Anaerobic digestion and energy

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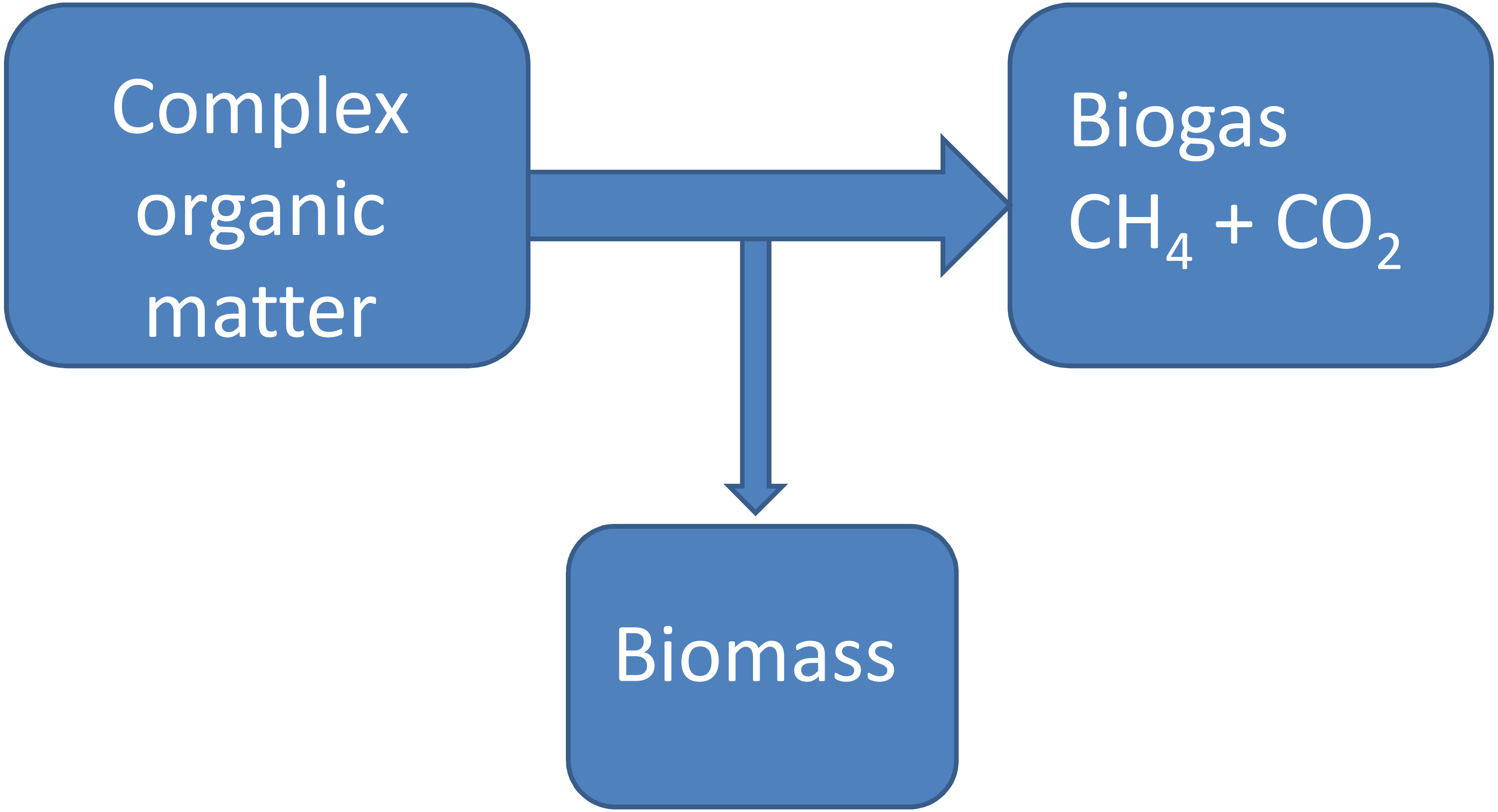
Carbon flow in anaerobic consortia



Energy

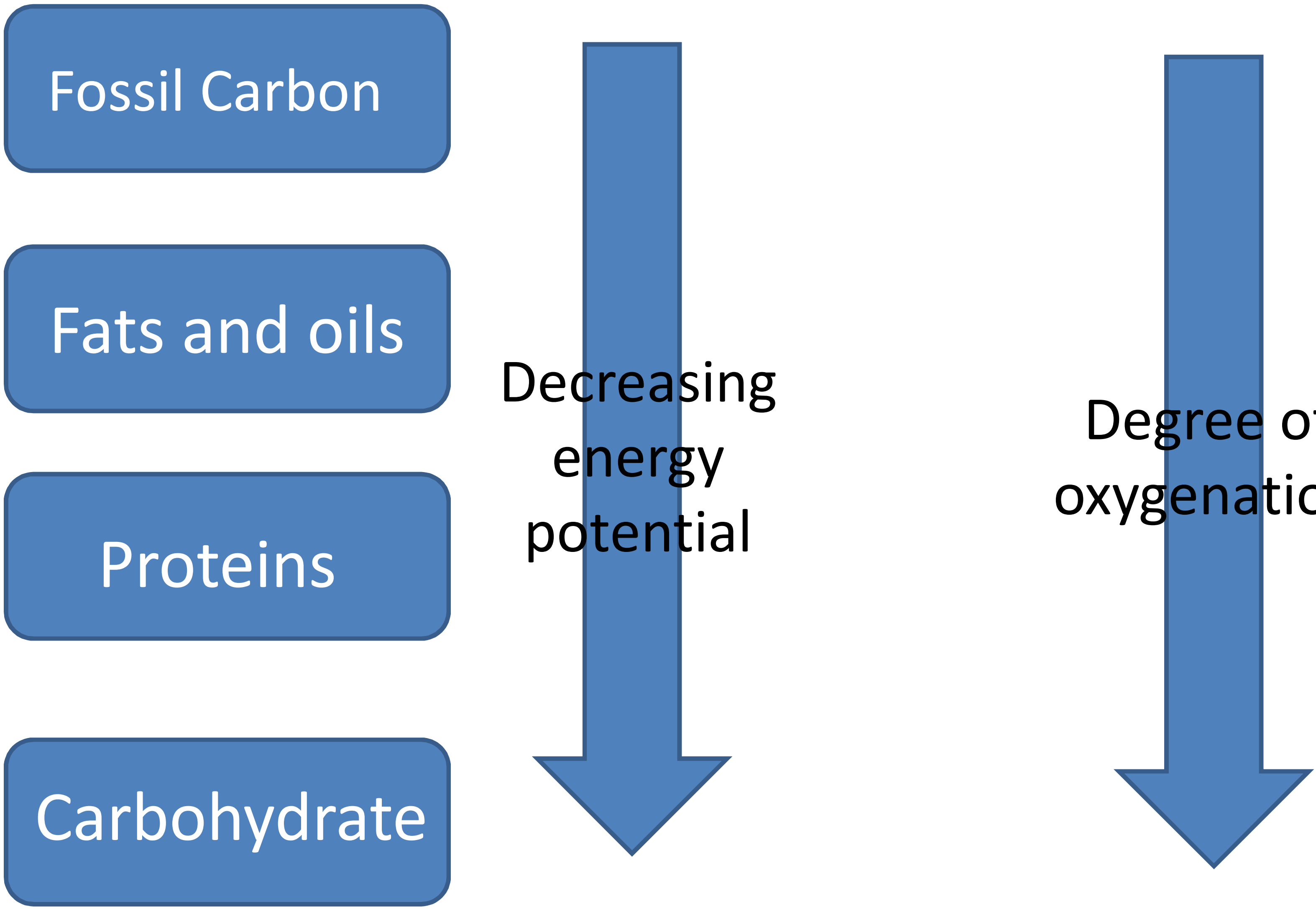
CO_2

Oxidised carbon – no energy value

CH_4

Reduced carbon – energy value

Energy potential of materials



Measurement of energy values

- Calorimetery is the study of enthalpy (energy) change– generally denoted as ΔH
- Rely mainly on detection of temperature change
- Many types of calorimeter exist for different purposes
- In measuring the energy potential of materials we are interested in the enthalpy of combustion or calorific value (CV) of a materials

Calorific value

- Measurement of the heat generated on combustion
- Different values can be obtained for the same material depending on the water content of the material
- The difference is due to the amount of water needed to vaporise the water present in the sample

Calorie

- The original scientific unit in which changes in energy were measured

- The heat energy required to raise the temperature of 1 gram of water by 1^oC

Higher and lower heat values

- "***higher heat value (kJ/g)*** [HHV] is determined on a dry sample.
- "***lower heat value (kJ/g)*** [LHV] is the net energy released on combustion:

LHV = HHV - (2.766 x W) kJ/g

where:

W = moisture content

2.766 kg/g = coefficient of heat requirement for evaporation

(Enthalpy of vaporisation)

N.B. We have switch or unit of measurement

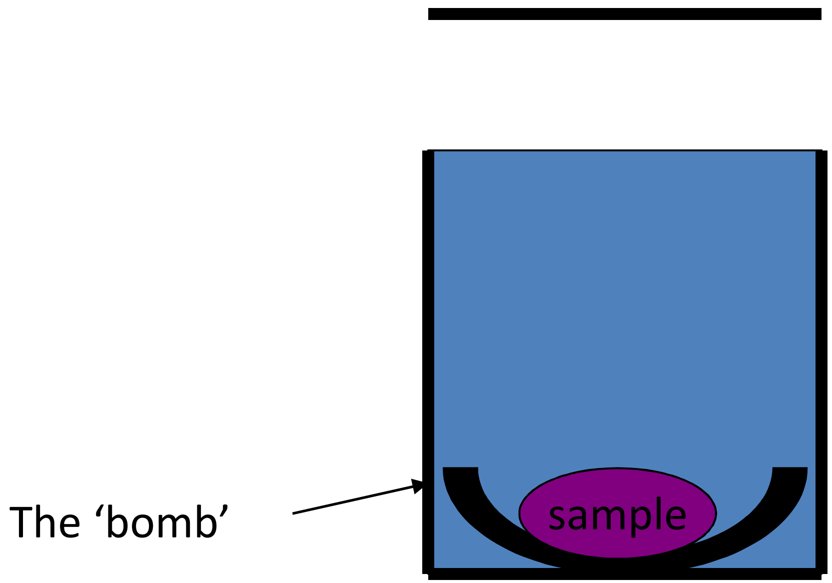
Joule

1.0 joule (J) = one Newton applied over a distance of one meter (= 1 kg m^2/s^2).

1.0 joule = 0.239 calories (cal)

1.0 calorie = 4.187 J

Bomb Calorimetery - Procedure



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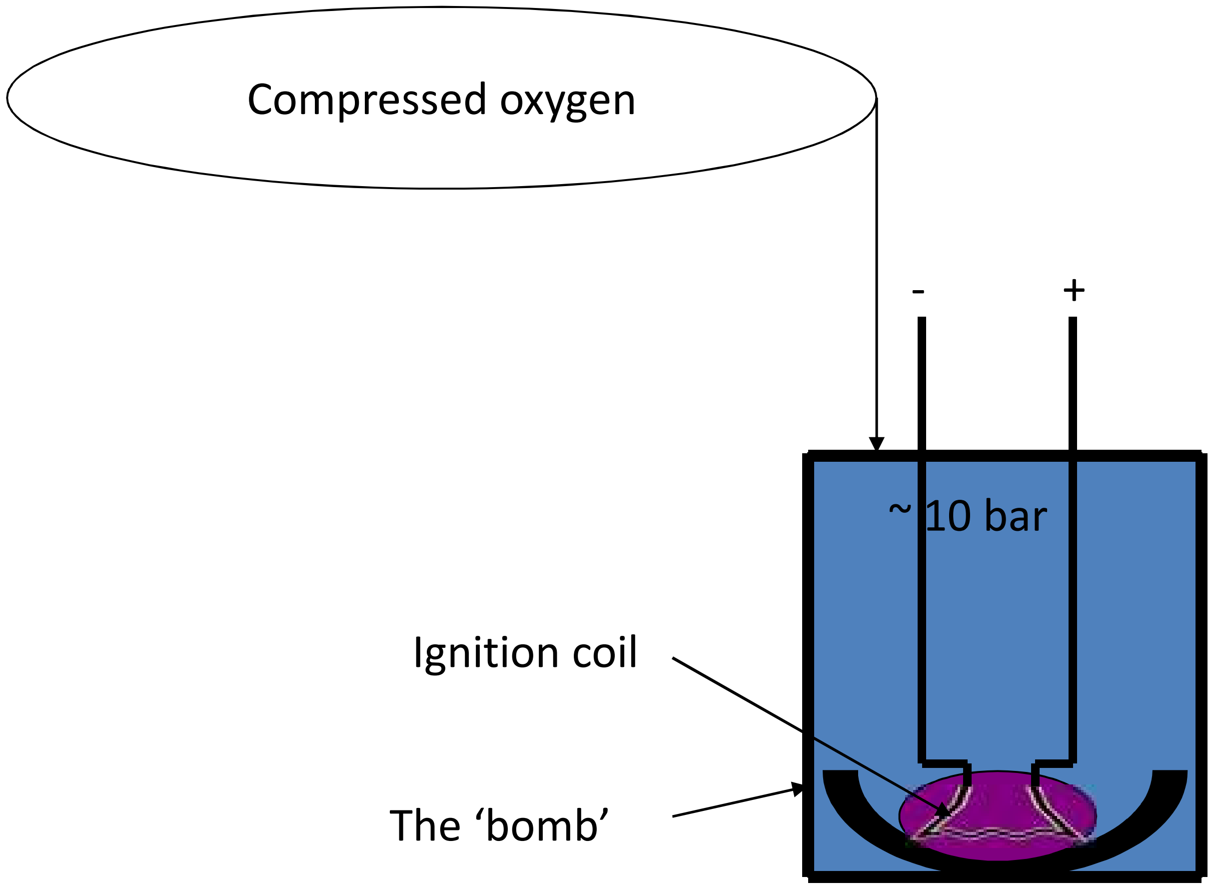

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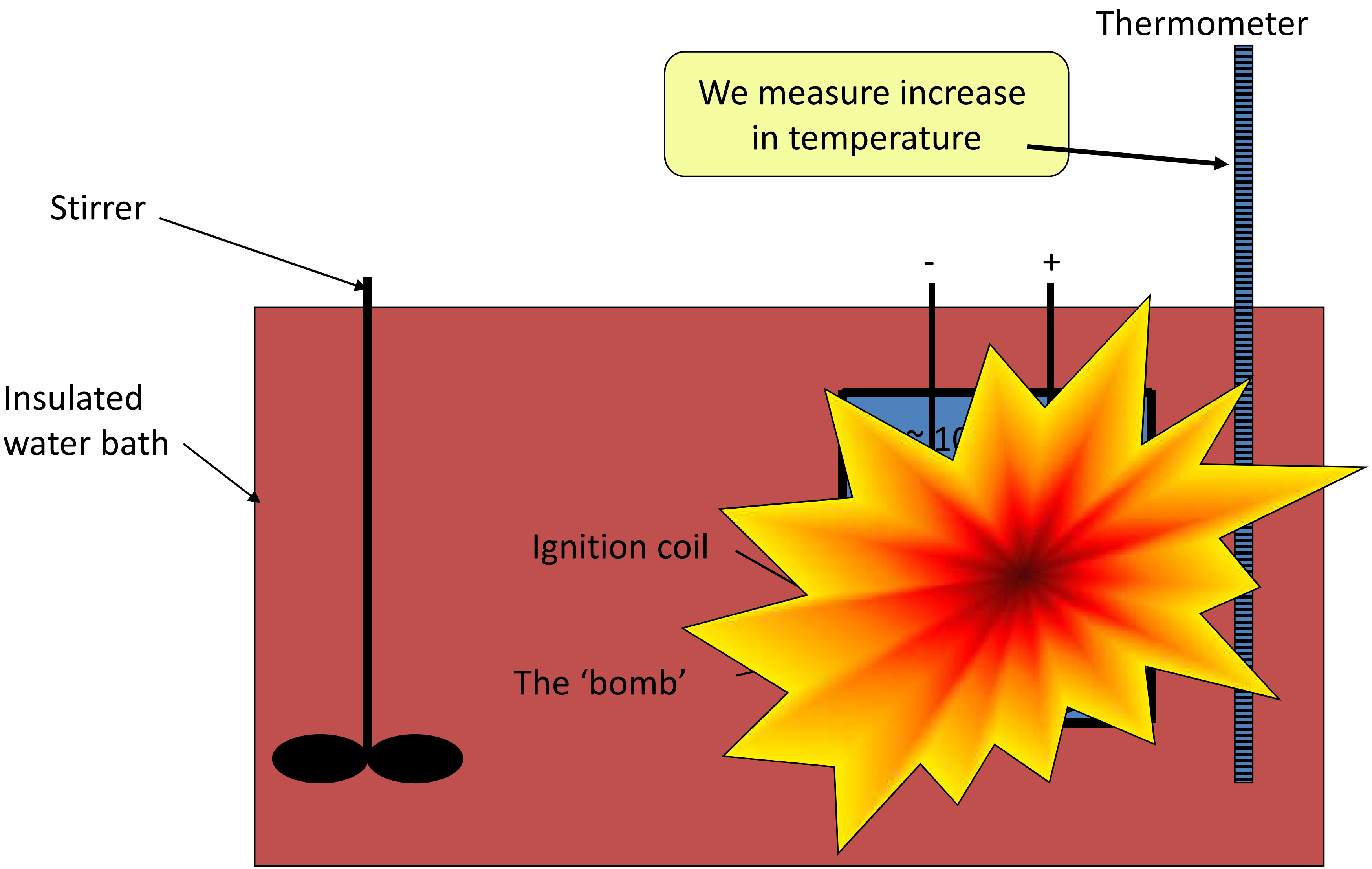
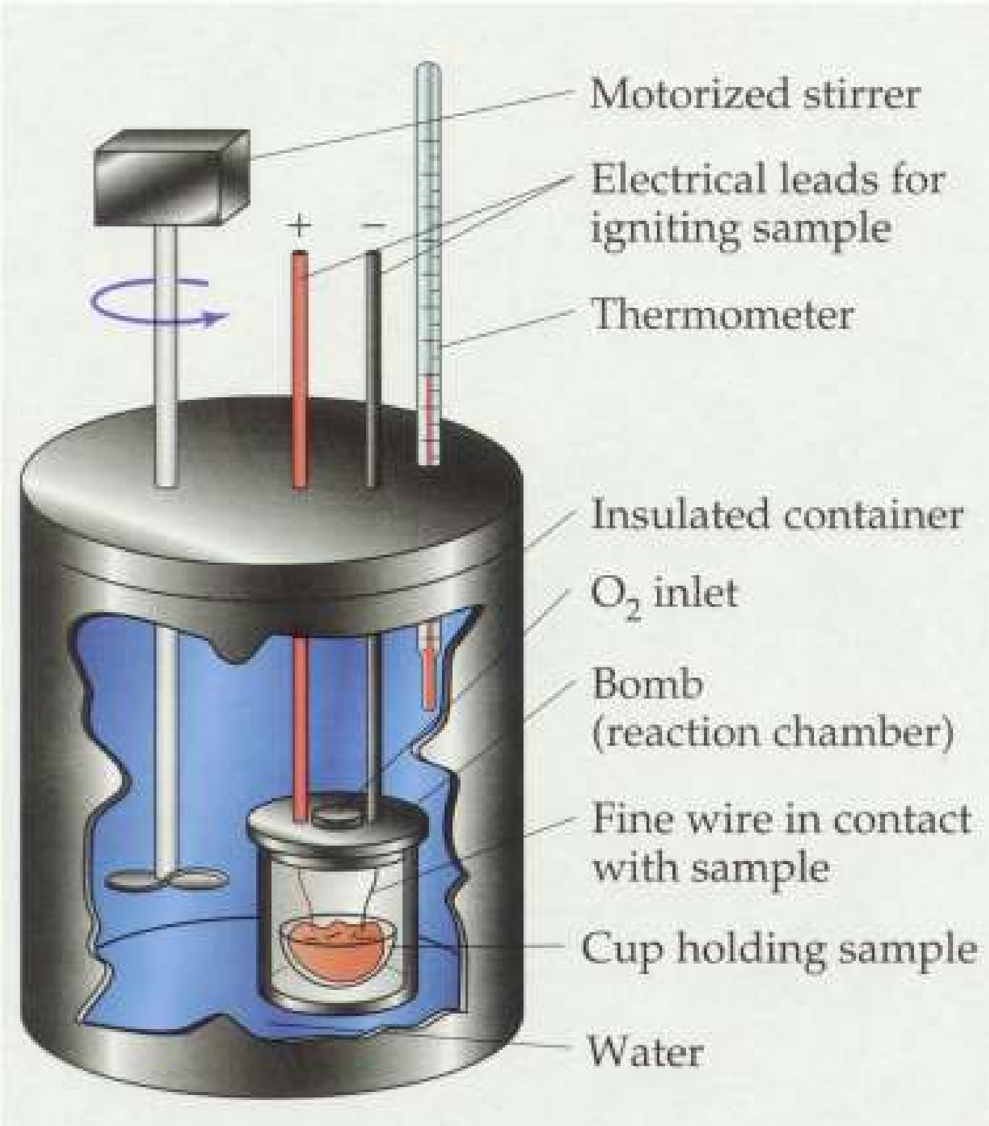


The Bomb Calorimeter



- Temperature increase is used to calculate the energy released
- Other data needed;
  - Heat capacity of the system including the water, bomb, coil etc.
  - Amount of energy input by the ignition coil
  - The sample weight added
- Modern bomb calorimeters do this for you!

The Bomb Calorimeter

Calorimetery – Example Calculation

A sample of maize has a Total Solids (TS) content of 20% and a VS content of 92% of TS. After analysis of the dry material in a bomb calorimeter the calorific value (CV) was found to be 16.31 kJ/gTS. Calculate the calorific value and lower heating value per gram VS.

1. All energy output comes from the volatile solids which are 92% of the maize (0.92 gVS/gTS), the VS content of the wet maize is 0.92*0.2=0.184 = 18.4%
2. CV per gram VS = CV per gram TS / (gVS/gVS) = 16.31 / 0.92 = **17.54 kJ/gVS**

Calorimetery – Example Calculation (continued)

1. The maize sample is 80% water and therefore contains 80 / 18.4 = 4.34 g water/gVS (grams of water per gram volatile solids)

2. Energy required to vaporise the water = weight of water * enthalpy of vaporisation = 4.34 * 2.766 = 12.02 kJ/gVS

3. LHV = HHV – energy to vapourise water = 17.54 – 12.02 = **5.52 kJ/gVS**

Ultimate analysis

we can also determine the calorific value of a material from its elemental composition in terms of:

Carbon	(C)
Hydrogen	(H)
Oxygen	(O)
Nitrogen	(N)
Sulphur	(S)
Ash	

The HHV can then be calculated using the Dulong equation:

$$HHV = 337C + 1419\ (H2 - 0.125\ O2) + 93\ S + 23\ N$$

Use of calorimetry in anaerobic digestion studies

- The HHV is the maximum amount of energy contained in the chemical structure of the material
- The HHV will always be higher than can be obtained in terms of ‘energy product’ from a biological system as ‘energy’ is consumed in the catabolic and anabolic metabolic pathways
- It provides however a performance benchmark for AD systems

But we don't have a calorimeter or an elemental analyser ☹

Use of Chemical Oxygen Demand

- COD is commonly used in the water and wastewater industry to measure the organic strength of liquid effluents
- It is a chemical procedure using strong acid oxidation
- The strength is expressed in 'oxygen equivalents' i.e. the mg O_2 required to oxidise the C to CO_2

Using the COD concept to estimate methane yield

- One mole of methane requires 2 moles of oxygen to oxidise it to CO_2 and water, so each gram of methane produced corresponds to the removal of 4 grams of COD

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$$

$$16 \quad\quad 64$$

or:

1kg COD is equivalent to 250g of methane

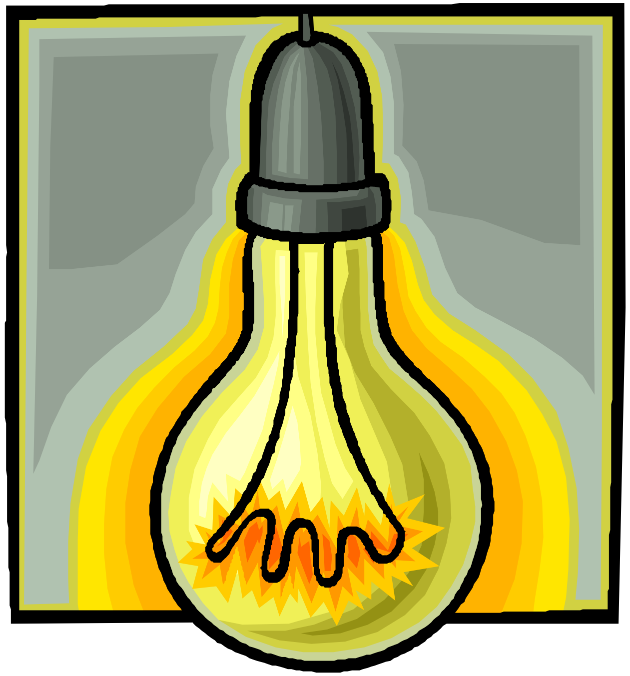
- 1kg COD $\Rightarrow$ 250g of CH_4
- 250g of CH_4 is equivalent to 250/16 moles of gas = 15.62 moles
- 1 mole of gas at NTP = 22.4 litres

  therefore 15.62 x 22.4 = 349.8 litres

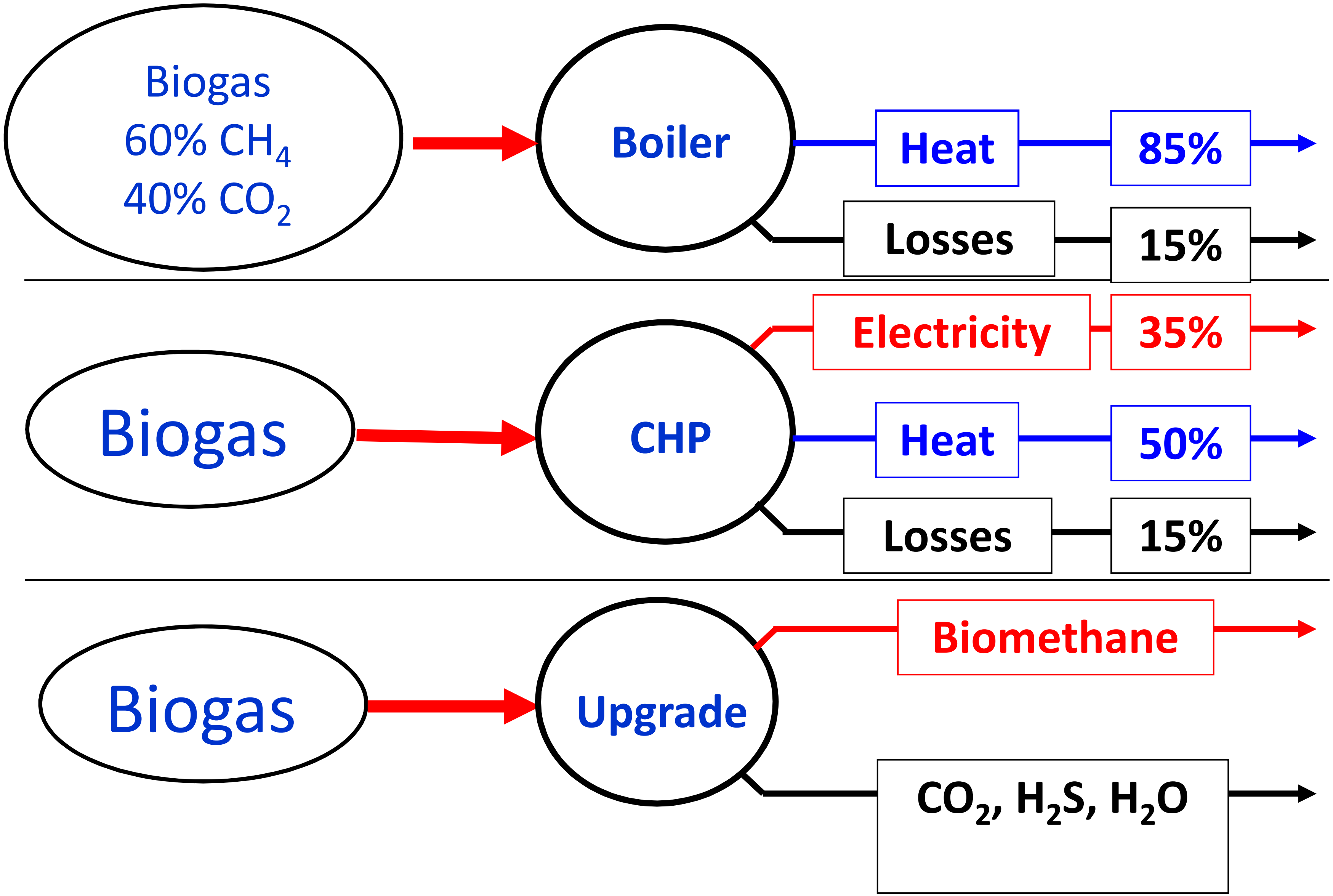
  = 0.35 m^3
- At standard temperature and pressure each kilogram of COD removed will yield 0.35 m^3 of gas

How much energy can we get from anaerobic digestion?

- Up to 75% conversion of organic fraction into biogas
- It has a methane content of 50-60% (but will depend on substrate)
- Biogas typically has a thermal value of about 22 MJ m^{-3}
- The thermal value of methane is 36 MJ m^{-3}



Uses of biogas



First estimate of digester energy yield

- Assume that 1 m^3 of biogas has a calorific value of 22 MJ

- Energy yield (MJ day^{-1}):

= daily gas production ($m^3\ day^{-1}$) x 22 MJ m^{-3}

Energy equivalents

- 1 Watt = 1 joule $second^{-1}$
- 1Wh = 1 x 3600 joules (J)
- 1 kWh = 3600000 J
- 1kWh = 3.6MJ
- 22MJ ($1m^3$ biogas) = 22/3.6 kWh
- = 6.1 kWh
- Electrical conversion efficiency = 35%

Therefore $1m^3$ biogas = 2.14kWh (elec)

The energy comes from the methane in the biogas

- To be more precise we need to know the biogas composition
- Can be done practically (gas chromatography, infrared analysis) of calculated

Theoretical – Buswell Equation

Buswell created an equation in 1952 to estimate the products from the anaerobic breakdown of a generic organic material of chemical composition $C_cH_hO_oN_nS_s$

$$\mathbf{C_cH_hO_oN_nS_s + 1/4(4c - h - 2o + 3n + 2s)H_2O}$$

$$\mathbf{\rightarrow \quad 1/8(4c - h + 2o + 3n + 2s)CO_2 + 1/8(4c + h - 2o - 3n - 2s)CH4 + nNH_3 + sH_2S}$$

The Buswell equation can be use to estimate biogas composition but not volume produced as it assumes 100% material breakdown

Calculations using Buswell formula

C	450			C	H	O	N	S	
H	2050		Glucose	6	12	6			
O	950		Alanine	3	7	2	1		
N	12		Trilauroglcerol	17	28	6			
S	1		waste	450	2050	950	12	1	
H2O	-528								
			Biogas %						
CO2	211		46.89						
CH4	239		53.11						
NH3	12								
H2S	1								

$C_cH_hO_oN_nS_s + 1/4(4c - h - 2o + 3n + 2s)H_2O = 1/8(4c - h + 2o + 3n + 2s)CO_2 + 1/8(4c + h - 2o - 3n - 2s)CH$

Theoretical - Method

- Carbon content of a feed material can be used in combination with the Buswell equation to estimate methane production

But…….

- We need to assume what proportion of the feed material is degraded in the process
- Can be based on typical values for different materials

  Food waste 85%, maize 80%, biodegradable municipal waste 70%......

Methane from waste

- $C_{450}H_{2050}O_{950}N_{12}S_1$

- From the Buswell equation
- 53% of CH_4
- 47% of CO_2

Steps to estimate gas and energy yield

We can calculate this based on the carbon content of the waste

1000 kg of wet waste

Water content = 650kg

Solids content = 350kg dry matter (35%TS)

$C_{450}H_{2050}O_{950}N_{12}S_1$

5400+2050+15200+168+32 = 22850

% carbon = 5400/22850

= 24% carbon

Carbon in 1000kg of wet waste
= 350 x 0.24kg C
= 84kg C

% of carbon biodegraded e.g. 70%
Then 84 x 0.7 = 58.8 kg C converted to biogas

From Buswell 53% CH_4 and 47% CO_2
Weight of methane carbon (CH_4-C)
58.8 x 0.53 = 31.16 kg C

Weight of methane (CH_4)
31.16 x 16/12
=41.55 kg CH_4

1 mol gas at STP = 22.4 litres

16g CH_4 = 22.4 litres

41550g CH_4 = 41550/16 mols = 2597 mols CH_4

2597 x 22.4 = 58172 litres CH_4 =58.2 m^3 CH_4

1000 kg wet waste = 58.2 m_3 CH_4

Energy value of methane and waste

$1m^3$ methane = 36 MJ

1 kWh = 3.6 MJ

$1m^3$ CH_4 = 10kWh

1 tonne (1000kg) wet waste

$58.1m^3CH_4$ x 10 kWh $m^{-3}CH_4$

=581 kWh

Theoretical - Example calculation

A sample of maize has elemental composition (weight as a percentage of VS) of 0.5, 0.08, 0.35, 0.06 and 0.01 of carbon, hydrogen, oxygen, nitrogen, and sulphur respectively. Use the Buswell equation to calculate the theoretical biogas composition and go on to apply a carbon balance to calculate the specific methane production. Assume 75% of the VS are degraded.

- The coefficients in the Buswell equation (C, H, O, N, S) can be calculated by dividing the proportion of weights by the atomic weights of the associated element (C=12, H=1, O=16, N=14, S=32) => $C_{0.5/12}H_{0.08/1}O_{0.35/16}N_{0.06/14}S_{0.01/32}$

=>

$$C_{0.0417}H_{0.0800}O_{0.0219}N_{0.0043}S_{0.0003}$$

- Calculate coefficients for CO_2 and CH_4

$1/8(4c - h + 2o + 3n + 2s) = 0.01801$

$1/8(4c + h - 2o - 3n - 2s) = 0.02530$

$0.0253 / (0.0253 + 0.01801) = 0.584$

= **58.4% CH_4, 41.6% CO_2**

Carbon balance

- 4 gVS contains 0.5g of carbon of which 75% is degraded = 0.375gC/gVS
- 58.4% of carbon is converted to methane = 0.375*0.584 = 0.219 gC/gVS
- 0.219 gC is (0.219/12) = 0.01825 moles C and 1 mole of C ≡1 mole of CH_4 so 1gVS produces 0.01825 moles of methane
- 1 mole of gas occupies 22.4 litres at STP => 0.01825 moles occupy (0.01825*22.4) = 0.408 litres. Specific methane production **= 0.408 l/gVS**

1	2	3	4	5	6	7	8	9	10
Waste input (tonnes)	Proportion dry solids	Proportion fixed carbon	Fixed C (kg)	Proportion converted	Proportion to CH4	CH4 carbon (kg)	CH4 (kg)	CH4 (Nm3)	Energy value (MJ)
1.000	0.35	0.24	84.00	0.70	0.53	31.16	41.55	58.17	2094.22

Pasteurisation

1	2	3	4	5	6	7	8	9	10
Waste input (tonnes)	ratio of make-up water	Make-up water (tonnes)	Input temperature (oC)	Pasteurisation temperature (oC)	Temp difference (oC)	Thermal efficiency	Pasteurisation energy requirement (MJ)	Pasteurisation energy requirement (KWh)	Heat energy available from gas (MJ)
1.000	5	0.0	20	70	50	0.8	261.25	72.57	2094.22

Digestion

1 Tonnes of wet waste (can be per unit of time e.g. per hour, day, year)
2 Dry weight of the waste (105 oC to constant weight)
3 This is the total carbon content derived from elemental or proximate analyisis. A value of 0.4 is fairly typical for MSW.
4 Calculates the available carbon (kg) that could theoretically find its way to methane or carbon dioxide.
5 This is the factor reflecting the conversion of fixed carbon in the digester (equivalent to the volatile solids destruction). Typical figures 0.3
6 Depends on the biochemical pathway. 50:50 split if all goes via acetic acid. 60:40 split would reflect 80% via acetoclastic methanogens
7 Calculates the weight of carbon going to methane
8 Calculates the weight of methane produced
9 Calculates the volume of methane at STP
10 Calculates the energy value of the methane @ 35.82 MJ per Nm3
11-13 calculates the volume of carbon dioxide
14 Calculates the total biogas volume at STP
15 Electrical conversion efficiency

VALORGAS

SEVENTH FRAMEWORK
PROGRAMME