Biogas Impurities and Cleanup for Fuel Cells

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Biogas is the product of anaerobic decomposition of organic waste

Municipal solid wastes (MSW)

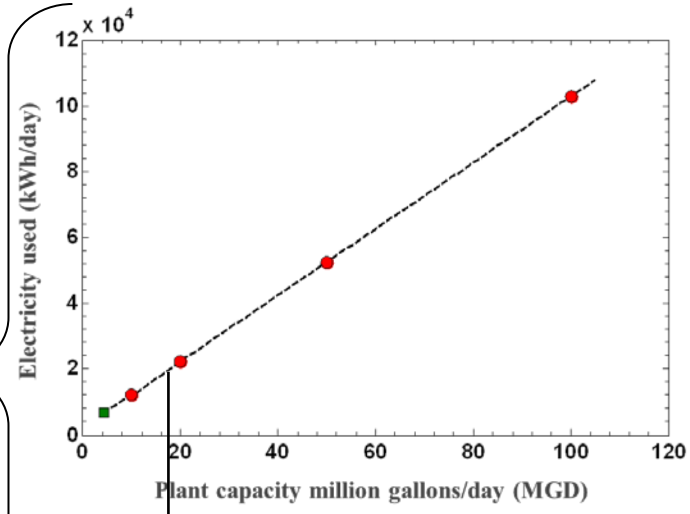
- For every 1 million tons of MSW:
  - 432,000 cubic feet per day of landfill gas (LFG) for a period of 20 years
  - 1 MW of electricity[1]

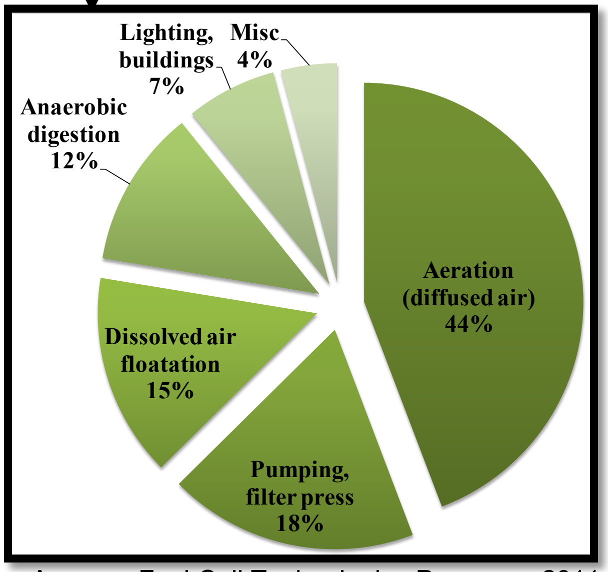
Sewage sludge/waste water (WWTP or ADG)

- A typical WWTP processes 100 gallons per day (GD) for every person served
  - 1 cubic foot of digester gas can be produced per 100 gallons of wastewater
- 100 kW of electricity[1] can be generated from 4.5 MGD of waste water

Agricultural waste (i.e. dairy waste)

- About 70-100 ft^3/day of digester gas is produced per milking cow
  - A dairy farm of 500 cows can generate 100 kW of electricity[1]





[1] Assuming 30% conversion efficiency

Argonne Fuel Cell Technologies Program - 2011

There is a significant energy recovery potential from the biogas at the waste water treatment plants

WWTPs by Flow Rates (MGD)	Total WWTPs	Total wastewater flow (MGD)	Wastewater flow to WWTPs with ADG (MGD)	WWTPs with ADG utilizing biogas (%)	Power wasted[a)] (MW_{th})
>200	15	5,147	3,783	50	159
100 - 200	26	3,885	2,652	53	84
75 – 100	27	2,321	1,350	44	52
50 – 75	30	1,847	1,125	28	56
20 – 50	178	5,375	2,573	29	132
10 – 20	286	3,883	2,039	13	125
5 - 10	504	3,489	1,728	15	103
Total	1,066	25,945	15,247	19	711

www.epa.gov/chp/publications. "Opportunities for and Benefits of CHP at Wastewater Treatment Facilities," 2011, p.48

Outline

- Impurities in biogas
- Fuel Cell Tolerances
- Biogas Clean-up
- Cost of Clean-up

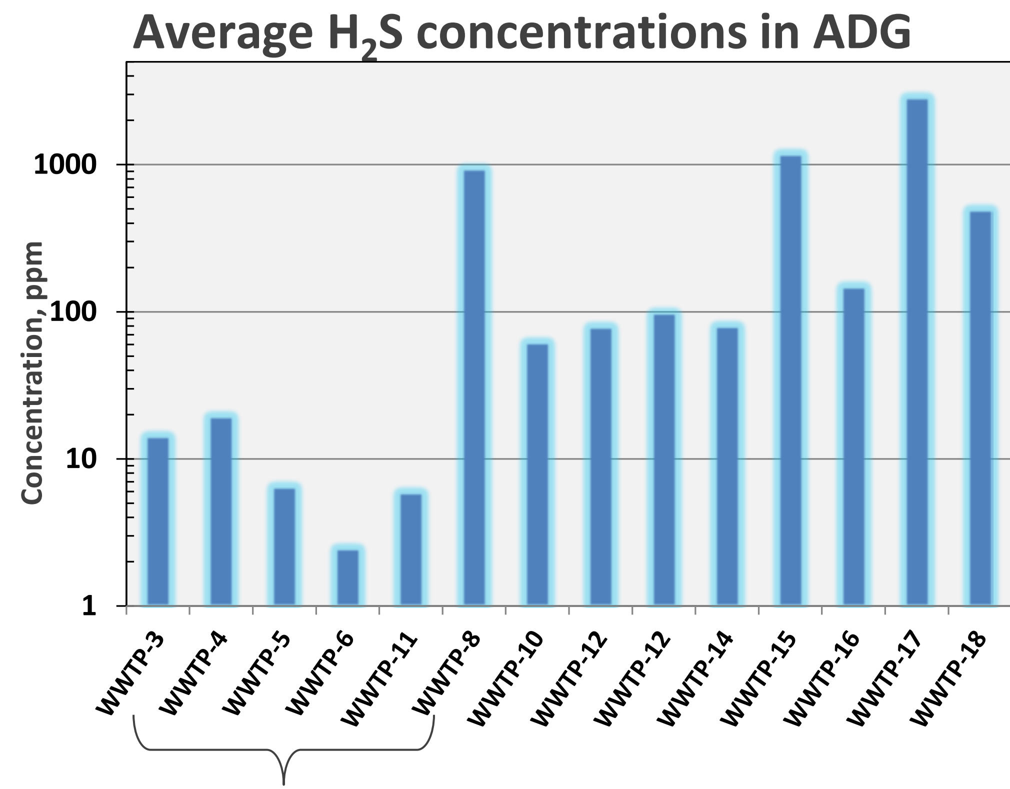
Biogas contains impurities that can damage the fuel cell system

- Large variability of trace impurities from different biogas source
  - *Factors affecting concentration are i.e. temperature, pressure, type/origin of waste, age of waste (LFG)*

  - **Sulfur**
    - Common to all biogas sources
      - LFG/ADG in ppm range
      - Highest levels in agricultural sector (up to vol-%)
    - H_2S bulk of sulfur species, organic sulfur range from ppb to few ppm (DMS>Mercaptans>COS)
  - **Organosilicon**
    - Biologically stable, found in many personal hygiene products, detergents, lubricants
    - Cyclic species (D3-D5), linear (L2-L4) and trimethylsilanol most frequently encountered
    - Newer sources of biogas (LFG, ADG) are showing higher concentrations
    - Analytical techniques are lab based and time consuming
  - **Volatile Organic Compounds (VOC)**
    - Aromatics, oxygenates, alkanes, halogens in the range of ppm
    - Distribution affected by the type of waste and age of the landfill
    - Halogens arise from volatilization of compounds in plastics foams, solvents, refrigerants,…
    - CFC's are stable compounds and evaporate slowly from landfill waste

Sulfur – ADG contains mainly H_2S

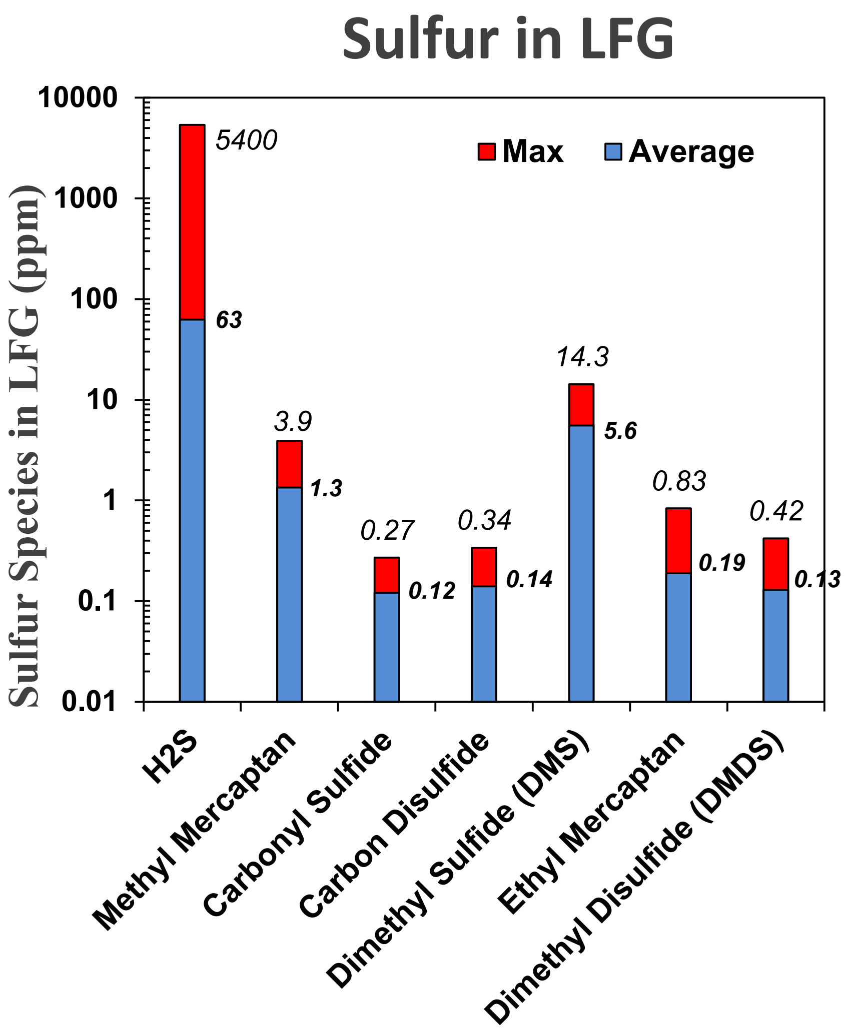
- H_2S concentrations vary by 3 orders of magnitude
- DMS, Mercaptans can vary from ppb to few ppm
  - Other species at < 1 ppm
- Iron salts used in the water treatment process sequesters sulfide
- Impacts reformer, fuel cell catalyst, electrolyte
  - Sulfur impurities need to be reduced to levels of ~0.1-1 ppm



Low H_2S content due to iron salt used in the waste water treatment process, i.e. for sludge thickening, phosphate precipitation

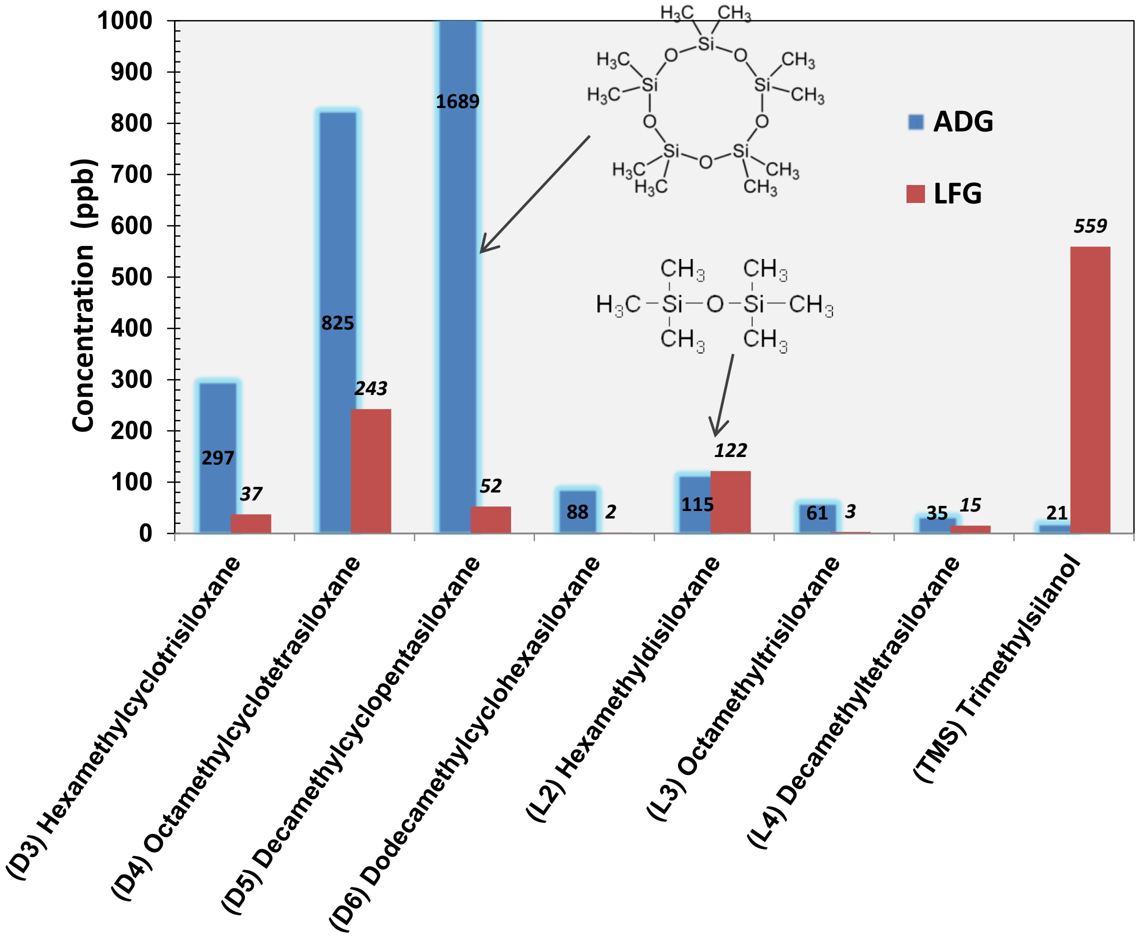
Sulfur – LFG contains different sulfur species in significant concentrations

- LFG has a variety of organics sulfur species at higher concentrations (than in ADG)
  - H_2S content is lower
- Dimethyl Sulfide is the dominant organosulfur
- DMS is difficult to adsorb



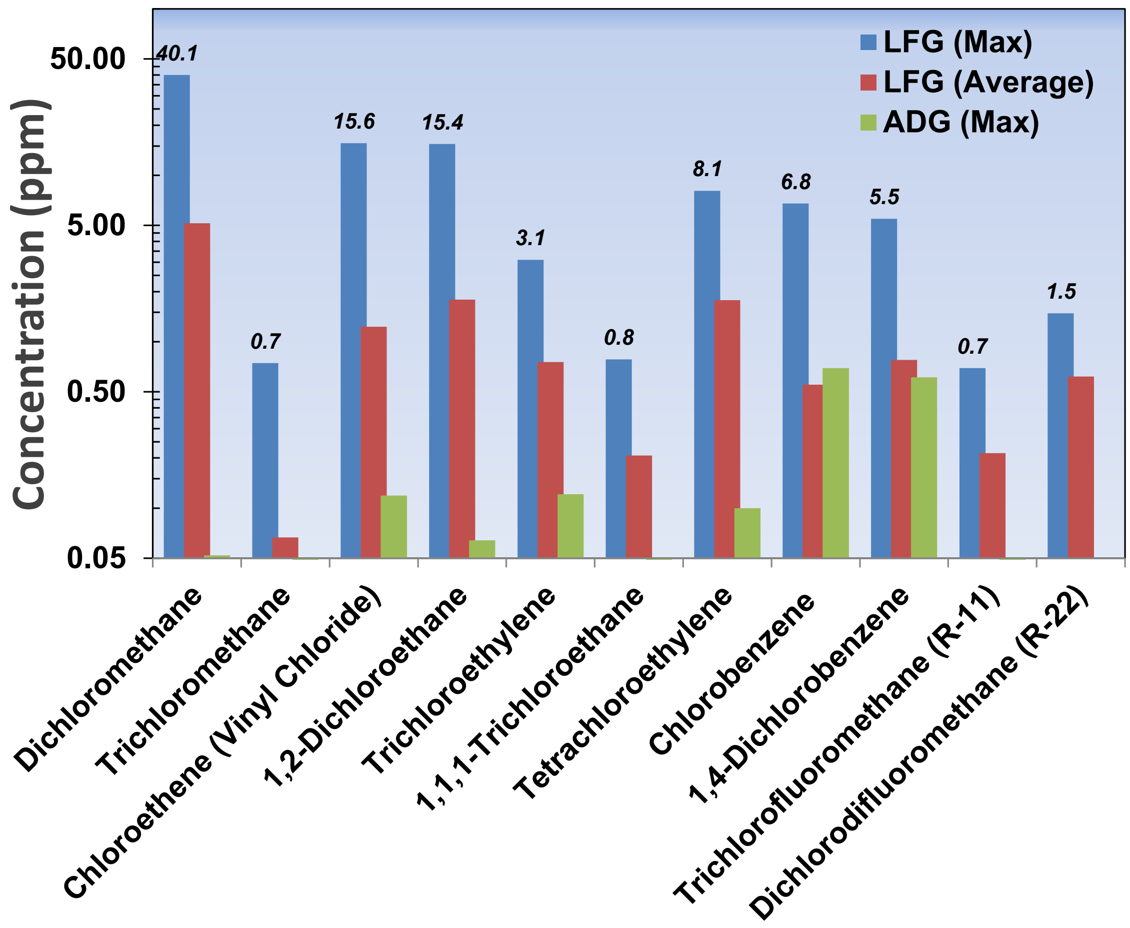
Siloxane content in ADG is higher than in LFG

- Cyclic compounds (D4 & D5) are dominant in ADG
- Concentration of linear compounds and TMS are usually low
- ADG temperature affects speciation and concentration of siloxane compounds
- Solid silica deposits on surfaces. Tolerance level often require “below detection limit”



Landfill gas contains a variety of halocarbons and at much higher concentrations than in ADG

- Concentration of halogens are generally much lower in ADG than in LFG
- Chlorine is the dominant halogen species
- Forms corrosive gases from combustion or reforming
- Affects long-term performance of fuel cell



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What are the tolerance limits for the FCs?

- ***Sulfur***
  - Corrosive, affects catalyst and electrolyte
  - Rapid initial followed by slower voltage decay
  - More severe effect with CH_4/CO rich fuels to Fuel Cell and anode recirculation
  - Tolerance limits 0.5-5 ppm
  - Effect may be recoverable
- ***Siloxanes***
  - Fouls surfaces (HEx, sensors, catalysts)
  - Thermally decompose forming glassy layers
  - Few studies on the effects on FC's, but tolerance limits may be practically zero
- ***Halogens***
  - Corrosive, affects electrolyte
  - Long term degradation effect
  - Tolerance limits, 0.1-1 ppm

Impurity	Tolerance	Reference
Molten Carbonate Fuel Cells		
H_2S	0.1 0.5 0.1-5 ppm	(Tomasi, *et al.*, 2006) (Abe, Chaytors, Clark, Marshall and Morgan, 2002) (Moreno, *et al.*, 2008) (Desiduri, 2003)
COS, CS_2, mercaptan	1 ppm	(Tomasi, Baratieri, Bosio, Arato and Baggio, 2006)
Organic Sulfur	<6 ppm	(Lampe, 2006)
H_2S, COS, CS_2	0.5-1 <10 ppm	(Cigolotti, 2009) (Lampe, 2006)
Halogens (HCl)	0.1-1 ppm	(Moreno, McPhail and Bove, 2008) (Desiduri, 2003), Lampe, 2006) (Abe, Chaytors, Clark, Marshall and Morgan, 2002)
Halides: HCl, HF	0.1-1 ppm	(Cigolotti, 2009)
Alkali Metals	1-10 ppm	(Tomasi, Baratieri, Bosio, Arato and Baggio, 2006) (Moreno, McPhail and Bove, 2008)
NH_3	1 1-3 %	(Moreno, McPhail and Bove, 2008) [Desiduri, 2002], [Fuel Cell Handbook, 2002] (Cigolotti, 2009)
[illegible]	[illegible]	(Moreno, McPhail and Bove, 2008)
Siloxanes: HDMS, D5	10-100 <1 ppm	(Cigolotti, 2009) (Lampe, 2006)
Tars	2000 ppm	(Cigolotti, 2009)
Heavy Metals: As, Pb, Zn, Cd,Hg	1-20 ppm	(Cigolotti, 2009)
Solid Oxide Fuel Cells		

⋮

Some tolerance data is available

Type of Fuel Cell	PAFC	MCFC	SOFC
H_2S	2	0.1-5.0	1
COS, CS_2, Mercaptan		1	
Organic Sulfur		6	
H_2S, COS, CS_2		0.5-10	
HCl, ppm		0.1	"few"
Halogens	4	0.1-1.0	1-5
Halogenated Organics		0.1	
NH_3	1	10,000	5000
Siloxanes		1	0.01
Tars		2000	

Units: ppm

The data and its variability reflects the vulnerability of the materials and the conditions at which they were tested

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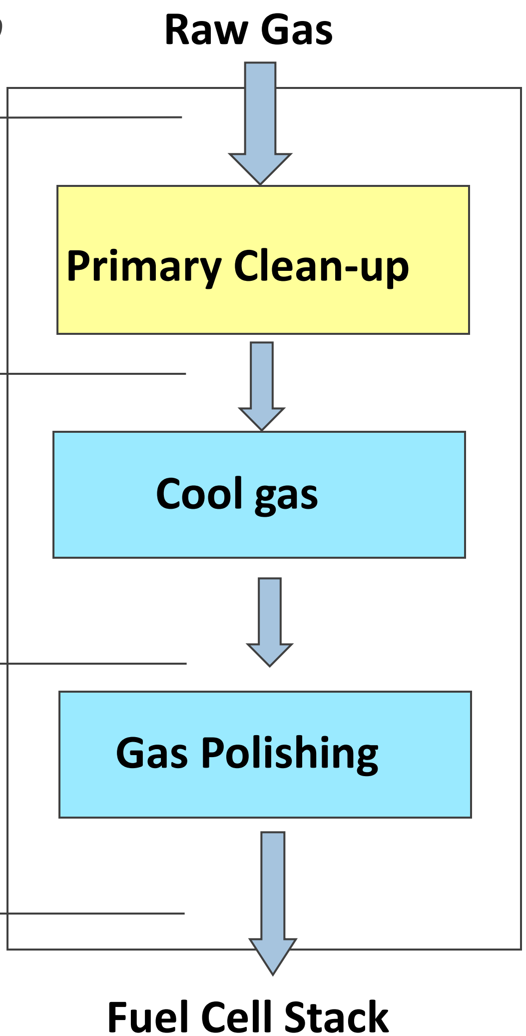
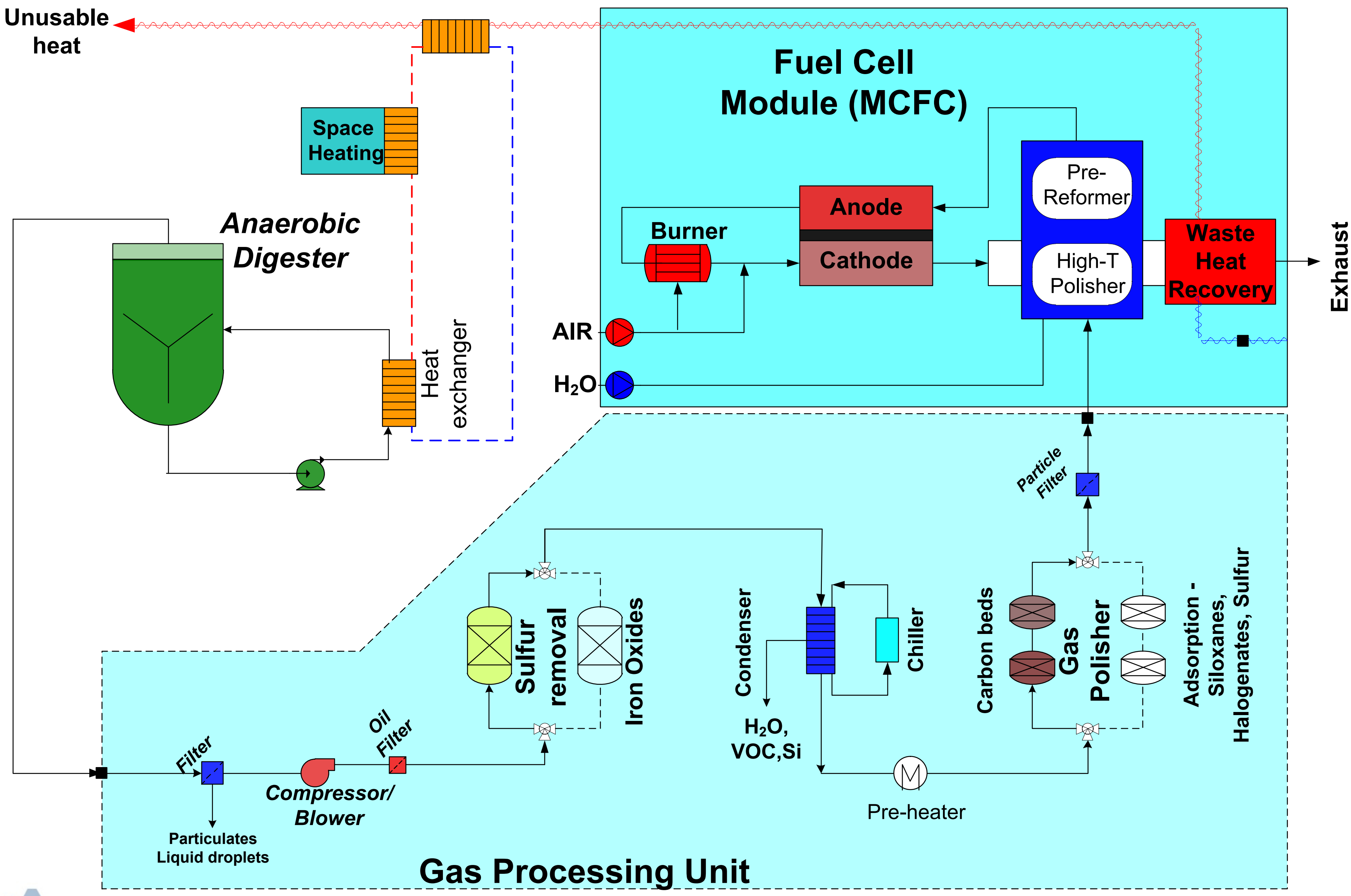
Clean up processes mostly rely on bulk removal and polishing solutions

Example of strategy commonly employed for biogas clean-up

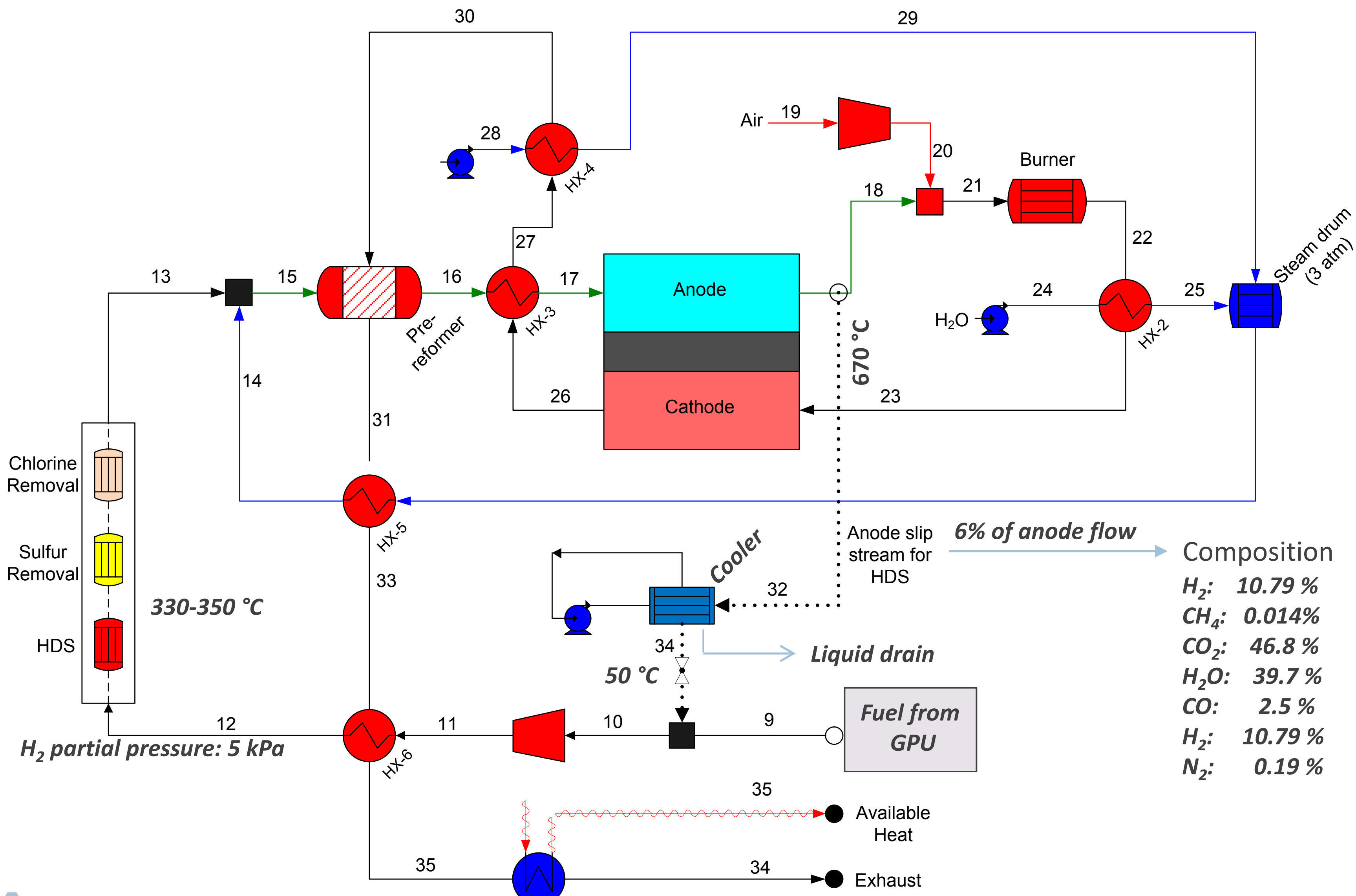
- Remove bulk of sulfur (to ~5-10 ppm)
  - **Precipitation, Iron oxides, Impregnated carbon**
  - *(Biological, washing)*
- Remove moisture (dry gas for polishing)
  - **Cooling may condense some VOCs and siloxanes**
  - *(Deep refrigeration effective for some siloxanes)*
- Remove Sulfur, Halogens, Siloxanes
  - **Active carbon, Silica gel, ZnO …**
  - **Throw away / regenerable options**



The base case system operates on Anaerbic Digester Gas coupled with a 300 kWe MCFC



The process includes a high temperature gas polisher: Part of the anode tail-gas (6% or less) need to be recycled for the HDS unit



Composition

H_2: 10.79 %
CH_4: 0.014%
CO_2: 46.8 %
H_2O: 39.7 %
CO: 2.5 %
H_2: 10.79 %
N_2: 0.19 %

The adsorption capacity of activated carbon varies dramatically with the impurity species, and further by their interactions

Maximum capacity for the individual species

Strong

Adsorption affinity

Weak

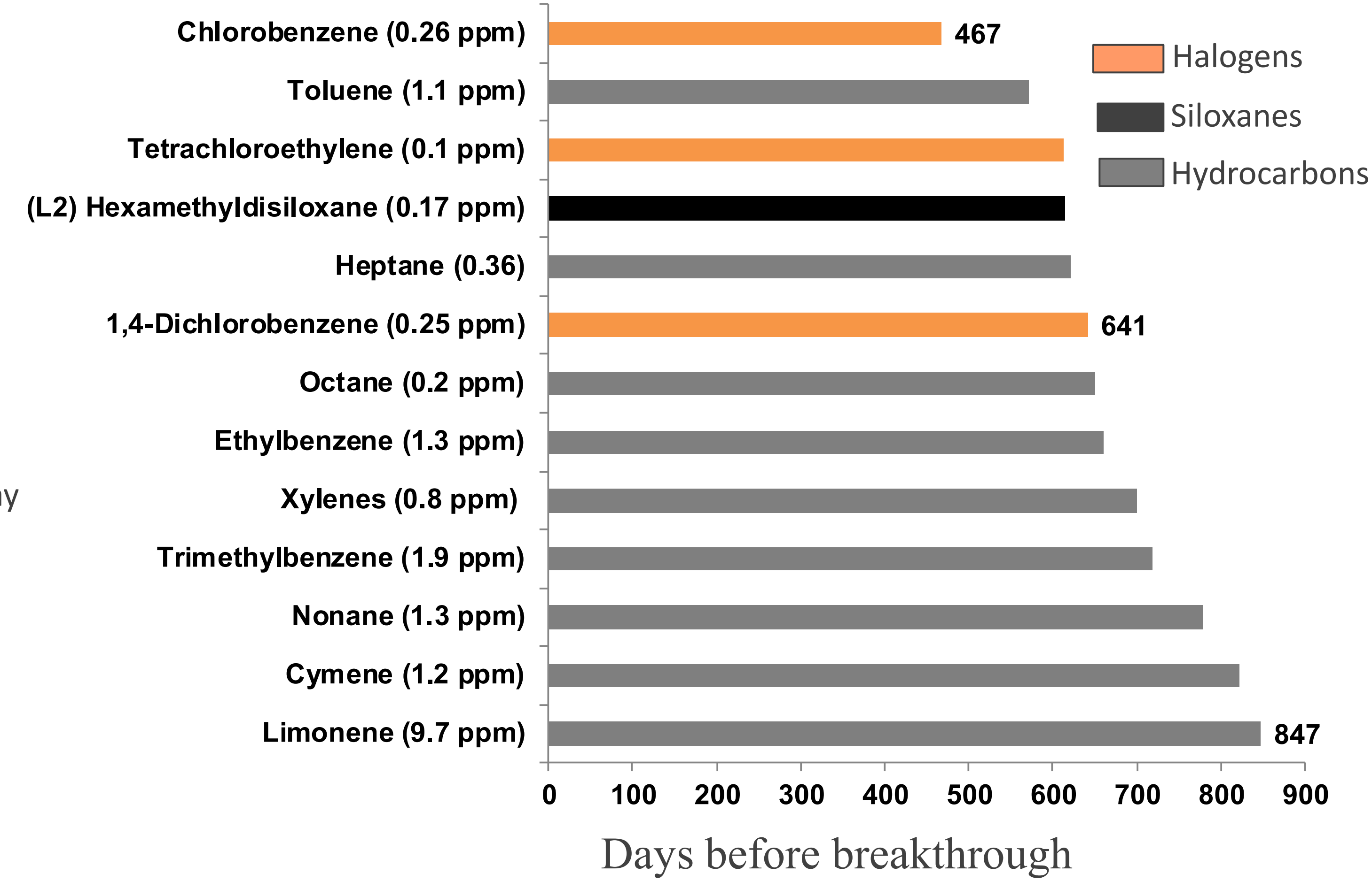
Species	Capacity[a)] (Nm^3/g)	Capacity Wt.%	Boiling Point °C
Xylene	4.9	21.8	144
Toluene	4.6	17.2	110
Tetrachloroethylene	3.4	23.8	121
Hexane	2.8	9.7	68
D4 (Octamethylcyclotetrasiloxane)	2.3	26	173
Trichloroethylene	2.2	12.2	360
Acetone	0.7	1.7	87
Vinyl Chloride	0.5	1.3	-13
Dichloromethane	0.1	0.5	39
Hydrogen Sulfide[b)]	~0	~0	-60
Ethane	~0	~0	-89

[a)] Biogas processed to remove 10 ppm of impurities per g-carbon, T=298 K, 0% humidity

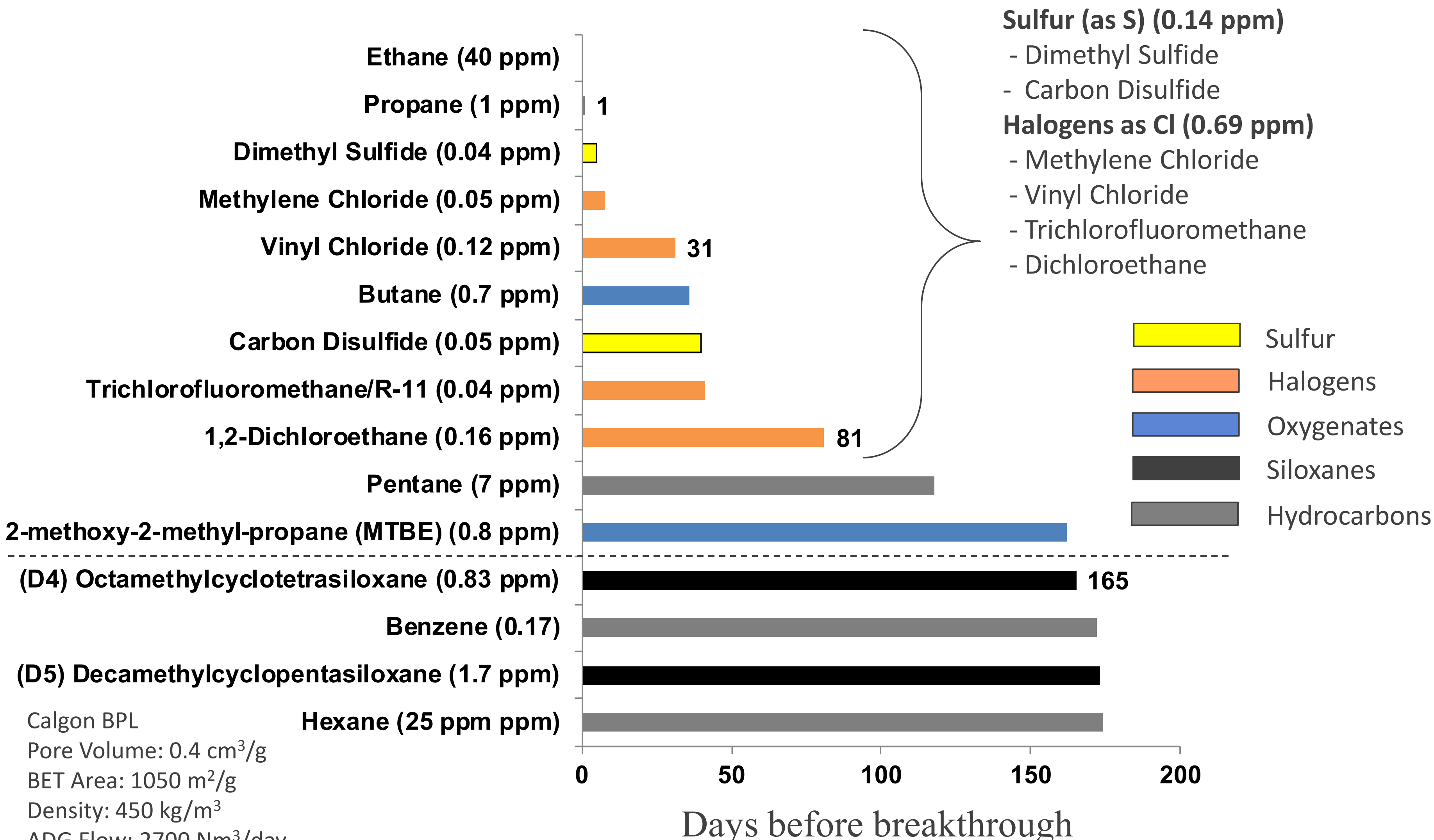
[b)] Capacity for non-impregnated carbon

The hydrocarbons are effectively removed by activated carbon

Calgon BPL
Pore Volume: 0.4 cm^3/g
BET Area: 1050 m^2/g
Density: 450 kg/m^3
ADG Flow: 2700 Nm^3/day
Carbon Loading: 700 kg



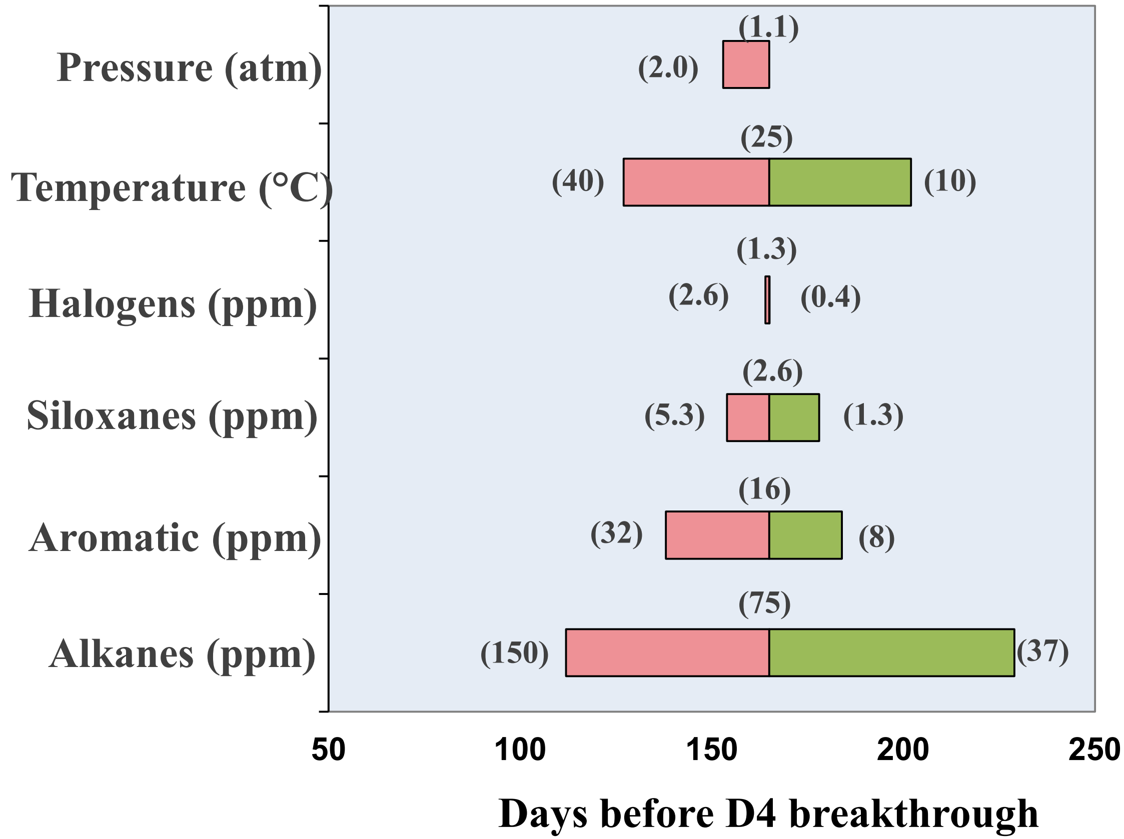
The carbon beds were replaced before D4 and D5 siloxanes break through



Calgon BPL
Pore Volume: 0.4 cm^3/g
BET Area: 1050 m^2/g
Density: 450 kg/m^3
ADG Flow: 2700 Nm^3/day
Carbon Loading: 700 kg

The hydrocarbons reduce the capacity of the carbon

- Higher temperatures reduce capacity
- Variations in inlet concentrations are common
- Online sensors can help
  - Avoid break-through
  - Effective use of media



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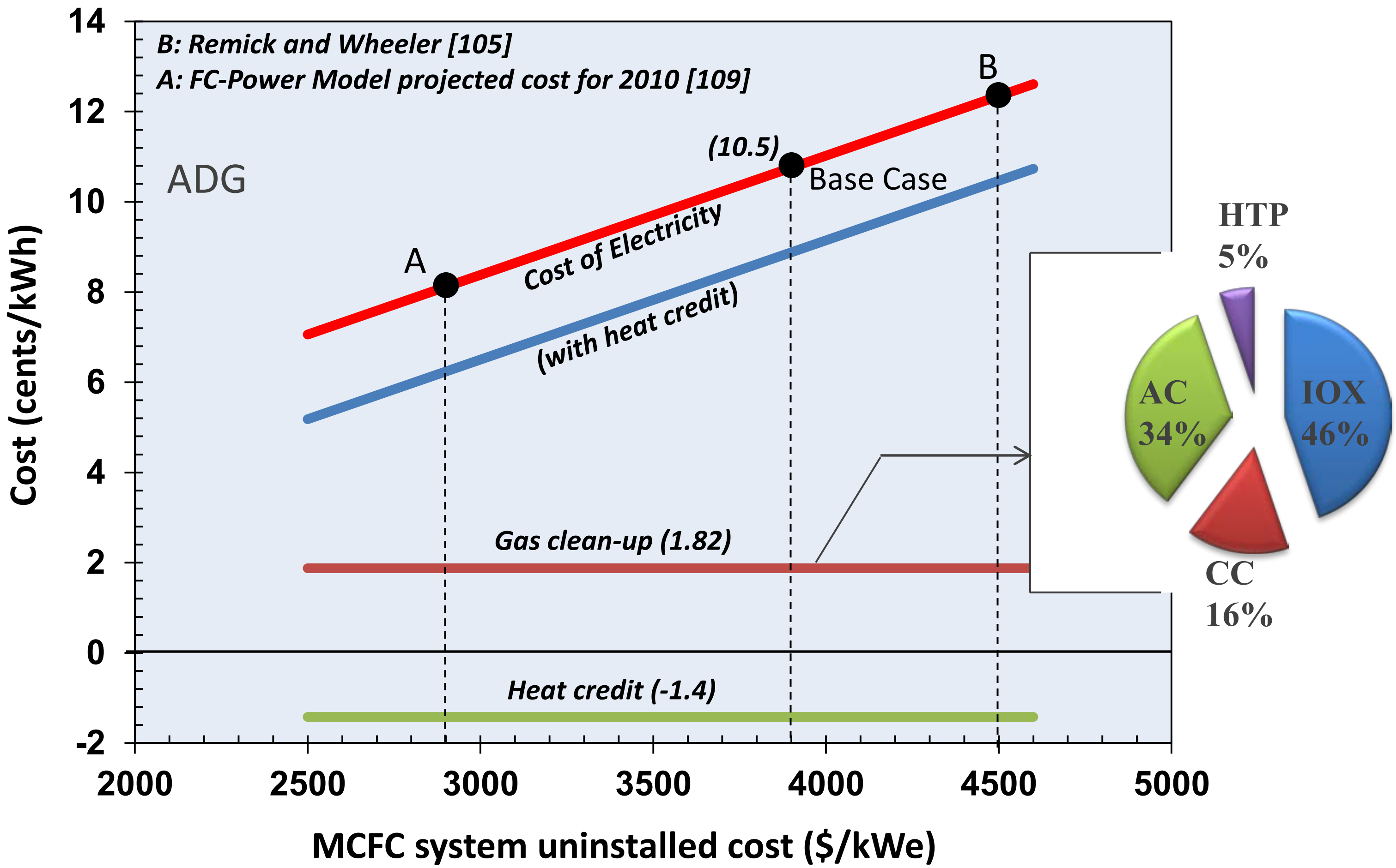
- ❑ Cost of Clean-up

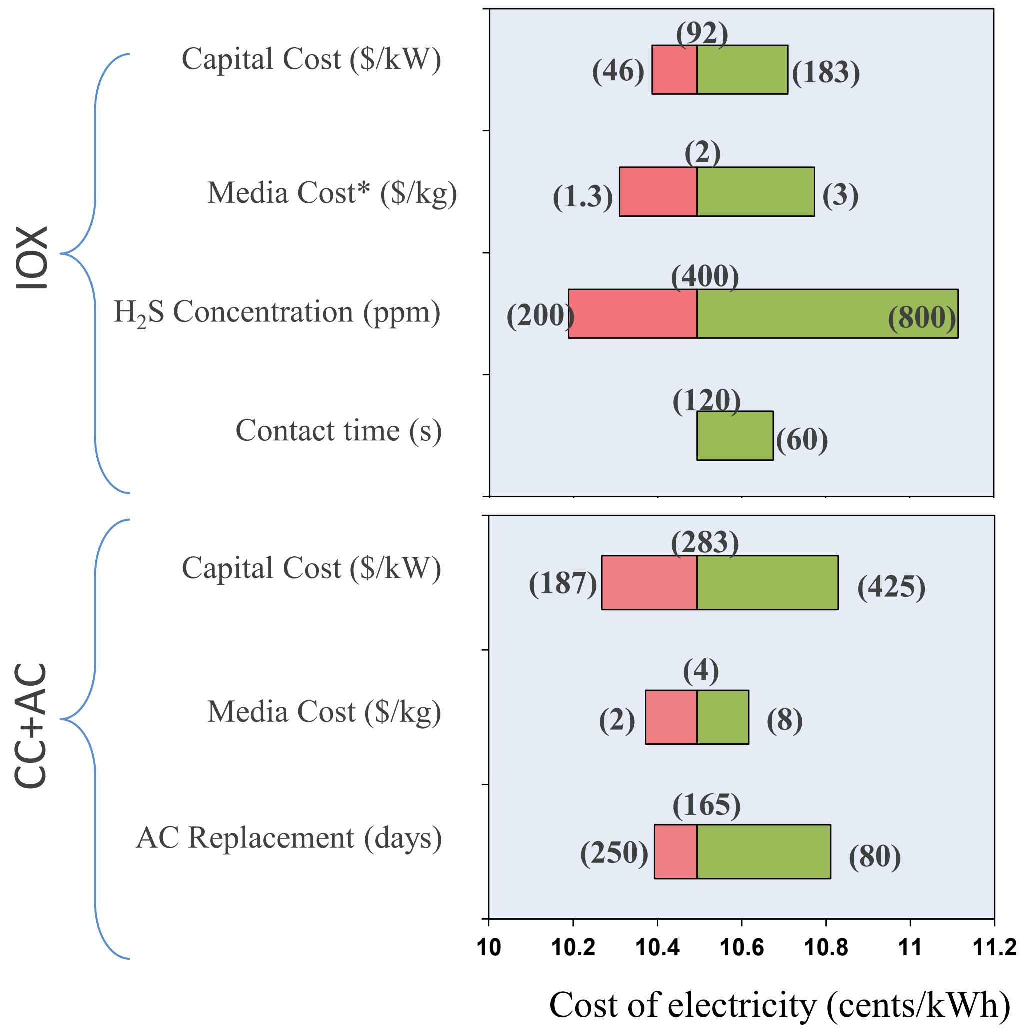
Gas clean-up adds ~2 cents per kWh, which can be partly offset if credited for available heat



AC = Activated Carbon, CC = Chiller / Condenser,
IOX = Iron Oxide, HTP = High Temperature Polisher

The cost of electricity is most sensitive to the H_2S content

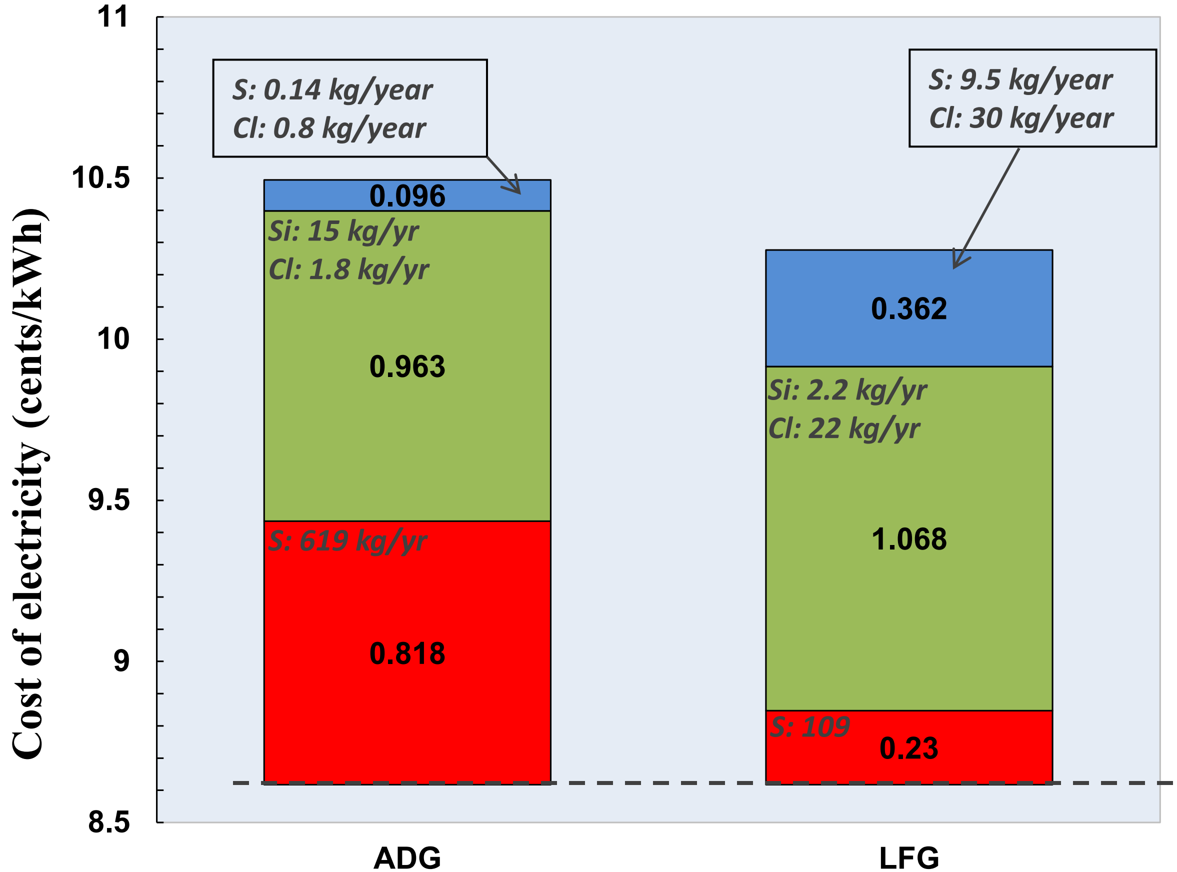
- Increasing contact time increases capital cost
  - Net effect: higher cost
- Replacement frequency depends on operating conditions (T, P, RH, …)



*Includes replacement cost

IOX – Iron Oxide; CC – Chiller/Condenser; AC – Activated Carbon

H_2S removal dominates cost of ADG clean-up
The carbon bed is the most expensive part of LFG clean-up



	ADG	LFG
CH_4 %	58	50
CO_2 %	38	48
O_2 %	1	1
N_2 %	1	1
Impurities, #	47	47

If NG costs $4/MMBtu, then the cost of electricity from NG-MCFC would be ~11 c/kWh

Custom clean-up solutions are complex and costly

- Sulfur, organosilicon, and halocarbons need to be removed to ensure durability of the fuel cell
  - Moisture, most hydrocarbons, do not damage the fuel cell but degrade the capacity of the media
- Fuel cells have little (if any) tolerance for these impurities
- There are technology options for removing the impurities
  - Clean-up process needs to be designed based on impurity distributions
  - Increased complexity of the system due to impurity interactions with sorbents
- Clean-up costs represent ~20% of the cost of electricity

- Technology needs
  - Sensors
  - Sorbents
    - Adsorption data to support calculations
    - Higher capacity
  - Generic clean-up strategies

Acknowledgment

- Fuel Cell Technologies Program, Energy Efficiency and Renewable Energy, U.S. Department of Energy
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