



# HYGEAR

## GAS CLEANING EUROPE

ELLART DE WIT



# 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 m<sup>2</sup> System test facilities
  - Rapid prototyping shop
  - Flexible system assembly line

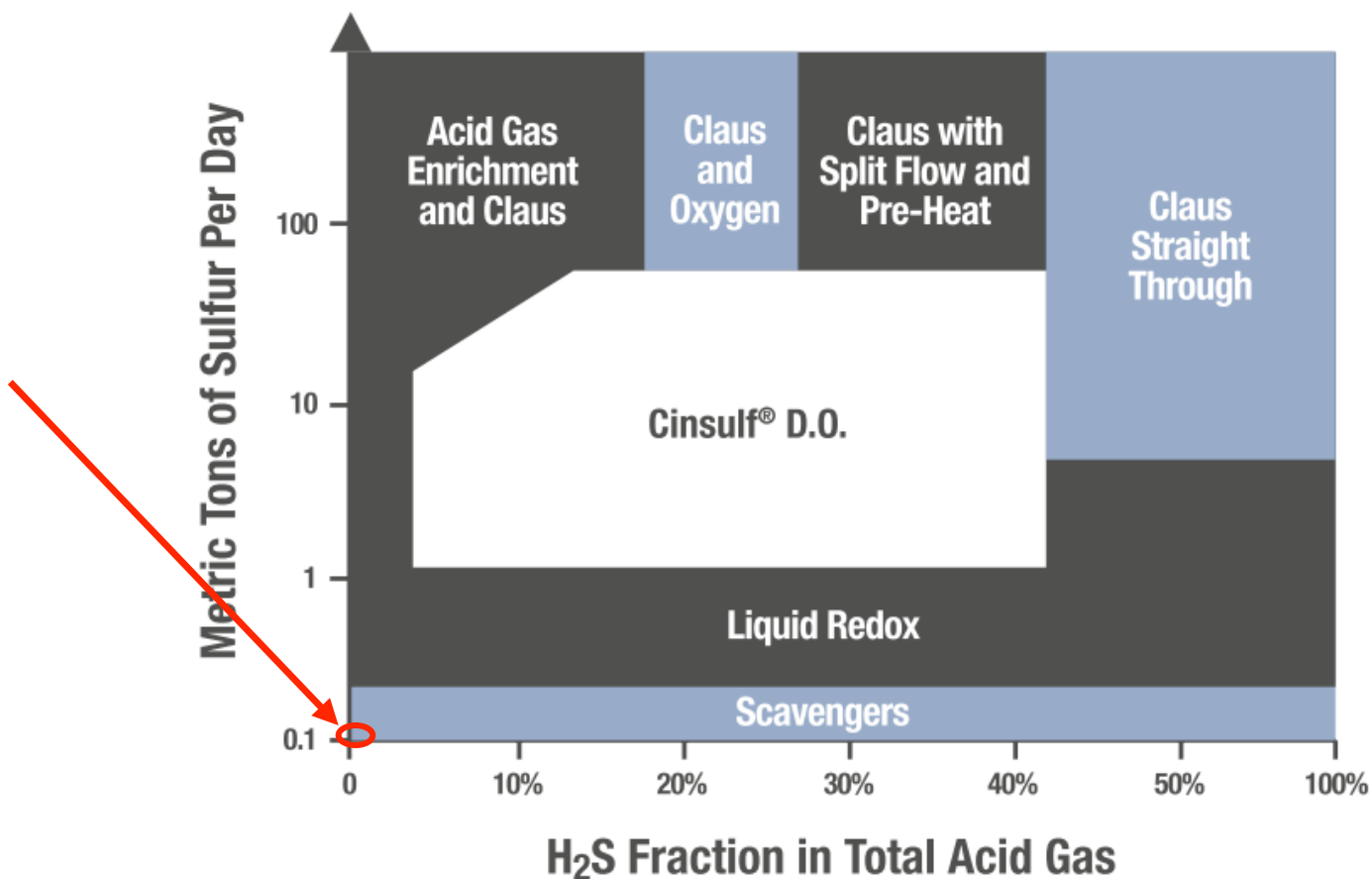


# NATURAL GAS CLEANING - SULFUR

- Most sulfur is removed at well!!
- What is in pipeline depends on source:
  - Netherlands: sulfur removed at well
  - Russia: small amounts  $H_2S$  &  $COS$
  - North Africa: all sulfur removed (LNG source)
  - North Sea: small amounts of  $H_2S$  &  $COS$
  - 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%  $CH_4$ ,  $CO_2$  +  $N_2$ ,  $C_2$ - $C_3$
  - H-Gas:  $\pm 100\%$   $CH_4$  (plus  $C_2$ - $C_3$ )
  - Peak shaving: propane + air

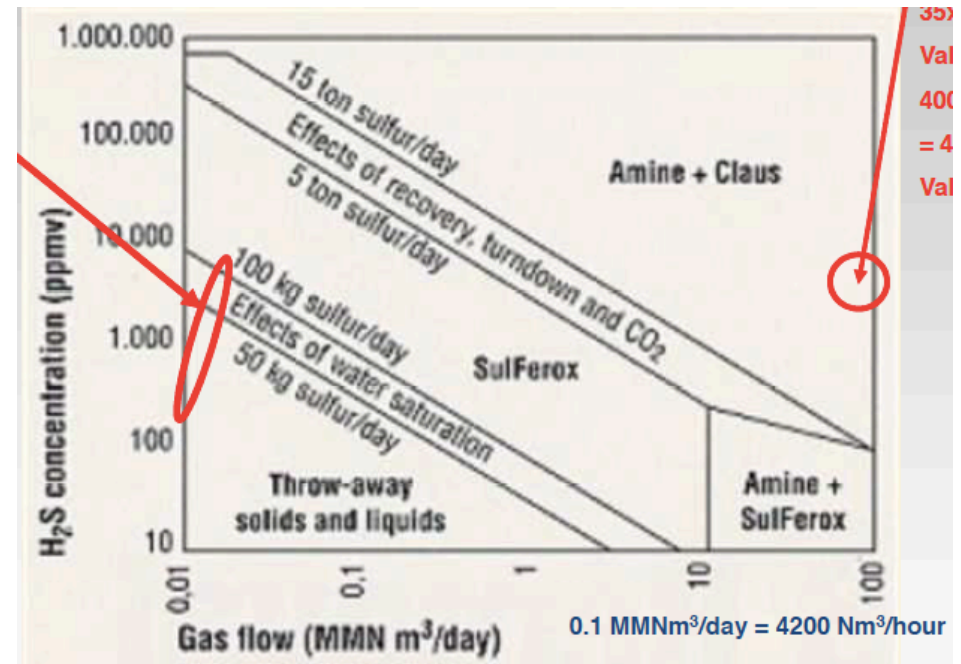
# WHERE ARE WE ON THE MAP OF SOLUTIONS?

- 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 ( $H_2S$ , 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

# TESTS OF ADSORPTION MATERIALS

- ❖ >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, H<sub>2</sub>S and COS
  - Ni-based: non flammable after use, high capacity for mercaptans, H<sub>2</sub>S and COS, **carcinogenic**



# ALTERNATIVE SOLUTION: HYDRODESULFURIZATION

- Major impact on system design
  - Needs  $H_2$
  - Needs heat  $350^{\circ}C$ 
    - 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 reformat not suitable for most catalysts & ZnO
  - complex solution (reliability, sensing)



# SIMPLIFY LIFE

- 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) UPGRADING

- Remove CO<sub>2</sub> by
  - Water / amine washing (large plants, 500-1500m<sup>3</sup>/h)
  - (V)PSA (mid-size, 200-700 m<sup>3</sup>/h, landfills)
  - Membranes (small size, <200 m<sup>3</sup>/h)
  - 137 plants in Europe (2011)
- Remove S by
  - One step (<200ppm):
    - active carbon with O<sub>2</sub> 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<sub>2</sub>: 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

HyGear

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