Hydrogen and Fuel Cell Based Energy Systems

THE USAGE OF BIOGAS IN FUEL CELL SYSTEMS

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Outline

- Biogas as renewable fuel
- Application to fuel cells
- Fuel cells requirements
- Upgrading biogas
- Future perspectives

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Biogas as renewable energy source

- Sustainable development: limitation of fossil fuels use
- Renewables
  - Biofuels: can be stored and transported more easily than other renewable energy sources.
    - Biogas
      - Landfill gas
      - Anaerobic digestion gas:
        - » Industrial waste water treatment
        - » Stabilisation of sewage sludge
        - » Recycling of biowaste, agricultural waste and manure as organic fertilizers

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Biogas composition

- Main components:

CH_4, CO_2, H_2S, NH_3

- Other:

N_2, O_2, H_2, CO, HC, HC-X, H_2O,

siloxanes, dust particles

- Its energy content is defined by the methane concentration:

10% $CH_4 \Rightarrow 1\ kWh \cdot m^{-3}$

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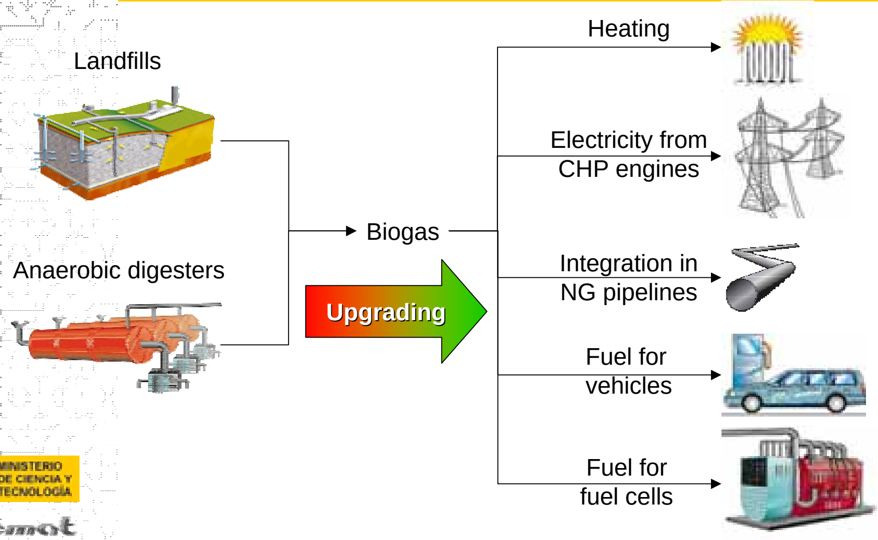
Options for biogas utilisation



Biogas upgrading

- Depending on the final application the biogas quality have to be improved.
- Main components to remove as general rule:

H_2S, H_2O, HC-X, CO_2

H_2S: Corrosion; Toxic H_2S concentrations; SO_2/SO_3 formation in burners

H_2O: Condensation in gas lines; Formation of acid solutions

HC-X: Corrosion

CO_2: Reducing energy content

Biogas components

High-grade biogas
Medium-grade biogas
Low-grade biogas
Raw biogas

• **CH_4**	30-60 % vol.
• **CO_2**	20-50 % vol.
• **N_2**	< 10% vol.
• **O_2**	<2% vol.
• **H_2**	Trace
• **CO**	Trace
• **H_2S, mercaptanes**	Trace
• **NH_3**	Trace
• **HC/HC-X**	Trace
• **Siloxanes**	Trace
• **H_2O**	saturation
• **Particles**	Trace

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Biogas purity grades

- Options for its final use depend on the degree of processing.
- Level of processing affects the economics of the application:

Low-grade:	Heating (end-user must be in the proximity)
Medium-grade:	Heating Gas engines Combined heat and power (CHP)
High grade:	Pipeline quality gas Production of chemicals Fuel for vehicles Fuel for FC

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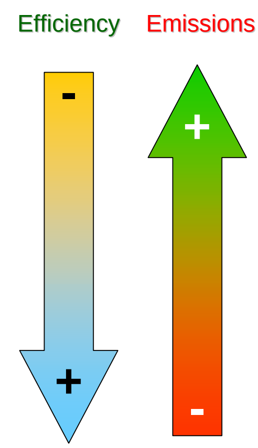
From biogas to electricity

Options:

- Gas engines and turbines
- Combined heat and power plants
- Fuel cells

Require upgrading to medium grade biogas

Require biogas upgrading & processing to obtain hydrogen



LFG and AD biogas revalorization

- Main problem associated to biogas:

variability of its composition:
depends on the source and varies with time

- For low CH_4 contents:

ignition problems in ICE:
mixtures usually vented after being burned in flares

can be used in FC after upgrading by using CO_2 instead of water as source of oxygen for producing H_2/CO by reforming

Fuel Cells for biogas conversion

- High temperature FCs: MCFCs, SOFCs
  - Upgrading before reforming: removal of sulfur compounds, NH_3, halogenated HC, siloxanes
  - More tolerant to impurities
  - May operate with $H_2/CO/CO_2$ mixtures
- Low temperature FCs: PEMFCs
  - Upgrading before reforming: removal of sulfur compounds, NH_3, halogenated HC, siloxanes
  - Fuel processing after reforming to reduce CO levels below 10 ppm.

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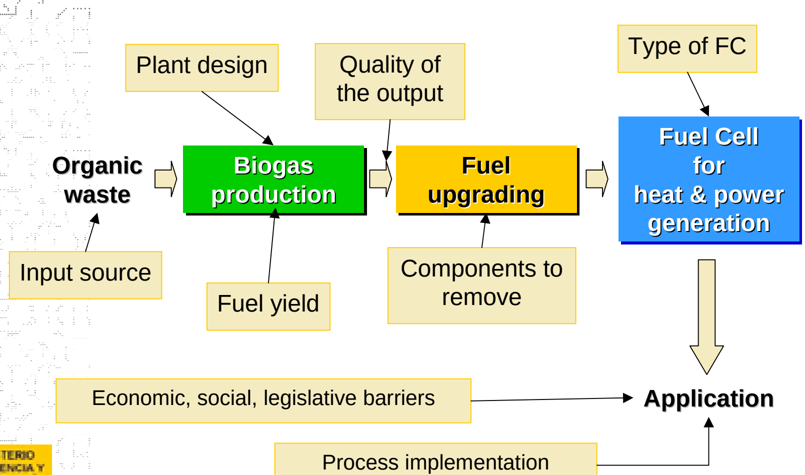
Multidisciplinary research area



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Fuel Cell feeding requirements

Component	PEMFC	PAFC	MCFC	SOFC
H_2	Fuel	Fuel	Fuel	Fuel
CO	Poison (10 ppm)	Poison (10 ppm)	Fuel	Fuel
CH_4	Inert	Inert	Fuel	Fuel
CO_2, H_2O	Diluent	Diluent	Recycled	Diluent
Sulfur	< 200 ppb	Poison <50 ppm H_2S+COS	Poison 0.1-0.5 ppm H_2S	Poison < 1 ppm H_2S
Halogens	----	Poison 4 ppm	Poison < 0.1-1.0 ppm	Poison < 1 ppm

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Fuel cell types

Fuel cell type	Electrolyte	Charge carrier	Operating temperature	Fuel	Power range/ applications	Electrical efficiency % today (target)
Alkaline FC (AFC)	KOH	OH^-	50-100°C	Pure H_2	Aerospace	40-60
Proton exchange membrane FC (PEMFC)	Solid polymer (such as Nafion)	H^+	50-100°C	Pure H_2 (tolerates CO_2)	Automotive, CHP, (5-250 kW) portable	35 (45)
Phosphoric acid FC (PAFC)	Phosphoric acid	H^+	~ 220°C	Pure H_2 (tolerates CO_2, approx. 1% CO)	CHP (200 kW)	<42
Molten carbonate FC (MCFC)	Lithium and potassium carbonate	CO_3^2	~ 650°C	H_2>, CO, CH_4, other hydrocarbons (tolerates CO_2)	200 kW - 2 MW range, CHP and stand-alone	47 (60)
Solid oxide FC (SOFC)	Solid oxide electrolyte (yttria, zirconia)	O^{2}-	~ 1000°C	H_2, CO, CH_4, other hydrocarbons (tolerates CO_2)	2-1000 kW range, CHP and stand-alone	47 (65)

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Biogas upgrading technologies

- Removal of moisture and particles
- Removal of trace gases:

  sulfur compounds, halogen compounds, siloxanes

- Carbon dioxide stripping

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Moisture removal techniques

- **Moisture separators:** reduce the gas flow velocity and allows liquid droplets to condensate in the vessel walls.
- **Mist eliminator:** filters with high surface area allows frther condensation. It also allows particles removal. In combination with moisture separators removes 99.9% of the liquids.
- **Gas cooling and compression:** decreases the dew point of the gas.
- **Absorption technology:** liquids with high water affinity: glycols: EG, DEG, TEG. Require regeneration
- **Adsorbent materials:** silica gel, alumina, molecular sieves. Require regeneration.

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Removal of H_2S

- **Adsorbents: activated carbon impregnated with KI** (high affinity with H_2O reduces its potential for traces removal the moisture removal step is not efficient)
- **Iron sponge, Fe_2O_3 pellets:** removal of H_2S by formation of iron sulphide (25-50ºC). Adsorbent regeneration by oxidation: Fe_2O_3 + S (highly exothermic).
- **Selective solvents:**
  - Water scrubbing
  - NaOH scrubbing (Na_2S, HNaS)
  - Alkanolamine process: selective solvents mainly for for H_2S and CO_2: MEA, DEA, TEA
  - Selexol scrubbing (polyethylene glycol)

2-column system for H_2S scrubbing with iron oxide

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H_2S removal

- **Addition of $FeCl_3$ in digesters:** very effective method but needs to be complemented with another removal method to reduce H_2S level.
- **Biological desulphurisation: *thiobacillus***
  Autotrophic organism consuming CO_2 and producing S and SO_4^{2-}. Requires addition of some amount of O_2 (2-6%) and reduce H_2S level below 50 ppm. (Biogas in air is explosive in the range of 6 – 12 % depending on the methane content.) It is suitable for gas engines but not for FC.
- **Biological filters:** combination of water scrubbing and biological desulphurisation

Biological desulphurization unit

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Siloxane removal

Organic silicon compounds are occasionally present in biogas and may affect adversely to FC performance: are widely used in cosmetics, pharmaceuticals and in anti-foaming agents in detergents

- Adsorption in a mixture of hydrocarbons: adsorbent regenerated by heating and desorption
- Cooling to -2ºC and adsorption in charcoal

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Halogenated hydrocarbons removal

Higher hydrocarbons and chlorinated and fluorinated compounds are commonly found in LFG: corrosive agents

- Removal by pressurized tube exchangers filled with activated carbon: PSA units

  Regeneration by desorption at 200ºC.

PSA unit for biogas, for H_2S, halogenated carbons, and CO_2 removal

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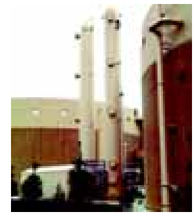
Carbon dioxide stripping

- **Solvent extraction:**
  - **Water scrubbing**
  - **Polyethylene glycol scrubbing (Selexol)**
- **Adsorption:**
  - uses a series of molecular sieves to reduce CO_2 level below 1%.
- **Membrane separation:**
  - High pressure: selective permeation membranes typically composed of cellulose acetate have been used for these purposes.
  - Gas-liquid absorption membranes: (NaOH). Operate at low pressure (1 atm) and temperature (35ºC).



Renton plant
Seattle, USA
4000 m^3/day

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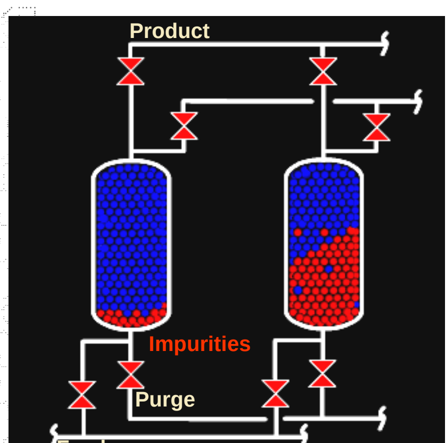
PSA systems
(Pressure Swing Adsorption)



1. **Pressure adsorption**
2. **Co-current despressurisation**
3. **Counter-current despressurisation**
4. **Purge**
5. **Pressurisation**

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Adsorbents in PSA systems

Adsorbent	Application: removed component
Silica gel	H_2O
Activated alumina	H_2O
Activated carbon	CO_2, CH_4, (CO)
Zeolites	CO, N_2, CH_4
ZnO	H_2S, sulfur containing compounds

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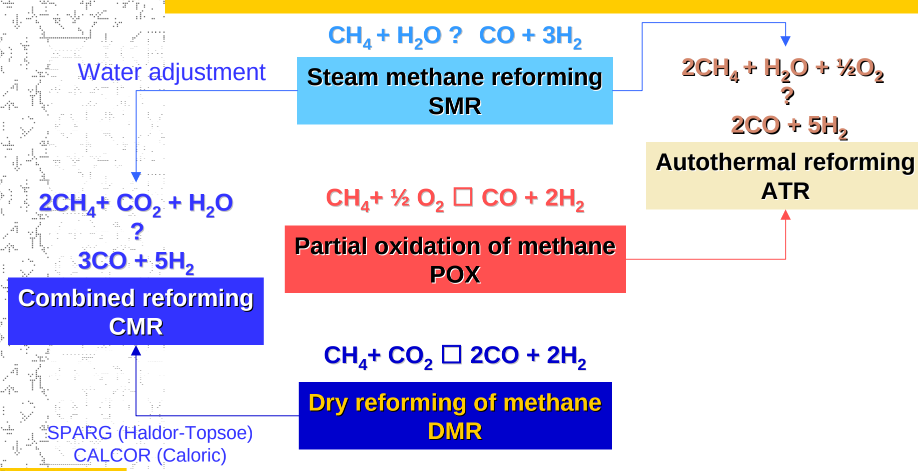
Biogas reforming



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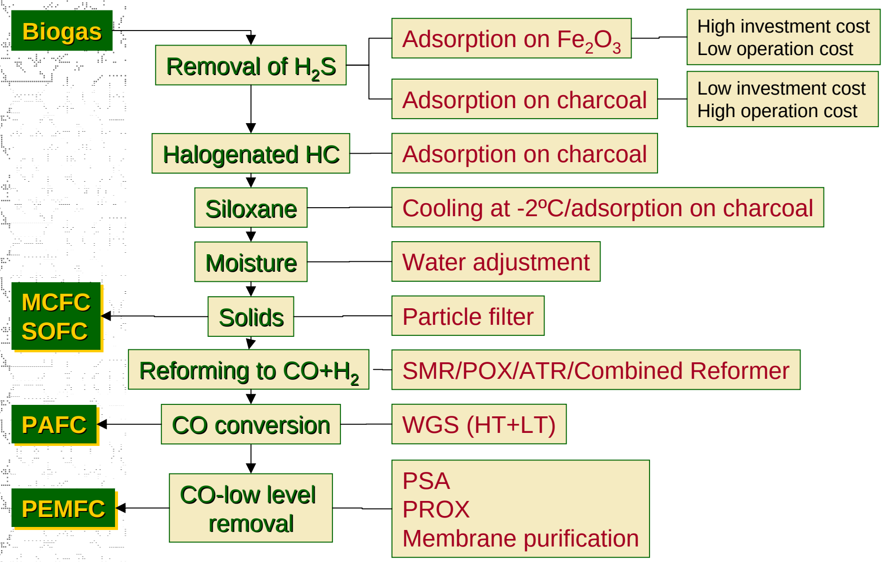
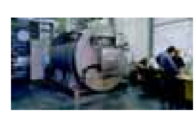
Upgrading processes for FCs



Future perspectives

- High temperature fuel cells are more suitable for biogas use:
  - Higher tolerance to impurities
  - Higher efficiency
  - Simpler purification systems for biogas
  - Simpler reformers
  - CO_2 use for reforming: lower steam requirements


PAFC


MCFC


SOFC

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