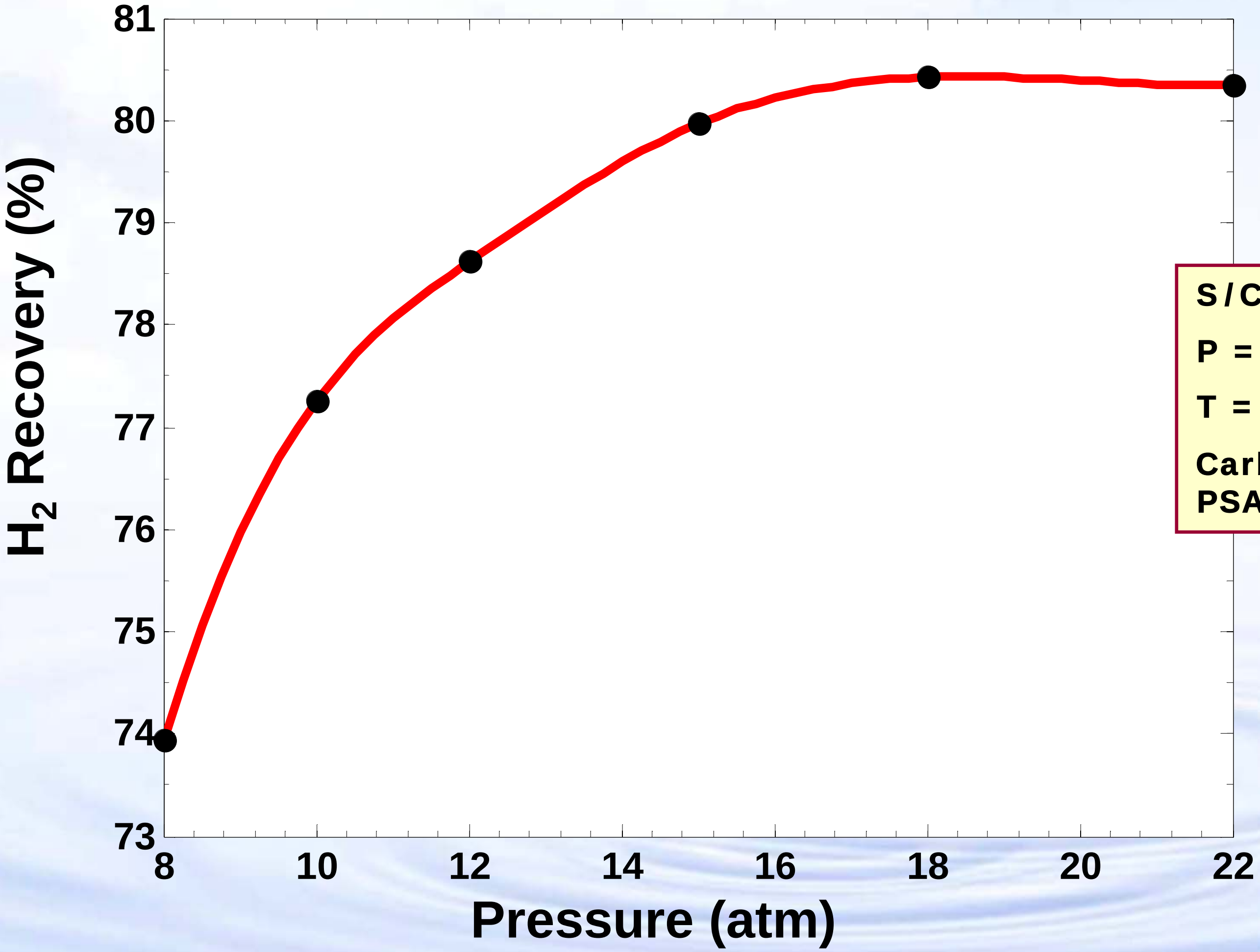
Impact of Distributed SMR Operating Pressure on Outlet Hydrogen Concentration

Increased SMR outlet pressure reduces the SMR outlet hydrogen content

Steam / Carbon, molar ratio	S/C	4		
Steam Reformer Exit Temperature, °C	T_{SR}	750		
WGS Exit Temperature, °C	T_{WGS}	435		
Steam Reformer Pressure, atm	P_{SR}	**8**	**15**	**22**
PSA Pressure, atm	P_{PSA}	**8**	**15**	**22**
PSA Inlet Temperature, °C	T_{PSA}	25		
Carbon in PSA Bed, fraction (balance is zeolite)		0.8		
Composition of Gas Entering PSA, %				
H_2		76.4	73.9	71.8
CH_4		2.8	6.0	8.7
CO_2		17.5	17.4	17.2
CO		2.8	2.3	1.9
N_2		0.36	0.39	0.43
H_2S		100	100	100

Impact of Operating Pressure on Hydrogen Recovery

Maintaining CO at 0.2 ppm, hydrogen recovery increases with increasing pressure to ~17 atm, and then decreases at higher pressures



S/C = 4

P = variable

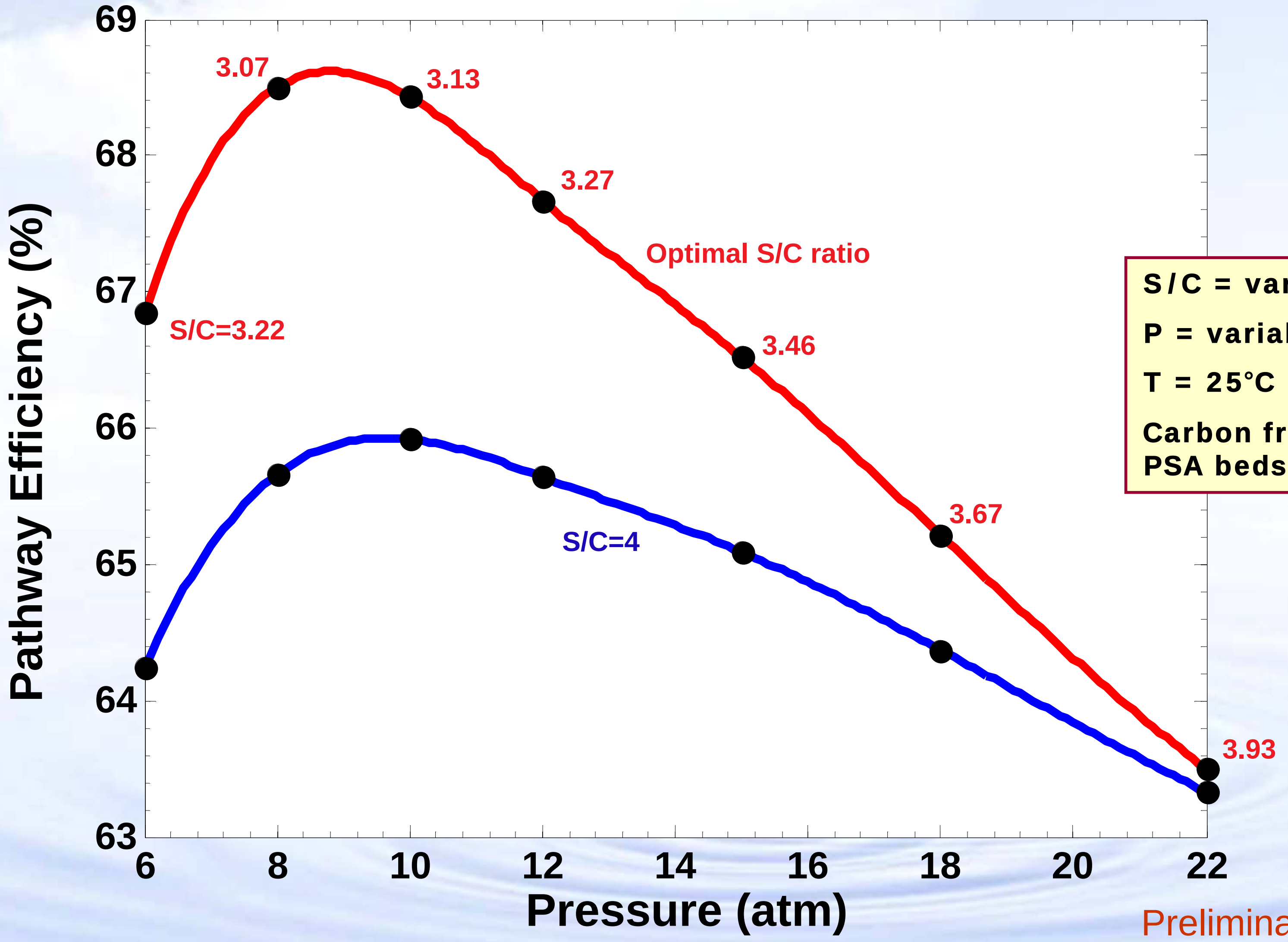
T = 25°C

Carbon fraction in PSA beds = 0.8

Preliminary Data

The SMR+PSA Pathway Efficiency vs. Pressure

Pathway efficiency reaches a maximum at a system pressure of 8-10 atm



S/C = variable

P = variable

T = 25°C

Carbon fraction in PSA beds = 0.8

Preliminary Data

Impact of Different Natural Gas Compositions on the Reformate Composition

Variation of natural gas composition (%)

Species	Mean	10th percentile*
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

*10% of NG may have these compositions or lower CH_4 and/or LHV

Blazek, C.F., Kinast, J.A. and Freeman, P.M., "Compressed natural gas measurement," A.G.A. Distribution/Transmission Conference, Orlando, FL, May 16-19, 1993.

Steam Reformer

P : 8 atm
S/C : 4
T_{SMR} : 750°C
T_{WGS} : 435°C

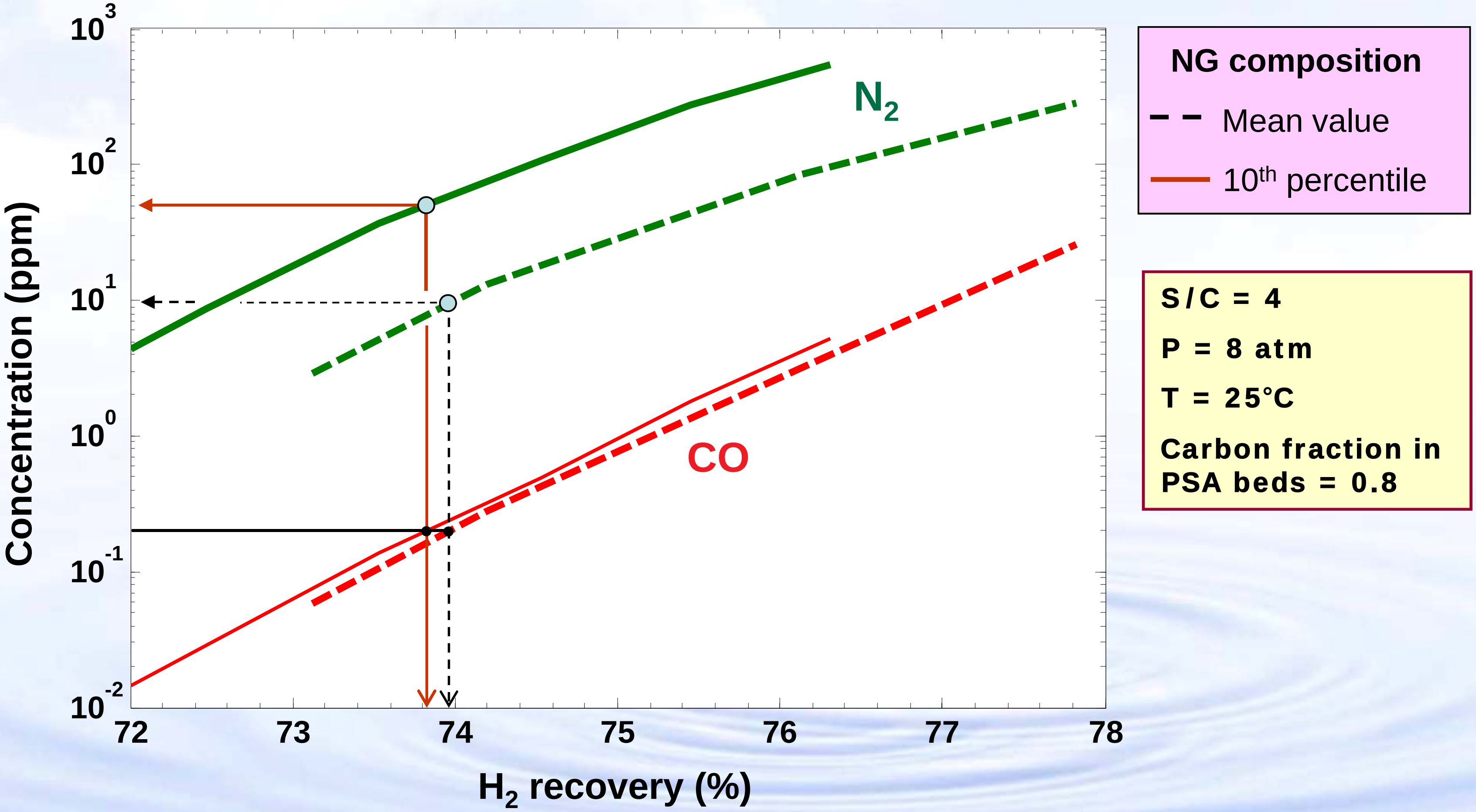
Reformate composition to PSA (%, dry basis)*

Species	Mean	10th 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

*Also, arbitrarily added 100 ppmv H_2S to PSA feed

Impact of Higher Nitrogen Content in the Feed Natural Gas

Higher levels of N_2 in NG feedstock lower the hydrogen recovery to meet product specifications



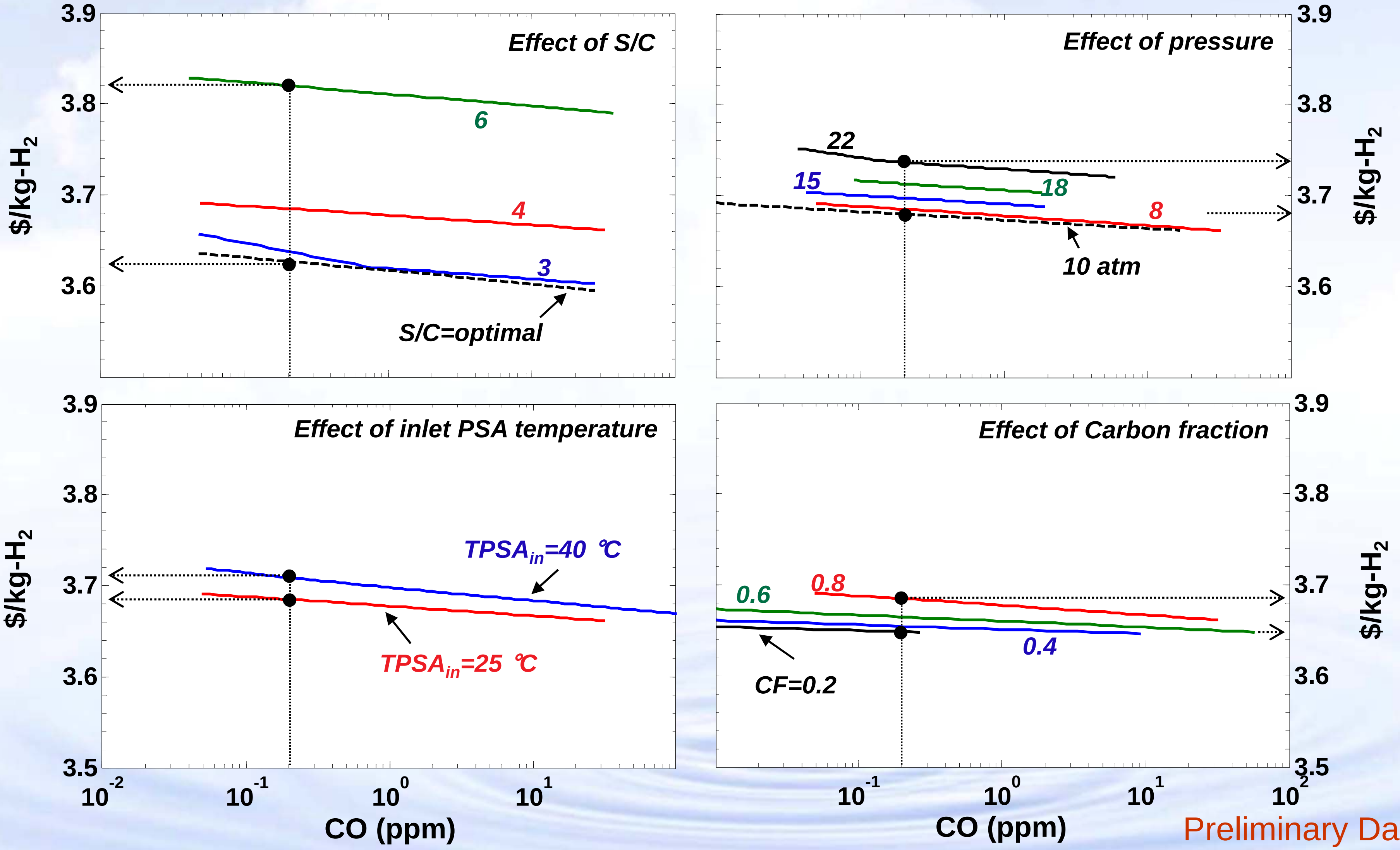
S/C = 4

P = 8 atm

T = 25°C

Carbon fraction in PSA beds = 0.8

The Cost of Hydrogen is not Found to be Very Sensitive to the Level of CO in the Product Hydrogen



Preliminary Data

(Basis: 2007 average NG price = $7.60/1000 ft³): Data from EIA

Impact of CO Specification on Cost of Hydrogen and Life-Cycle Cost of Fueling the FCV

Meeting the fuel cell CO requirement has little impact on hydrogen cost

			Fuel Cell CO spec.		
CO Concentration in Hydrogen	**ppm**	**0.1**	**0.2**	**0.5**	**1.0**
Cost of Hydrogen	$/kg	3.63	3.63	3.62	3.62
Fuel Cell Stack Efficiency[1]	% (LHV)	51	49	48	46
FCV/ICEV[2] Fuel Econ. Multiplier		2.54	2.50	2.46	2.42
Fuel Economy	mpgge	51	50	49	48
Hydrogen Required (Life = 100,000 miles)	kg	1,970	2,000	2,030	2,070
Cost of Fuel (Vehicle Life)	$	7,150	7,250	7,360	7,470
Fuel Cost Multiplier		**0.99**	**1.00**	**1.02**	**1.03**

[1] R. K. Ahluwalia and X. Wang, “Effect of CO and CO_2 Impurities on Performance of Direct Hydrogen Polymer-Electrolyte Fuel Cells,” Journal of Power Sources, 180, 122-131, 2008.

[2] SUV type ICEV achieving 20 mpg. R. K. Ahluwalia, X. Wang, A. Rousseau, and R. Kumar, “Fuel Economy of Hybrid Fuel Cell Vehicles,” Journal of Power Sources, 152, 233-244, 2005.

Preliminary Data

Impact of Hydrogen Contaminant Analysis on Cost of Hydrogen

CO Concentration in Hydrogen	ppm	0.2	0.5	1.0
Grab Samples, Off-Site Analysis				
Analytical Cost[1] per Analysis	$	150	150	150
Intervals between Analysis	Days	1	1	1
Plant Capacity	kg/day	1500	1500	1500
Cost of Analysis	**$/kg**	**0.10**	**0.10**	**0.10**
On-Site Instrumental Analysis				
Instrument Cost[1]	$	10^5	10^5	5×10^4
Instrument Life	Years	5	5	5
Operation / Maintenance	$/year	3000	3000	3000
Cost of Analysis	**$/kg**	**0.04**	**0.04**	**0.03**

[1] The cost of analysis and instrument cost are estimates based on private communications with vendors and experience at Argonne.

Preliminary Data

Summary

Accomplishments

- **A mathematical model has been developed to correlate desired impurity limit with hydrogen recovery and production efficiency**

- **Selected parameters have been studied based on industry feedback**
  - **Steam/carbon ratio (S/C), pressure, PSA temperature, carbon/zeolite proportions, and natural gas composition**
  - **Fixed: cycle and timing and number of beds**

Summary

Findings

- **Based on the parameters studied so far:**
  - **Given current guideline values**
    - **CO specification for SAE hydrogen purity guidelines can be met with a PSA unit**
    - **Reducing CO concentration to the SAE purity guidelines reduces the hydrogen recovery**
    - **Reducing CO from 1 ppm to 0.2 ppm has minimal impact on the cost of produced hydrogen**
  - **By meeting the CO concentration levels required for the fuel cell, meeting the required Sulfur concentration will not be a problem**
    - **Sulfur is an easier compound to remove**
  - **Nitrogen can become the limiting species if the natural gas feedstock to the steam methane reformer (SMR) contains high levels or the adsorbent proportions are changed**
    - **A high concentration of nitrogen in the feedstock can reduce the hydrogen recovery and system efficiency**
  - **The PSA system can be optimized to operate at higher efficiencies (compared to the reference case scenario presented here)**

Next steps

- **The results (efficiency) from this model will be incorporated into H2A production model**
  - **To generate cost of hydrogen correlated to contaminant type and level**

Backup

Sulfur and Ammonia (NH_3) are easier to remove in the PSA than Nitrogen (N_2)and CO

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

Courtesy of B. Balasubramanian, Chevron Technology Ventures