BIOENERGY

Chapter 1. Photosynthesis. Process description.

Chapter 2. Biomass. Definition, biomass composition, biomass as a carbon dioxide storage, types of biomass.

Chapter 3. Biofuels. Introduction. Definition, classification. World markets, production, basic technologies for biofuel production. Relative production efficiency. Energy balance. Biofuels from the environmental point of view.

Chapter 4. Definition and composition of bioethanol, raw materials, production technologies, industrial processes, applications.

Chapter 5. Biodiesel. Definition, the transesterification process. Raw materials. Industrial production. Uses and applications.

Chapter 6. Definition and composition of biogas. Sources, process of biodegradation, production technologies, applications.

Chapter 7. Thermochemical technologies for solid biomass processing.

1. DEFINITION OF BIOGAS. COMPOSITION

Biogas: gaseous product obtained from **anaerobic digestion** of organic matter.

Anaerobic digestion: biological process where organic matter, in **absence of oxygen**, with the help of specific bacteria, decomposes organic matter giving these products:

- "Biogas" (CH_4, CO_2, H_2, H_2S, etc.)
- Digestate: solid mixture of inorganic elements (N, P, K, Ca, e.a.) and matter that can be used as a fertilizer.

Biogas composition: It will depend on the substrate and the used technology.

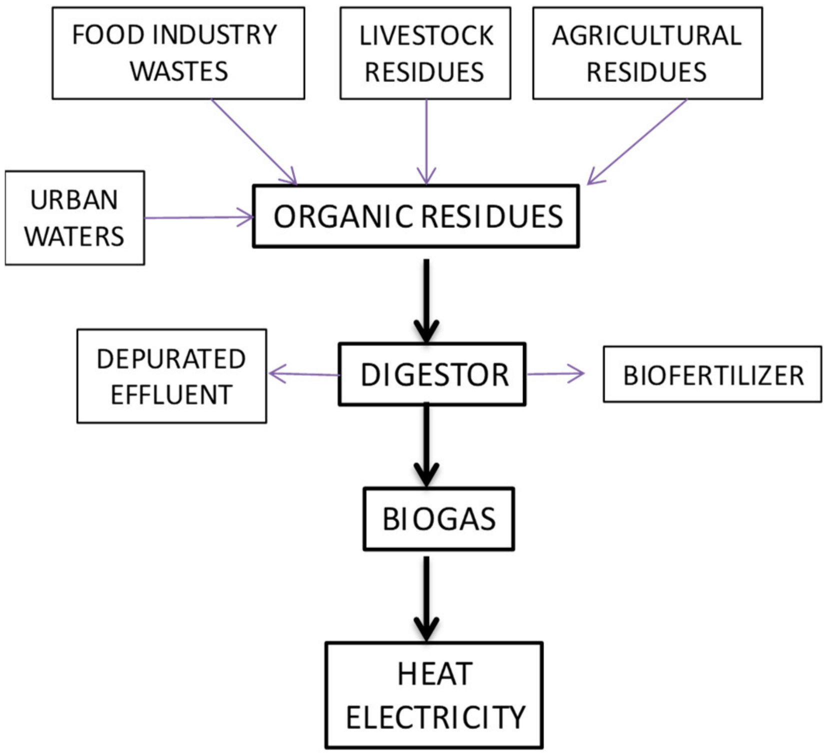
50-70% **methane** (CH_4).
30-40% **carbon dioxide** (CO_2).
≤ 5% hydrogen (H_2), H_2S and some other gases

Biogas has a high methane concentration CH_4 (%50-70), so it can be used to obtain energy through combustion, in engines, turbines or furnaces, pure or mixed with other fuels.

2. Raw materials for biogas production

Raw materials: animal, agricultural or industry residues.

For instance: manure, agricultural refuse or excedent materials, organic fraction of urban refuse and industrial residual waters.



2. Raw materials for biogas production


Livestock residues. Manure

Farming residues


Residues from food-industry


Organic phase of municipal solid waste

Sewage sludge


Waste water from industry

2. Raw materials for biogas production

We can produce biogas from anaerobic digestion of raw materials as far as:

- The matter is in **liquid state**
- There is **organic material** that can be digested
- It has a stable composition and concentration

"Co-digestion": processing of different raw materials for biogas producing.

2. Raw materials for biogas production

2.1 Organic fraction of urban solid waste

The organic faction of urban solid waste can be used as a substrate for anaerobic fermentation. This process is called **bio-methanization or bio-gasification** .

In this process, the **organic matter** will turn into **biogas** and a **solid fraction** with **poorer** quality than **compost**.

In **bio-methanization plants**, it will be necessary to make a **pre-treatment** before starting the process: a separation of the degradable organic matter and grinding to obtain the correct size of the material and insure homogeneity.

Composition of the urban waste: organic matter, paper and cardboard, plastics, metals, textiles and wood.

2. Raw materials for biogas production

2.2 Sludges from the treatment of urban residual water

They are the semi-solid residue that remains after treating the urban residual waters.

They have a rich composition in nutrients, such as N, P and K and present organic matter percentages higher than 60% .

2.3 Industrial residual water

Water is used in almost all the **industrial processes**, during which its composition and quality changes.

The **industrial residual water** is normally **rich** in nutrients, suspended solid matter, bacteria, **organic matter** and, in some cases, toxic compounds.

If the organic matter content is high enough, they will be susceptible of being fermented to produce biogas.

Examples: Food industry water (tin, dairy, meat, wheat industries).

2. Raw materials for biogas production

2.4 Manure and livestock residues

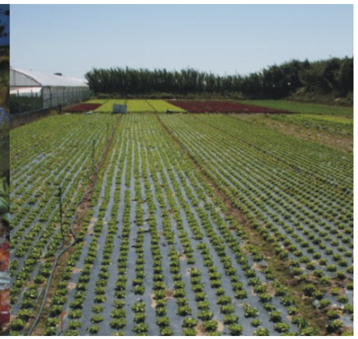
They constitute an important source of organic matter and they need to be treated or eliminated from the environment due to their toxicity and negative impact in the environment.

Feedstock	Dry matter, DM (%)	Organic matter (% of DM)	Biogas yield (m^3/t ODM)	Biogas yield (m^3/t wet)	Average biogas yield (m^3/t wet)
Cow manure	7–15	65–85	200–400	9–51	25
Pig manure	3–13	65–85	350–550	7–61	27
Chicken manure	10–20	70–80	350–550	24–88	51

2. Raw materials for biogas production

2.5 Agricultural residues

- Prunings
- Herbs and stalks
- Cereal straw
- Fruits and vegetales residues

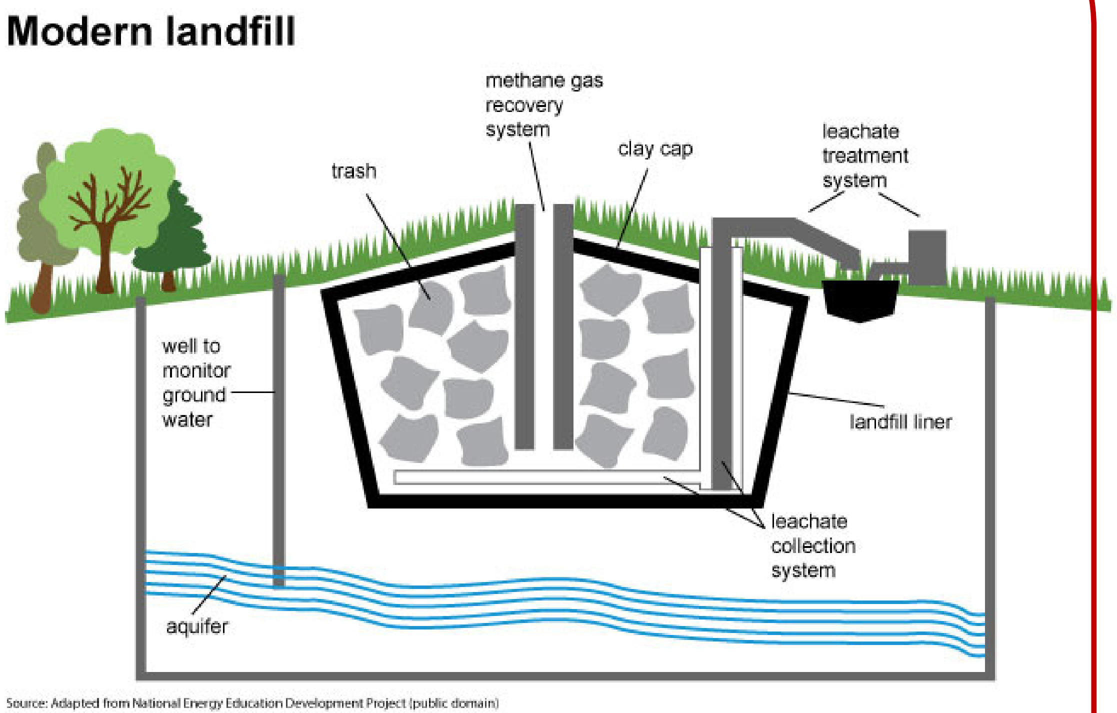


2. Raw materials for biogas production

2.6 Biogas from landfills

- Biogas is produced naturally by anaerobic bacteria in municipal-solid-waste landfills and is called ***landfill gas***.

- Landfill gas, due to its high methane content, can be dangerous to people and the environment because methane is flammable. Thus, it must be removed form landfills and it is interesting to take advantage of its heating power.



www.eia.gov/energyexplained/biomass/landfill-gas-and-biogas.php

2. Raw materials for biogas production

2.5 Biogas composition

The chemical composition of biogas will be determined by the origin and conditions of the formation process.

Table 1: Biogas chemical composition depending on the origin.

Component	Agricultural residues	Urban Waters sludges	Industrial waters	Dumping site gas
Methane	50-80 %	50-80 %	50-70 %	45-65 %
Carbon dioxide	30-50 %	20-50 %	30-50 %	34-55 %
Water	Saturated	Saturated	Saturated	Saturated
Hydrogen	0-2 %	0-5 %	0-2 %	0-1 %
Hydrogen sulfide	100-700 ppm	0-1 %	0-8 %	0,5-100 ppm
Ammonia	Traces	Traces	Traces	Traces
Carbon monoxide	0-1 %	0-1 %	0-1 %	Traces
Nytrogen	0-1 %	0-3 %	0-1 %	0-20 %
Oxygen	0-1 %	0-1 %	0-1 %	0-5 %
Other organic compounds	Traces	Traces	Traces	5 ppm

2. Raw materials for biogas production

2.5 Biogas composition

The biogas production is determined by the organic load of the substrate and its biodegradability.

Residue	Organic content	Volatile solids	Biogas production
Pig manure	Carbohydrates, lipids and proteins	3 -5 %	10-20 m^3 / Tm
Residual sludges	Carbohydrates, lipids and proteins	3 -4 %	17-20 m^3 / Tm
Concentrated residual sludges	Carbohydrates, lipids and proteins	15 -20 %	85-110 m^3 / Tm
Solid urban residues organic fraction	Carbohydrates, lipids and proteins	20 -30 %	150-240 m^3 / Tm

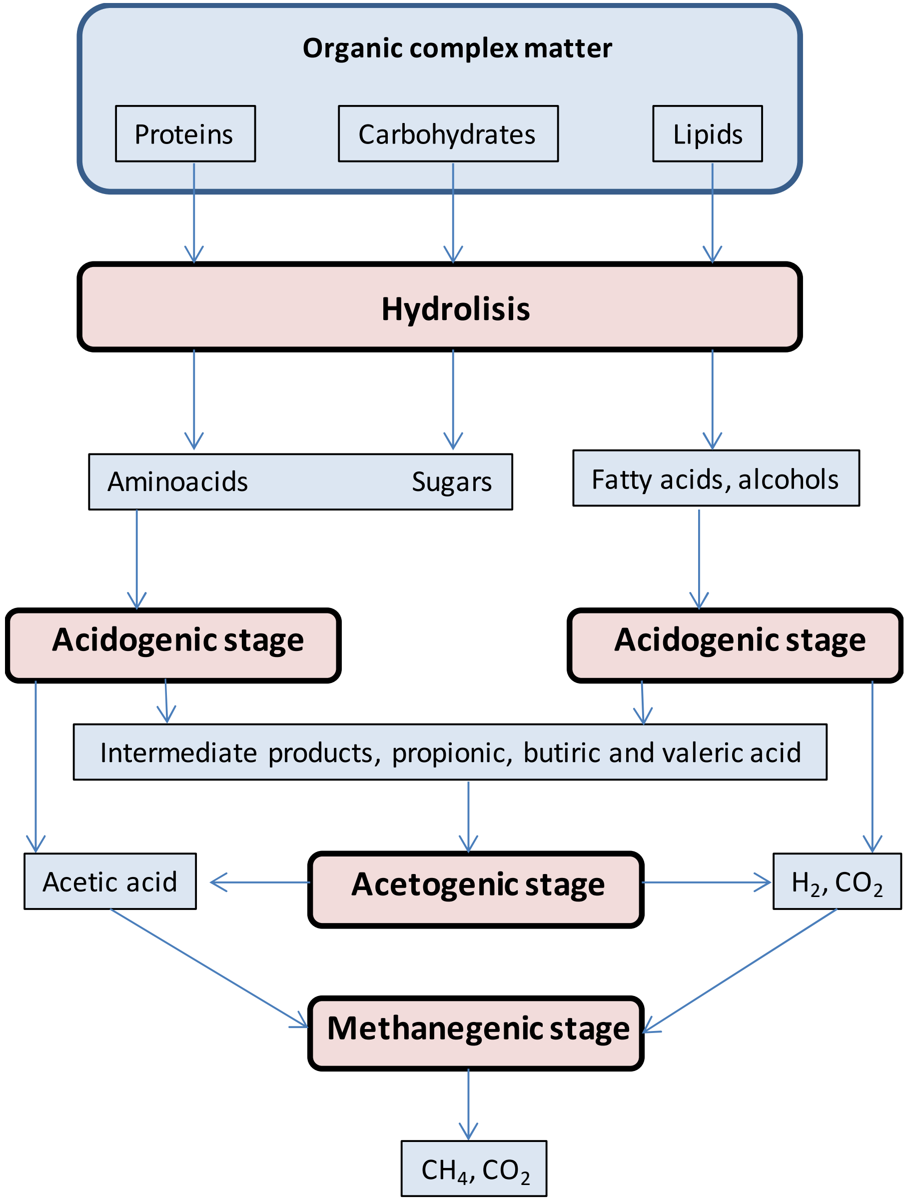
3. BIODEGRADATION PROCESS

3.1. Anaerobic fermentation steps

Organic matter fermentation process is divided in 4 stages.

Every stage is ruled by a different bacteria type.

1. Hydrolisis
2. Acidogenesis
3. Acetogenesis
4. Methanegenesis



3. BIODEGRADATION PROCESS

3.1. Anaerobic fermentation steps

3.1.1. Hydrolisis

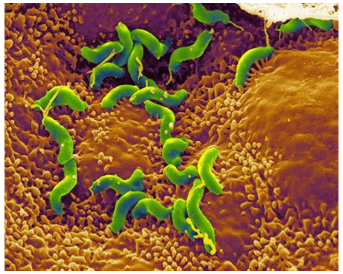
- It is the first neccesary step for the fractionation of complex organic matter into smaller molecules.

- The hydrolitic bacteria depolymerize the organic matter into their monomer constituents.

- Lipids are degradated by lipases into long chain fatty acids and glycerine.

- Proteins are hydrolized by proteases into peptides and aminoacids.

- Polisaccarides are converted in monosaccarides.



3. BIODEGRADATION PROCESS

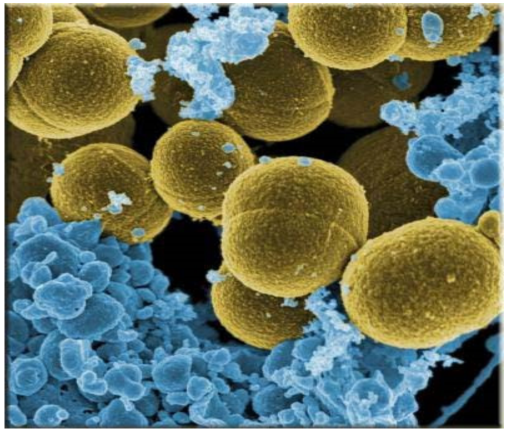
3.1. Anaerobic fermentation steps

3.1.2. Acidogenic stage

- The obtained soluble compounds from the previous step are transformed by acidogenic bacteria into short chain fatty acids (volatile fatty acids), alcohols, ammonia, hydrogen and carbon dioxide.

- The main volatile acids are acetic, propionic, valeric and butiric acids.

- In this step it is important to control the quantity of present hydrogen because the metabolism of acetogenic bacteria strongly depends on it.



3. BIODEGRADATION PROCESS

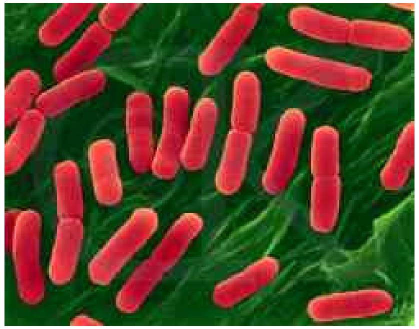
3.1. Anaerobic fermentation steps

3.1.3. Acetogenic stage

- Some fermentation products, such as hydrogen and acetic acid, can be directly metabolized by methanegenic organisms but other intermediate products can't (butiric, propinic acids for instance).

- Acetogenic bacteria converts these intermediate products into smaller molecules giving acetic acid, hydrogen and carbon dioxide as main products.

- Acetogenic bacteria needs an exhaustive control of hydrogen concentration as high pressures of this compound entail the inhibition of acetates formation and propionic and butiric acids or ethanol are produced instead of methane.



3. BIODEGRADATION PROCESS

3.1. Anaerobic fermentation steps

3.1.4. Methanegenic stage

- In the last step of the process, **methanegenic bacteria** transforms **acetic acid**, **hydrogen** and **carbon dioxide** into **methane** and **carbon dioxide**.

- In this step the bacteria type is totally anaerobic.

- Two types of microorganisms can be distinguished:
  - Those that degradate **the acetic acid** into **methane** (CH_4) and **carbon dioxide** (CO_2) (**classic methanegenic bacteria**)
  - Those that degradate $\mathbf{CO_2}$ in the presence of H_2 to form $\mathbf{CH_4}$ and $\mathbf{H_2O}$ (hydrophilic methanegenic bacteria).

$$CH_3COOH \rightarrow CH_4 + CO_2$$
$$CO_2 + H_2 \rightarrow CH_4 + H_2O$$

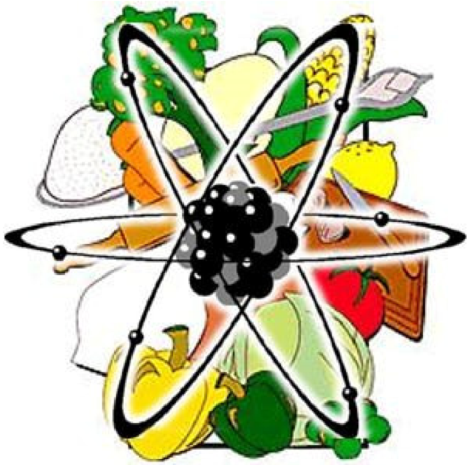
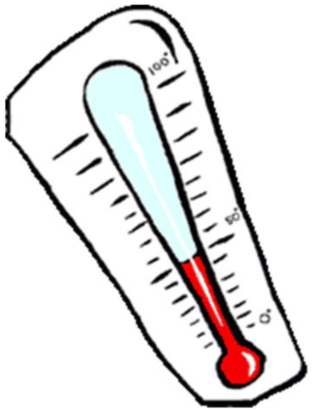
The main reaction for the production of **methane** is the first one with about the 70% of the total produced methane. It is an slow process and the limiting step of the global process.

3. BIODEGRADATION PROCESS

3.2 Process conditions

Several physical and chemical factors influence the process:

- Nutrients
- Temperature
- pH
- Solids content
- Residence time
- Process inhibitors
- Stirring


3. BIODEGRADATION PROCESS

3.2 Process conditions

Nutrients

- Mineral nutrients (nytrogen, sulphur, phosporus, potassium, calcium, magnesium, etc.) are required in this process, appart from an organic carbon source and energy.

- A proper nutrients ratio must be present for the proper growing of the bacteria.

-**C/N ratio** should be from 15/1 to 45/1, as lower values decreases the reaction speed.

- **P/N optimum ratio is** 150/1.

- The organic fraction of the urban residues, the manure and the water sludges present proper nutrient ratios.

- Industrial residues often need to add some elements to obtain a proper ratio.

3. BIODEGRADATION PROCESS

3.2 Process conditions

Temperature

Anaerobic digestión can be performed in a wide range of temperaturas but, depending on the bacteria type used, three ranges are typically defined:

Bacteria	Temperature range	Sensibility
Psicrophilics	Less than 20 ºC	± 2 ºC / hour
Mesophilics	20-40 ºC	± 1 ºC / hour
Thermophilics	More than 40 ºC	± 0,5 ºC / hour

Generally, **mesophilic bacteria** type is the more widely used, even if the **thermophilics** give the highests biogas productions, but this last type is very sensitive and needs strict temperature control and a more expensive maintenance of the system.

3. BIODEGRADATION PROCESS

3.2 Process conditions

pH

- It is a typical controlled parameter in this kind of processes. In each phase of the process the optimal pH for the working bacteria is different.

- **Optimal pH ranges**
  - Hydrolitic microorganisms: 7.2 to 7.5
  - Acetogenic microorganisms: 7 to 7.2
  - Methanegenic microorganisms: 6.5 to7.5.

Solids content

It is a very influencing factor as the mobility of bacteria in the media is limited by existing solid content and, thus, the biogas production is limited too.

3. BIODEGRADATION PROCESS

3.2 Process conditions

Retention time

- It is defined as the time during which the substrate is in contact with the different bacteria.

- This parameter can be precisely measured in batch reactors.

- In semi-continuous or continuous reactors the **residence time** is defined instead as the ratio between the reactor volume and the dairy load.

- The required time is highly dependent on the used substrate and the temperature. Higher temperaturas imply lower times or volumes.

3. BIODEGRADATION PROCESS

3.2 Process conditions

Inhibitors

- There are different inhibitor substances, among which, oxygen has an important negative influence.

- If the used substrate has **high nitrogen** contents, the formation of **ammonia** may happen and **inhibit** the process.

- **Heavy metals** are **toxic** to methanegenic organisms.

- Some organic substances, such as **antibiotic**s or **detergents** can **inhibit** the process as well.

- **High content** of **volatile acids** can be **harmful**.

3. BIODEGRADATION PROCESS

3.2 Process conditions

Inhibitors

Inhibitors	Concentration (mg/mL)
Sulphur (S)	200
Cu	10-250
Cr	200-2000
Zn	350-1000
Ni	100-1000
CN	2
Na	8000
Ca	8000
Mg	3000

3. BIODEGRADATION PROCESS

3.2 Process conditions

Stirring

- Several aspects of the process are favoured by the stirring:

  - Mix and homogeneization of the substrate
  - Uniform heat distribution in order to have homogeneous temperature
  - Favour the gas transference
  - Avoid foam formation and solids sedimentation

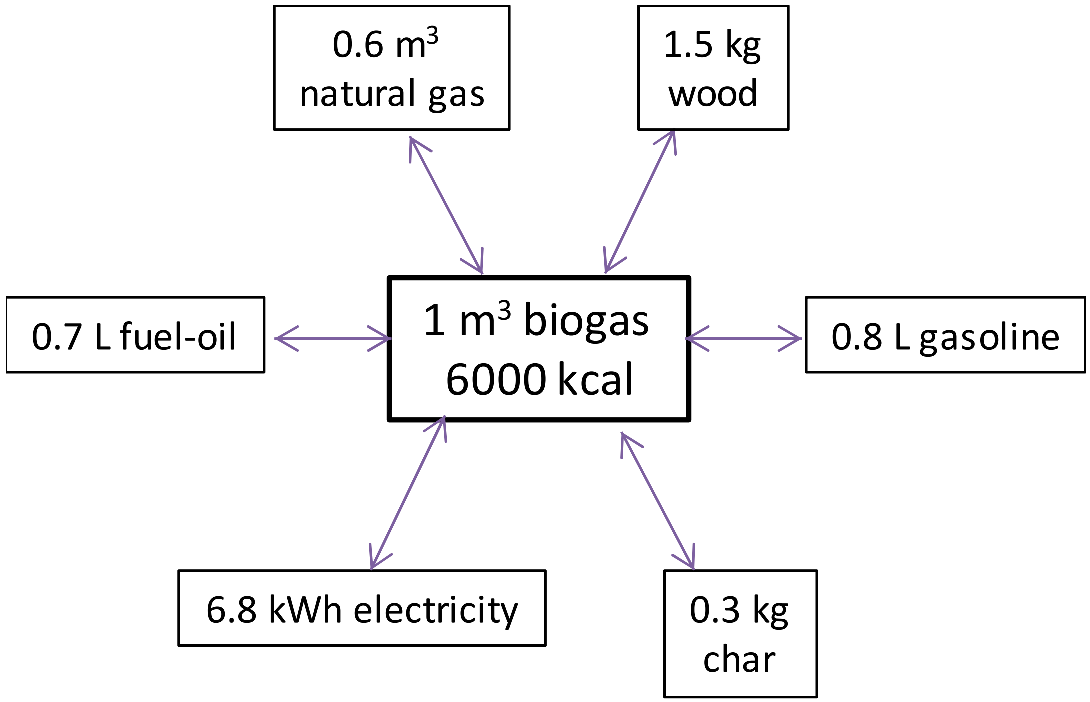
- Stirring can be mechanical or pneumatic, trhough gas bubbling up.

- It must be homogeneous and smooth in order not to destry the bacteria groups.

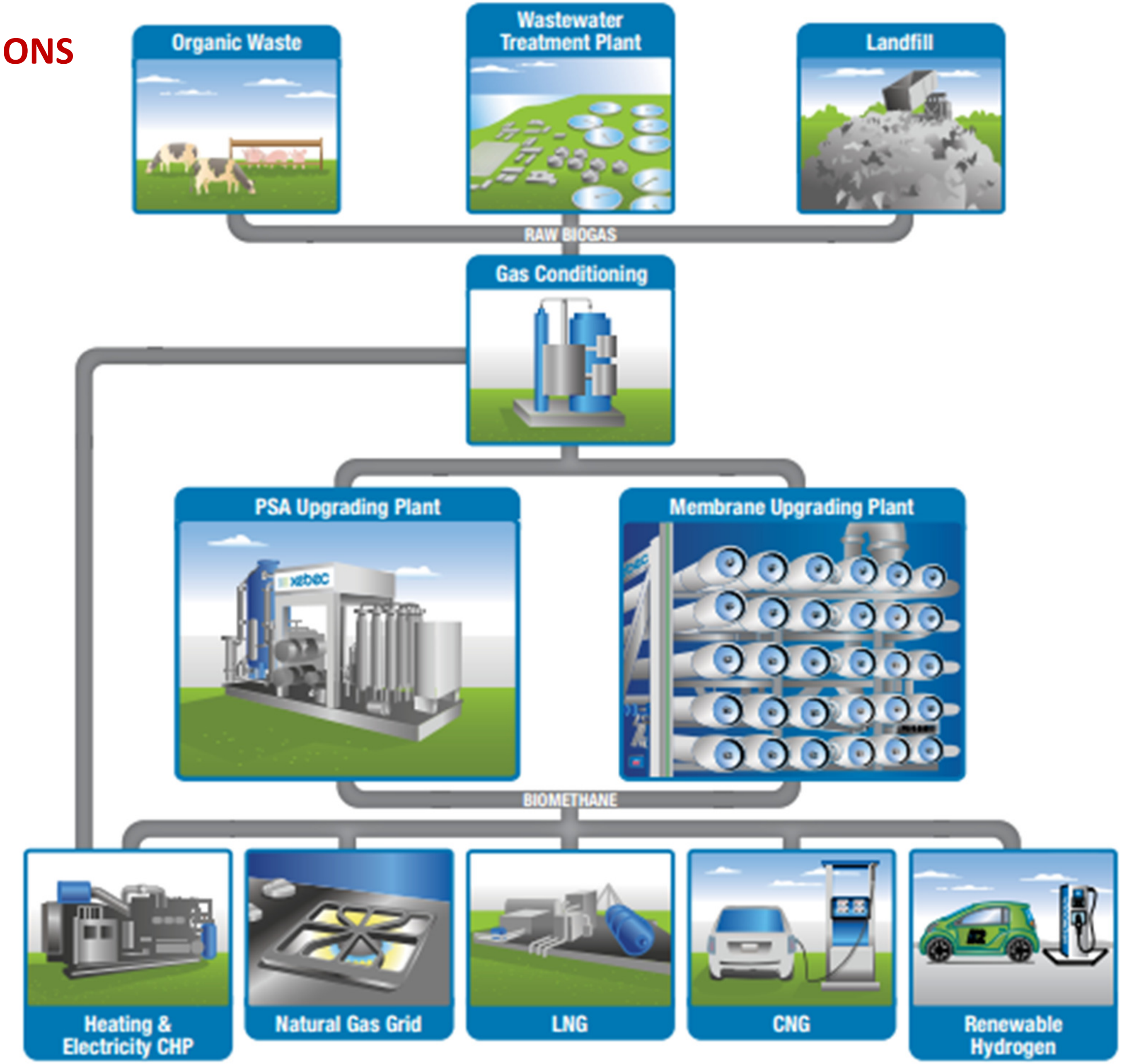
4. APPLICATIONS

Biogas

- → High methane content
- → Heating value ~ ½ the power of natural gas.
- → Biogas, formed by methane in a 60% has a calorific value of about 5.500 kcal/Nm^3 (6,4 kWh/Nm^3)
- → Except for the presence of H_2S, it is **an ideal fuel**



4. APPLICATIONS



https://www.xebecinc.com/applications-biogas.php

4. APPLICATIONS

4.1 Heat production from direct combustion

Biogas can be used for **heat generation** through **combustion**.

This heat might have different uses:

- Heating and Sanitary Hot Water obtaining in installations.
- Heating of the anaerobic digestion reactors.
- To incinerate or sterilise medical waste.
- For biomass drying.
- For space heaters, gas cookers, burners in both industrial or domestic areas.
- For domestic refrigerators.
- In refrigeration systems for dairy and other agricultural products.

Main problem:

The **heating value of raw biogas is quite low**, so it is **not economically viable to transport** it. This means it will have to be used as close as possible from the biogas source.

4. APPLICATIONS

4.2 Electricity generation

Right now, **the most interesting use for biogas.**

There are three main ways to obtain electricity from biogas:

· Electricity generators connected to **combustion engines.**
· Using gas **turbines or microturbines**.
· **Fuel Cells**

4.2.1 Electricity generation in combustion engines

Electricity can be generated thorugh combustion engines, both diesel and gasolina type ones.

The removal of some impurities is compulsory for this application.

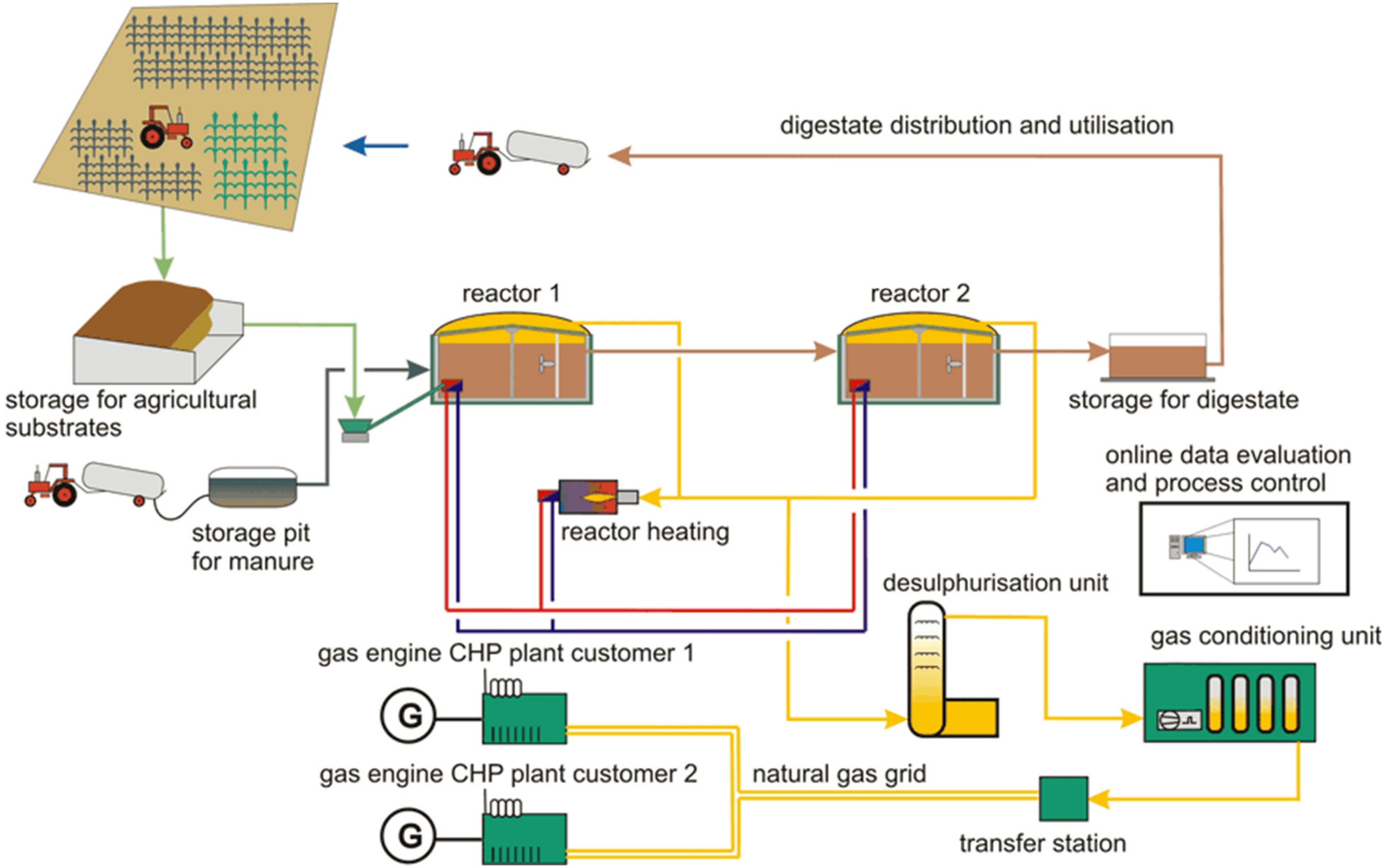
4. APPLICATIONS

4.3 Integration into the natural gas piping system

- As its main component is **methane**, it is possible to inject it into the natural gas piping system.
- It needs to be cleaned and refined: removal of CO_2, SH_2, NH_3, water and solid particles) to meet the quality criteria needed for injection into the system.
- Any system that works with natural gas should be able to use biogas.
- The natural gas net connects the production location with the high energy demand areas.
- It is possible to generate the biogas in remote locations and enhances the local provisioning.

4. APPLICATIONS

4.3 Integration into the natural gas piping system



https://www.bios-bioenergy.at/en/references/all-projects/bad-tatzmannsdorf.html

4. APPLICATIONS

4.4 Transport fuel

It is a promissing use for biogas, together with electricity generation.

It has beeen proven as a very good option for city public transportation and garbage collection trucks.

Once impurities of the biogas (CO_2, SH_2, NH_3, water and solid particles) have been removed and we reach a 95% methane purity, it can be compressed and used in vehicles that run on natural gas.

Compressed natural gas refuelling facility

www.cga.ca/news_item/canadas-natural-gas-utilities-propose-target-for-renewable-natural-gas-content/

4. APPLICATIONS

4.5 Use in fuel cells

Fuel cells are electrochemical systems in which chemical energy is converted into electricity.

The fuel cell is on while fuel and oxidant are present

It is formed by an **anode** in which the fuel is injected (normally hydrogen or ammonia) and a **cathode** in which an oxidant is injected (oxygen or air). Both electrodes are separated by and ionic electrolitic conductor.

The procedure is the reverse water electrolysis procedure, in which water si separated into hydrogen and oxygen under an electric current.

In fuel cells electric energy is obtained trhough the reaction of hydrogen and oxygen:

$$H_2 \quad + \quad O_2 \quad \leftrightarrow \quad H_2O \quad + \quad \text{electricity}$$

4. APPLICATIONS

4.5 Use in fuel cells

Efficiency is quite high (>60 %) and the only generated product is water vapour.

Heat is generated as well so co-generation can be considered as well.

When biogas is used in cell fuels, it is previously converted in hydrogen.

Methods to convert biogas into hydrogen

- *Water vapour reforming*
- *Partial oxidation*
- *Autoreforming*

4. APPLICATIONS

4.5 Use in fuel cells

Water vapour reforming: consist of mixing methane and water vapour in a high temperature reactor, by the following reaction:

$$CH_4 \quad + \quad H_2O \quad \leftrightarrow \quad CO \quad + \quad 3H_2$$

This is a high endothermic reaction and the reactors are limited by the heat transfer. Hydrogen concentrations of up to 70% are achieved.

Partial oxidation: methane reacts with oxygen in concentrations lower than the stoichiometric one through the following reaction:

$$CH_4 \quad + \quad 1/2O_2 \quad \leftrightarrow \quad CO \quad + \quad 2H_2$$

The generated heat can increase the gas temperature up to 1000ºC. The yield is lower than the first reaction one.

Autorreforming combines the two previous processes. The generated heat of the second reaction is used in the first part. A catalyst is used to model the reactions between the gas and vapour.

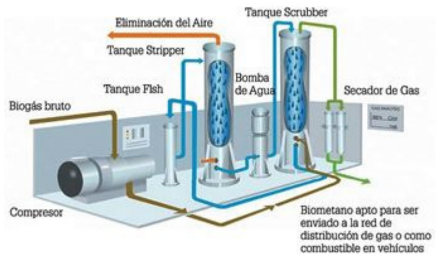
5. REFINING

Ordering biogas uses depending the degree in refinning, from less to most:

- Heat generation through direct combustion

- Electricity generation

- Injection into the natural gas network



- Transportation fuel

- Fuel in fuel cells

5. REFINING

Biogas refining

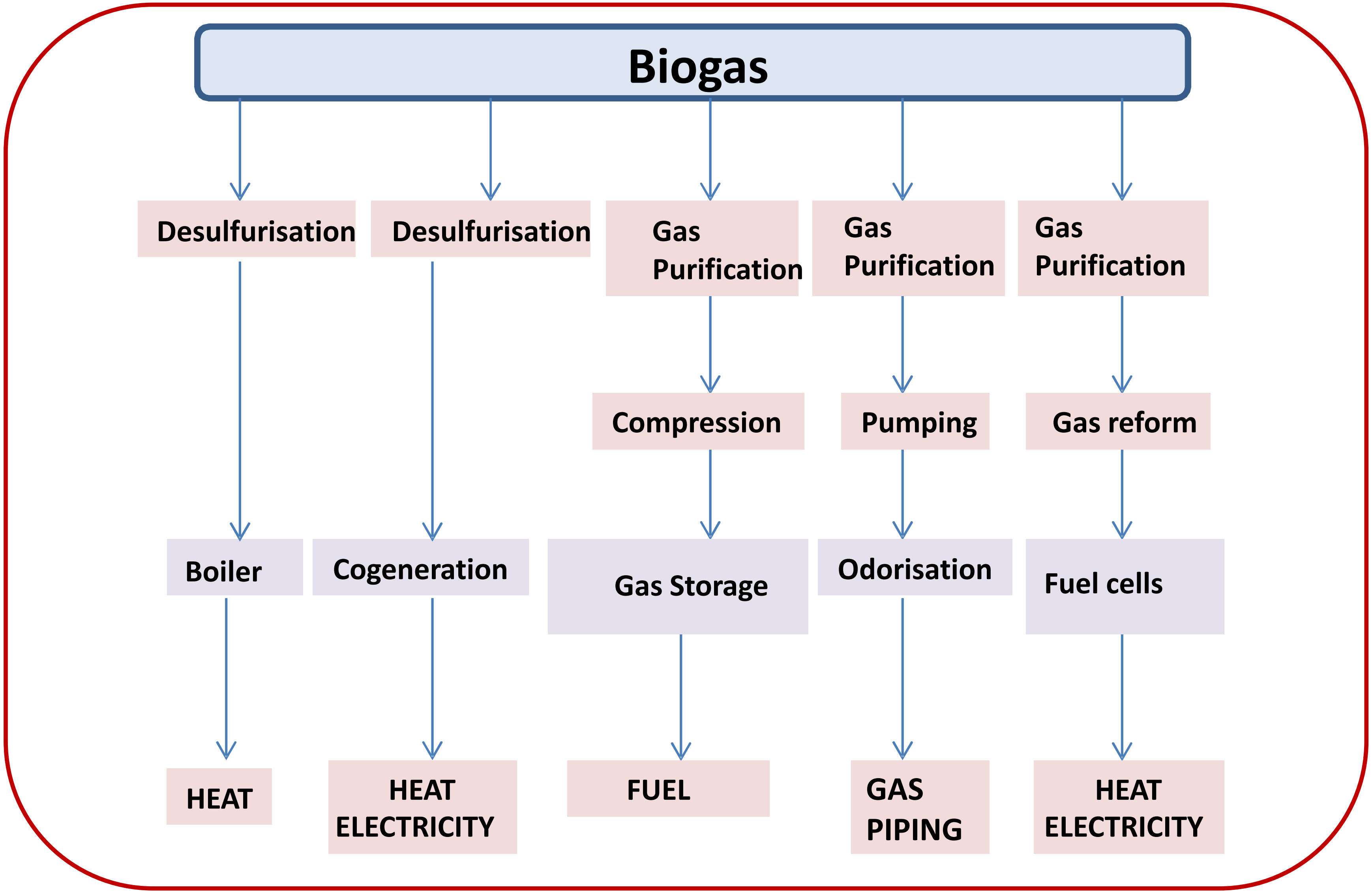
Biogas must be refined BEFORE any energy application.

Biogas purification includes the removal of CO_2, SH_2, NH_3, water and solid particles.

The purification operations will depend of the final use for the biogas.

The quality requirements will be most astringent for automotive fuel, injection into the natural gas network and for their use in fuel cells.

5. REFINING


Biogas
Desulfurisation
Desulfurisation
Gas Purification
Gas Purification
Gas Purification
Compression
Pumping
Gas reform
Boiler
Cogeneration
Gas Storage
Odorisation
Fuel cells
HEAT
HEAT ELECTRICITY
FUEL
GAS PIPING
HEAT ELECTRICITY