DESULF

Gas purification with adsorbents

Christian Frilund
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Gas purification

- Applications:
  - Industrial gases – Cleaning for downstream application
    - Syngas
    - Hydrocarbon gases – Refinery streams, SNG/NG
    - Niche industries
  - Air pollutant control – Emission control
    - Air purification
    - Combustion gases – SOx, NOx and VOC removal
      - Power plant flue gases
      - Combustion engine exhaust gases

Most typical gas impurities	
H_2S	Hydrogen sulfide
CO_2	Carbon dioxide
SO_2	Sulfur dioxide
H_2O	Water vapor
NOx	Nitrogen oxides
VOC's	Volatile organic compounds
HCl, Cl_2	Chlorine compounds
HF, SiF_4	Fluorine compounds
NH_3	Basic nitrogen
CO	Carbon monoxide
COS, CS_2	Organic sulfur
HCN	Hydrogen cyanide

Purification technologies

- Each gas purification application comes with their unique challenges and opportunities, depending on gas:
  - Composition
  - Impurity concentration
  - Purity requirement
- Technologies vary from simple single-unit operations to multiple step processes
- Purification technologies can be roughly divided into five groups :

Class	Example
Absorption into liquid	Solvent scrubbing of CO_2
Adsorption onto solid	H_2S removal by metal oxides
Permeation through a membrane	H_2 separation from gases
Reactive conversion	Selective catalytic reduction of NOx to N_2
Condensation	Steam (water) removal

Wärtsilä's flue gas scrubber

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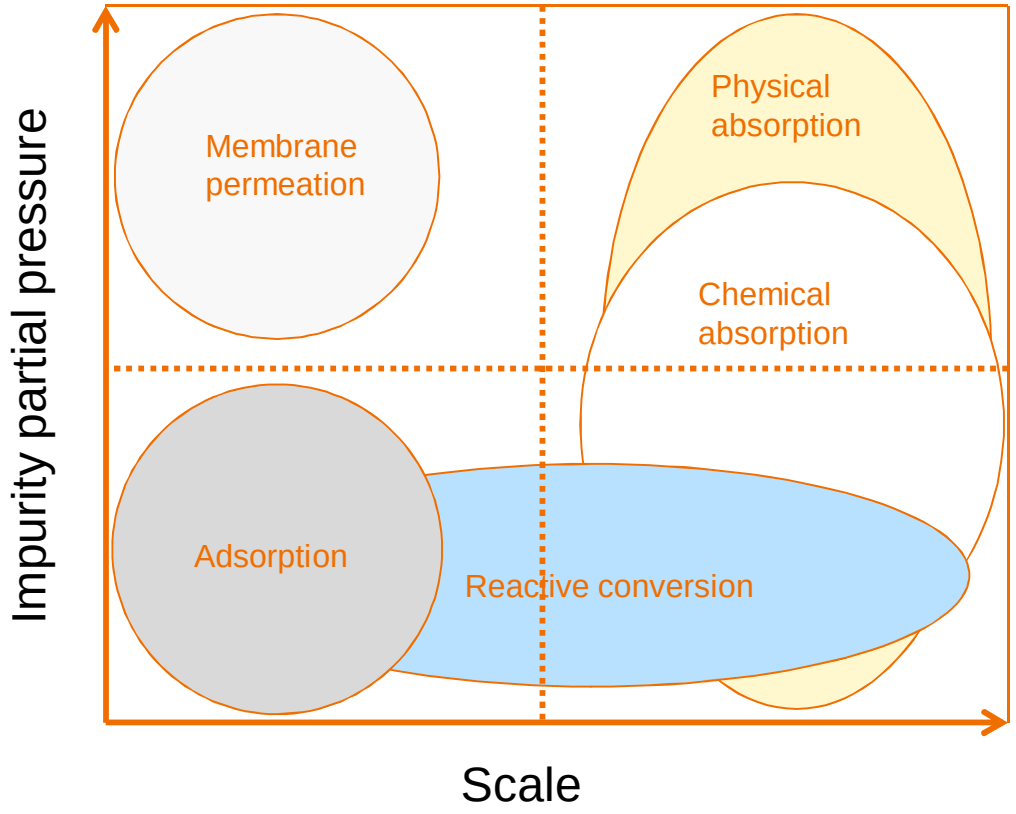
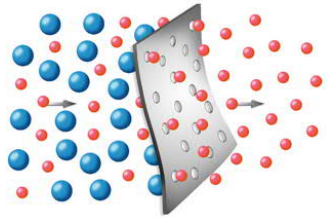


Adsorption

- Adsorbents can purify very low concentration species potentially selectively for deep purification purposes
  - Often used for trace component removal such as sulfurs, heavy metals etc.
- Occurs through:
  - Physical adsorption – Weak bonds, regenerable
  - Chemical adsorption – Strong bonds, often irreversible
- Typical adsorbents:

Adsorbent	Principle
Molecular sieves, eg. Zeolites	Molecular size difference
Metal oxides	Gas-solid reaction
Acticated carbons, silica gels	Physical adsorption



Molecular sieve

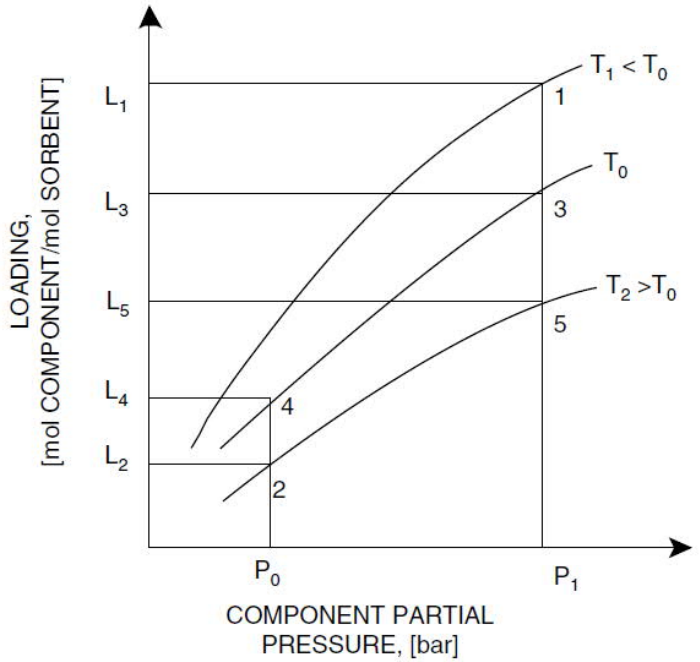
JM Mercury removal adsorbent

AdFis siloxane removal Activated carbon

Adsorption principles

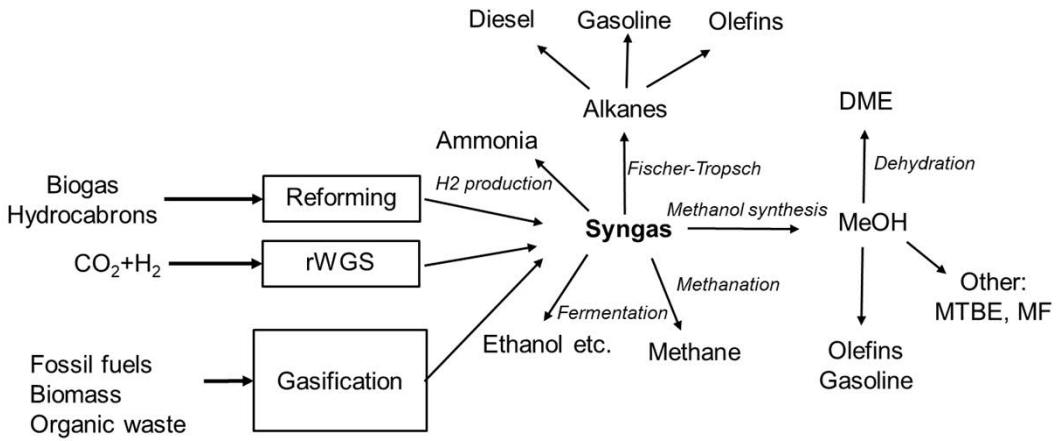
- Adsorption characteristics
  - Exothermic → Physical adsorption occurs readily at low temperature
  - Promoted by higher pressures
  - Chemical adsorption has a certain activation energy and requires higher temperatures
  - High solid surface area promotes adsorption

- Physical adsorption systems typically operate on a pressure swing cycle (PSA), where
  - Adsorption occurs at high P (3)
  - Desorption occurs at low P (4)



Higman, Gasification (2003)

Syngas (H_2+CO)



Formed gas species

	Combustion	Gasification
Carbon	CO_2	CO
Hydrogen	H_2O	H_2
Nitrogen	NO, NO_2	N_2, NH_3, HCN
Sulfur	SO_2, SO_3	H_2S, COS
Water	H_2O	H_2

- Syngas is a versatile platform – Especially for sustainable carbon-source conversion into value added products
- Several catalytic and biological routes available for syngas conversion to sustainable fuels and chemicals

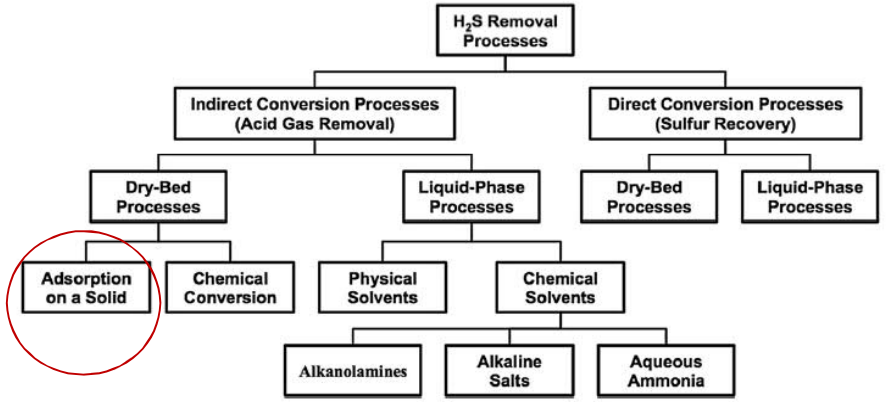
H_2S removal

- Sulfur is present in all biological and solid gasification feedstocks
- H_2S is formed in reducing atmospheres and is very corroding and a catalyst poison

Downstream sulfur tolerance:

Impurity	Turbine (electricity generation)	Methanol synthesis catalyst	Fischer-Tropsch synthesis catalyst
H_2S (ppm_v)	< 20	< 0.5	< 0.01
COS (ppm_v)		-	

- Most common H_2S removal technologies
  - Wet scrubbing for large quantities
  - Dry bed adsorption for small sulfur loads



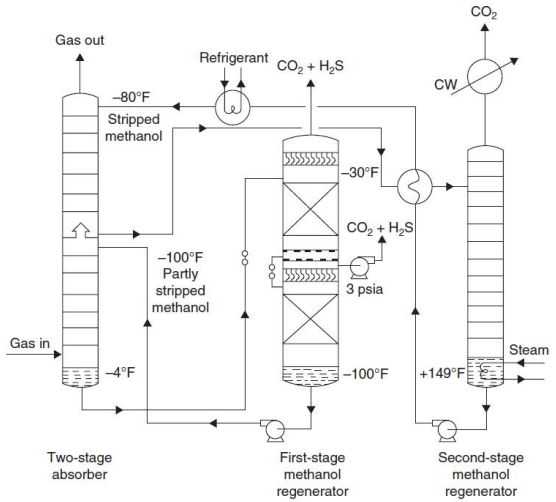
Woolcock, "A review of cleaning technologies for biomass-derived syngas," Biomass and Bioenergy, 2013

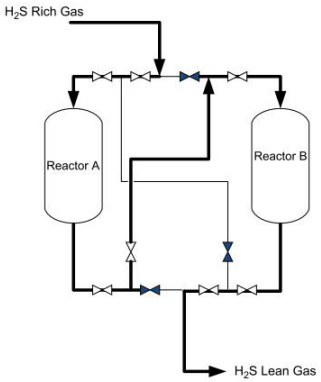
Syngas desulfurization

Wet scrubbing vs adsorbents

Wet scrubbing technologies eg. Rectisol (MeOH), Selexol (glycol)	
+	Effective acid gas removal (also removes CO2) to ppm levels
-	High CaPex and OpEx – Economies of scale apply
-	Sulfur recovery requires another process: Claus-type process

Adsorptive desulfurization	
+	Simple, selective dry-bed solution, low CapEx
+	Effective H_2S removal to sub-ppm levels
-	Likely only competetive at smaller scale operations
-	Spent adsorbent processing





Mokhatab, "Handbook of natural gas transmission and processing: principles and practices", 2015

Adsorbents for H_2S removal

A good adsorbent:

1) High H_2S adsorption capacity

2) Fast adsorption kinetics and favourable reaction equilibrium

3) Mechanical properties: low attrition rate and able to tolerate high temperatures

4) Chemical properties: stable in reducing environments, selective towards sulfidation

5) Cheap and readily available

Adsorbents
Metal oxides

- Most relevant adsorbents for complex gases
  → Selective H_2S removal possible
- Forms a stable stable metal sulfide at elevated temperatures:

$$MeO_x(s) + xH_2S(g) \rightleftharpoons MeS_x(s) + xH_2O(g) \qquad \Delta H_r < 0$$

Where *Me* suitable metal

Sulfidation kinetics: $r = k_o \exp\left(-\frac{Ea}{RT}\right) C_{H_2S}$

	ZnO	MnO	CaO	Fe	Cu-Ce_{2-x}
Ea (cal/mol)	7240	5690	5160	3300	3967
k_0 (cm/s)	0.11	0.47	0.039	0.0023	0.075

A. T. Atimtay and D. P. Harrison, *Desulfurization of Hot Coal Gas*. Springer, 1996.

Oxide	Cost ($/kg)
Fe_2O_3	< 0.5
TiO_2	1-3
ZnO	1-3
CuO	4-10
MnO	4-10
ZrO_2	4-16
NiO	6-10
CoO	14-20
CeO	16-20
Cr_2O_3	16-20
MoO_3	16-20

H. Hofbauer, "Report on Gas Cleaning for Synthesis Applications Work Package 2E : ' Gas treatment ,'2007.

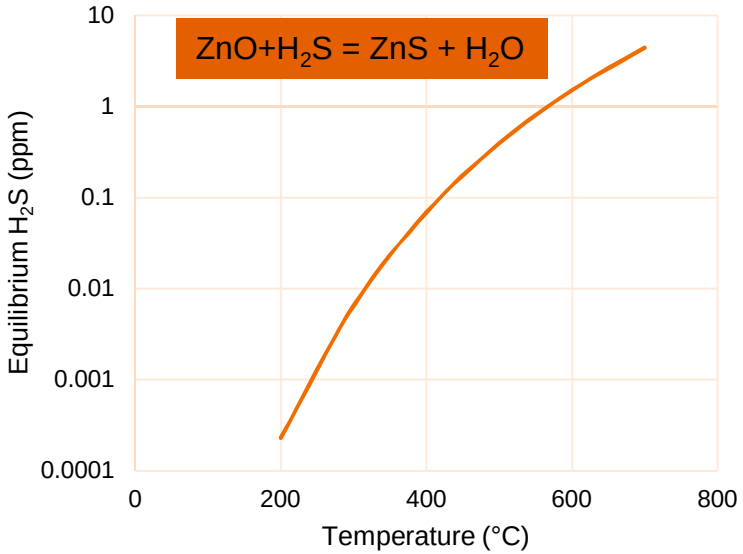
Zinc Oxide

- Used as a H_2S guard bed step in several applications
- Deep removal possible (ppb levels), good sulfidation kinetics, 0.39 g/g theoretical sulfur capture capacity
- Note! Also forms zinc chloride:

$$ZnO + 2HCl \rightleftharpoons ZnCl_2 + H_2O$$

- Challenging to regenerate
  - Issues with sulfate formation and sintering
    - Special ZnO-based adsorbents to tackle these issues exi
  - Many applications utilize adsorbents in a non-regenerable way → Waste problem

Equilibrium:



In syngas with 5 vol% H_2O

Outotec HSC Chemistry 8.0

Waste material valorisation to adsorbents

- While Zn-based materials are considered good desulfurization adsorbents, the price of primary ZnO prevents wider use
- Spent adsorbent material processing is an issue
- Zinc-rich metal industry EAF dusts are interesting adsorbent material candidates
  - Low-cost Zn-source
  - Provides viable spent material recycling pathway using existing EAF dust processing