ABOUT HYGEAR

• Established in 2002
  – 65 people
  – Acquired Plug Power Europe in 2009

• Products
  – Hydrogen Generation Systems
  – Biogas Cleaning systems
  – Fuel Cell Systems

• Facilities
  – Catalysis and Adsorbents laboratory
  – 2000 m² System test facilities
  – Rapid prototyping shop
  – Flexible system assembly line
NATURAL GAS CLEANING - SULFUR

• Most sulfur is removed at well!!

• What is in pipeline depends on source:
  – Netherlands: sulfur removed at well
  – Russia: small amounts H\textsubscript{2}S & COS
  – North Africa: all sulfur removed (LNG source)
  – North Sea: small amounts of H\textsubscript{2}S & COS
  – In all countries: TetraHydroTyofene (THT) added as odorant
    • South Germany and Italy add mercaptans (Tertiarybutylmercaptan)

• Different gas grids!
  – Every country own regulations
  – L-Gas: 81\% CH\textsubscript{4}, CO\textsubscript{2} + N\textsubscript{2}, C\textsubscript{2}-C\textsubscript{3}
  – H-Gas: ±100\% CH\textsubscript{4} (plus C\textsubscript{2}-C\textsubscript{3})
  – Peak shaving: propane + air
WHERE ARE WE ON THE MAP OF SOLUTIONS?

- Commercial solutions
DIFFERENT SOLUTIONS, DIFFERENT SPECS

• Scavengers
  – Remove sulfur down to ppm-range
  – Different solutions for different input amounts etc

• Polishers
  – Remove sulfur down to ppb-level
SOLUTIONS USED IN EUROPE

• Small scale fuel cells: adsorption
  – Active carbon (no COS, large volume)
  – Zeolites (mercaptans, THT)
  – Metal based (H$_2$S, COS)
  – Mixed beds (sequence is important! COS difficult)
CONCERNS / ISSUES / IMPROVEMENTS NEEDED

• Costs
• Interference by other compounds
  – water, higher hydrocarbons
• Non full use of material
  – Difference actual sulfur content in feed vs feed specifications
  – Sulfur sensing too costly for small units
  – Replace unused material
• Household
  – Major concern is toxicity/flammability of spent cartridges
  – Active carbon / zeolite as solution for households
    • Chemical company is starting service for replacements and logistics
• Industry
  – Ni-based solutions
    • Carcinogenicity of nickel subsulphides
>20 materials from 7 manufacturers were analyzed

>10 materials were tested in laboratory reactors

3 materials and combinations thereof proved to be acceptable

- Zeolite: flammable after use, captures THT and Mercaptans
- Metal-based: non flammable after use, captures Mercaptans, H₂S and COS
- Ni-based: non flammable after use, high capacity for mercaptans, H₂S and COS, carcinogenic
ALTERNATIVE SOLUTION: HYDRODESULFURIZATION

- Major impact on system design
  - Needs H₂
  - Needs heat 350°C
    - Guard-bed needed during start

- Dis- & Advantages
  - Cost benefits are minor
  - Converts all sulfur-species
  - No difficult waste!

- HDS/ZnO hardly used for fuel cells
  - no sulfur removal during start-up
  - water containing reformate not suitable for most catalysts & ZnO
  - complex solution (reliability, sensoring)
• Do not add sulfur....

• Use non-sulfur containing odorant
  – Gasodor®
  – Nitrogen based odorant. (m)ethylacrylate, methylethylpyrazine

• Only used in a few German cities
  – No expectations of wide use
  – High cost of introduction
BIOGAS (DIGESTER GAS) UPGRAADING

• Remove CO$_2$ by
  – Water / amine washing (large plants, 500-1500m3/h)
  – (V)PSA (mid-size, 200-700 m3/h, landfills)
  – Membranes (small size, <200 m3/h)
  – 137 plants in Europe (2011)

• Remove S by
  – One step (<200ppm):
    • active carbon with O$_2$ enrichment
    • Impregnated active carbon
      (high costs for waste removal)
  – Two step (>200ppm):
    1. Biological reduction / iron sponges
    2. Active carbon

• Siloxanes . Halogens removed by active carbon as well
• No more new landfills in Europe. Focus thus on digesters
PURIFICATION OF HYDROGEN STREAMS

• Traditional: bottled gas
  – PSA

• Fuel cell use
  – $O_2$: catalytic deoxidizer
  – Cl/chlorate: alkali water scrubbing
GASIFIER GAS CLEAN UP

- No mature market in Europe
- Technologies available for most contaminants

- A lot of research on tar removal
  - Today too costly
  - OLGA system is state of the art

- Quenching of gas to prevent tar formation results in low efficiencies

- Promising technologies for hot cleaning
  - Plasma cleaning
  - Catalytic candles
THANK YOU

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ENGINEERING FOR SUSTAINABLE GROWTH